FERROALLOYS AND OTHER ADDITIVES TO LIQUID IRON AND STEEL

Lampman/Peters, *editors*

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FERROALLOYS AND OTHER ADDITIVES TO LIQUID IRON AND STEEL

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sponsored by ASTM
Committee A-9 on
Ferroalloys and
Alloying Additives
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Foreword

This publication, *Ferroalloys and Other Additives to Liquid Iron and Steel,* contains papers presented at the symposium on Ferroalloys, Masteralloys, and Other Liquid Metal Additives which was held in Denver, Colorado, 20–21 May 1980. The symposium was sponsored by the American Society for Testing and Materials through its Committee A-9 on Ferroalloys and Alloying Additives. J. R. Lampman, Duval Sales Corporation, and A. T. Peters, Inland Steel Company, presided as symposium cochairmen and coeditors of this publication.

Related ASTM Publications

Impediments to Analysis, STP 708 (1980), $10.00, 04-708000-24

Toughness of Ferretic Stainless Steels, STP 706 (1980), $32.50, 04-706000-02

Fracture Mechanics, Proceedings of the Twelfth National Symposium, STP 700 (1980), $53.25, 04-700000-30

Properties of Austenitic Stainless Steels and Their Weld Metals (Influence of Slight Chemistry Variations), STP 679 (1979), $13.50, 04-679000-02

MiCon 78; Optimization of Processing, Properties, and Service Performance Through Microstructural Control, STP 672 (1979), $59.50, 04-672000-28

Rail Steels—Developments, Processing, and Use, STP 644 (1978), $45.00, 04-644000-01

Structures, Constitution, and General Characteristics of Wrought Ferretic Stainless Steels, STP 619 (1976), $7.50, 04-619000-02

Evaluations of the Elevated Temperature Tensile and Creep Rupture Properties of 12 to 27 Percent Chromium Steels, DS 59 (1980), $24.00, 05-059000-40

Unified Numbering System for Metals and Alloys and Cross Index of Chemically Similar Specifications, DS 56A (1977), $49.00, 05-056001-01

A Note of Appreciation to Reviewers

This publication is made possible by the authors and, also, the unheralded efforts of the reviewers. This body of technical experts whose dedication, sacrifice of time and effort, and collective wisdom in reviewing the papers must be acknowledged. The quality level of ASTM publications is a direct function of their respected opinions. On behalf of ASTM we acknowledge with appreciation their contribution.

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Introduction

In a normal year the U.S. iron and steel industry consumes in excess of one billion dollars' worth of ferroalloys and other additives intended to produce iron or steel of definite chemical composition.

A ferroalloy is usually defined as a metallic material containing a large proportion of a useful metal intended to be added to a melt and the balance being iron; however, the implication of iron being the other main component may or may not be true in modern practice. In a number of materials commonly regarded as ferroalloys, the proportion of iron is very low; calcium-silicon is a good example. Other additives vary from the definitely metallic pure chromium and manganese to the nonmetallic sulfur; most are obtained by a smelting process but some—titanium, for instance,—are often used as sized pieces of scrap.

Since virtually all steel and iron specifications call for manganese (contents exceeding those obtained in the molten metal and needed mainly to counteract the detrimental effects of sulfur)—manganese, usually as ferromanganese, is an additive without which the industry could not exist. The majority of steel grades call for levels of aluminum or silicon or both not obtainable from the steelmaking process; hence these two elements must be added to the liquid steel. Stainless properties can be obtained only from large chromium contents; modern high-strength low-alloy steels depend on columbium (niobium), vanadium, molybdenum, and sometimes other elements for the development of their properties. Consequently, while manganese is required in all steels and irons, the production of steel grades other than some nonalloy "plain carbon" ones is not possible without the use of other ferroalloys and additives.

It is surprising, therefore, with respect to the importance of the subject, that no comprehensive text on the use and properties of ferroalloys exists in English, while books on this subject are known in German, Russian, Polish, and reputedly Japanese. A number of papers discussing various aspects of ferroalloy use appeared in recent years in the *Journal of Metals, Iron & Steelmaking,* and *Iron and Steelmaker;* also, the subject was frequently but more or less in passing mentioned in many papers published in the *Proceed-*

ings of the National Open Hearth Conferences (later renamed Open Hearth and Basic Oxygen Steel Conferences and finally Steelmaking Conferences) and the Electric Furnace Conferences, published for many years by the American Institute of Mining and Metallurgical Engineers (AIME).

Since 1923, ASTM Committee A-9 on ferroalloys and alloying additives has been engaged in the formulation of standards for these materials. These standards are known and used throughout the world, although many national standards are now in existence. Cooperation of the committee with AIME resulted in sessions devoted exclusively to the usage of ferroalloys presented at the 1976 and 1977 Electric Furnace Conferences. It should be noted that sessions on the production (smelting) of ferroalloys were regularly included in these programs, but the use of the product was, as mentioned, covered only incidentally in some papers which discussed steel production.

The popularity of these two sessions led to a discussion within Committee A-9 regarding future work. The dependency of the United States on foreign sources of ferroalloys resulted at that time in a number of papers discussing the economics and trends of alloy usage. It was obvious to the practitioners of the art present in Committee A-9 that the conditions of use of the common alloys—manganeses, silicons, and chromiums—were well established in the industry. However, some managerial aspects of the field of ferroalloys were not well known and the technology of use of the "lesser" metals lacked any significant coverage.

With this in mind the presidium of A-9 developed plans for a symposium which would cover the less-well-known aspects of its subject.

It became obvious from the preliminary planning that discussing all alloys, even excluding the better-known ones, and all situations would not be practicable: a symposium would have to extend over an unacceptably long period and the resulting volume, unless severely abridged, would tax the resources of ASTM. Hence the program was limited to general coverage of the mentioned lesser aspects of the field and the present publication is the result of this effort.

The symposium took place 20–21 May in Denver, during an ASTM Committee Meeting week: 17 papers were presented. Since the discussions were intended to be very informal, no notes were taken and thus no discussions of the papers are included herein. By design, neither the manufacture of the materials nor the economics of supply were considered.

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ASTM Committee A-9 and the Steel Industry

REFERENCE: Huhn, W. P., "**ASTM Committee A-9 and the Steel Industry,**" *Ferroalloys and Other Additives to Liquid Iron and Steel, ASTM STP 739,* J. R. Lampman and A. T. Peters, Eds., American Society for Testing and Materials, 1981, pp. 3–31.

ABSTRACT: Since iron metallurgy began, constant effort has been expended to improve the normal product. A major method of improving the metallurgical properties of iron and steel is by alloying with other elements. Committee A-9 of ASTM on Ferroalloys and Alloying Additives is devoted to standardizing these alloying additives so that all within the industry will obtain comparable products.

The concept for A-9 occurred in 1923 when the first standards for ferroalloys were established. The next 50-odd years of operation have seen these standards expanded, deleted, altered, and new additions created to reflect the changes in steel technology. The complexity of this technology has involved A-9 with other ASTM committees and also with other domestic associations, not to mention the interrelationship with comparable foreign associations to establish worldwide standards on ferroalloys.

To prepare for the future of ferroalloys, A-9 will incorporate various facets into their present standards to constantly improve their performance and acceptance by not only domestic steel industry but worldwide as well. The flexibility of the committee's structure and membership permits attaining this goal.

KEY WORDS: standards, ferroalloys, world standards, Committee A-9

The purpose of this paper is to introduce Committee A-9, which is responsible for standards of ferroalloys consumed by the steel industry. By definition, the scope of A-9 is "the formulating and maintaining of specifications (that is, composition, definitions, sizing, classifications) covering additives such as ferroalloys, metals and metal compounds used in melting operations in the steel and other ferrous metal industries." Ferroalloy specifications, though relatively complete, have changed over the past 55 years to reflect the needs of the steel industry caused by changing technology and sophistication of operations. This encompasses not only the type of ferroalloy used, but its physical description as well. This is referenced particularly to chemical content, size, packaging, friability, and the sampling and testing methods as required by the industry and its suppliers.

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The first section of this paper contains a brief history of Committee A-9, including a description of some of the specifications and the way they were when A-9 was first formed. In later sections the present specifications and the current structure and modus operandi of A-9 are discussed, and a look taken at what the future might hold for ferroalloy specifications.

History

The first meeting of A-9 was held in November 1923 and the first formal minutes appear in Vol. 25 [*1*],[2] 1925 *Proceedings* of ASTM. The chairman of the committee at that time was F. C. Langenberg. F. C. Langenberg, Jr., is now president of Interlake Inc., located in Chicago—a steel producer as well as a ferroalloy producer.

At the time of the first meeting, the specifications for ferrovanadium, ferrochrome, chrome silicide, ferrosilicon, and ferromanganese as well as tungsten powder and ferrotungsten were initiated. Figure 1 gives an idea of exactly how these specifications were constructed and what facets of them were of interest to the committee at their initial formulation. The specifications initiated at this time were all considered tentative standards.

Almost paralleling the formation of ferroalloy specifications was the establishment of sampling and analytical technique for ferroalloys. Though these actually were not established by A-9, they were formulated in conjunction with ASTM Committees E-1 and E-8 [*2*]. This sampling procedure was initiated to insure both supplier and consumer that their samples would be representative of the product supplied. Simultaneously, analytical procedures were established so that both supplier and consumer would arrive at the same chemical analysis of the sample obtained from the material shipped. These techniques remained standard through 1949, when E-3 revised them to reflect new and more accurate methods for ferroalloys.

As mentioned previously, the initial standards which were formulated and referred to as "tentative" remained tentative standards until 1927. Because no objections had been raised by either consumer or supplier, these were adopted as ASTM standards for ferroalloys.

The scope of the A-9 Committee changed from its initial purpose to serve the steel industry to include standards used for both ferrous and nonferrous industries. For that reason it was decided to write a specification for molybdenum salts. In 1931 a ferromolybdenum specification was written which included not only ferromolybdenum but molybdenum salts as well. The ferromolybdenum specification included molybdenum content from 55 to 65 percent and molybdenum salts between 30 and 45 percent. The implications were that molybdenum was becoming an important part of steelmaking. Actually there were three specifications to cover molybdenum products being used by the steel industry; ferromolybdenum, low-carbon ferromolybdenum,

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

and molybdenum salts and compounds. At the 1938 meeting it was decided to consolidate low-carbon ferromolybdenum and ferromolybdenum together into one specification. In 1949 a revision of ASTM Specification A-146-39 was approved to include molybdenum oxide.

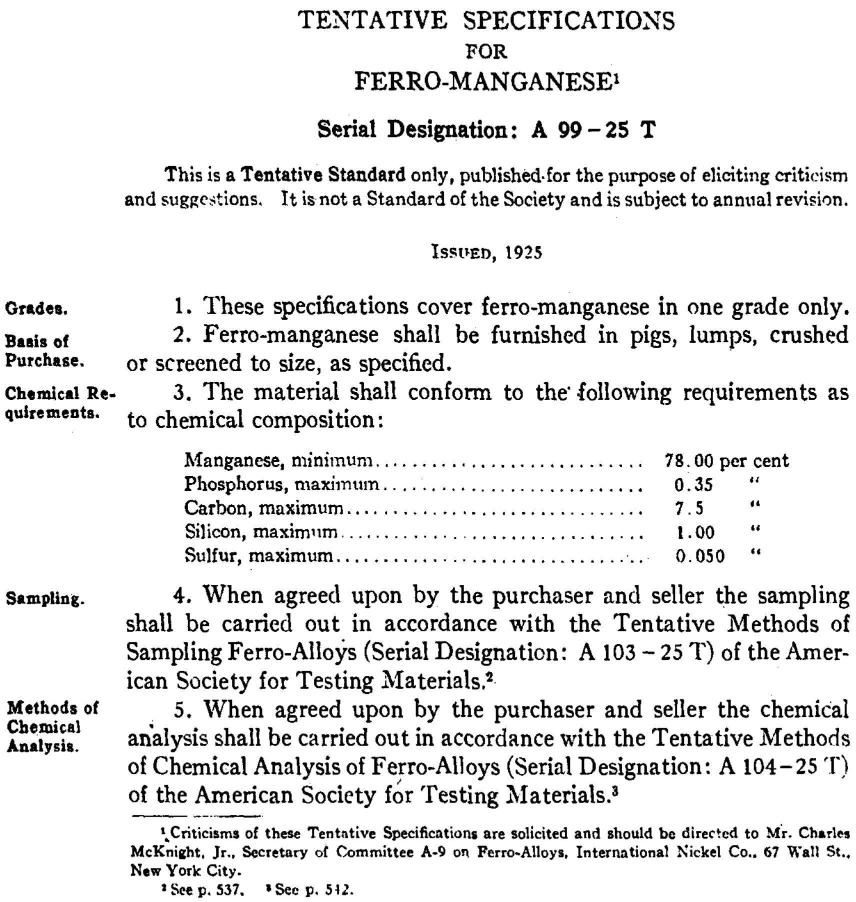
In 1934 specifications for ferrophosphorus, ferrotitanium, and high-purity nickel were considered but never developed until many years later. In fact, A-9 Committee has just concluded at their last meeting in 1979 that the need to write a specification for ferrophosphorus has outlived its usefulness. In 1938, E. A. Lucas, father of our present member, who formulated A-9 Bylaws, was charged with the responsibility of writing specifications for ferrotitanium, ferroboron, and ferrocolumbium.

These ferroalloys became very important, particularly during World War II. There were shortages of many critical elements and it was hoped that these products could be substituted for such things as nickel, chromium, and molybdenum. It may be recalled that tentative standards utilizing boron to replace nickel became very prevalent during the war. These were called the NE Grades, or National Emergency Grades. They were also known as TS Grades, Temporary Standards. Again, they were lean alloy steels utilizing boron to improve hardenability. In 1949, Subcommittee 1 on specifications had formulated the ferroboron and ferrotitanium specifications and in 1950 these were approved by the Society and became standards.

The standards for ferrocolumbium and ferrocolumbium-tantalum were begun in 1961 but were not approved until 1964. About this time a new physical dimension of ferroalloys had received considerable attention—friability. This is the ability of a ferroalloy to withstand handling without deteriorating in size from when the product was initially packaged or sized for customer shipment. Many steel companies had become concerned with ferroalloy sizing with fines and lumps. Shipments of products produced in Ohio, for example, were shipped as lumps and received as fines in Texas.

Earl Saunders of Union Carbide accepted the challenge of determining the friability of various ferroalloys. He developed the tumbling test which was vital in establishing the strength of ferroalloys from one of the hardest—low-carbon ferrochrome—to the softest—calcium silicon. The rating system developed by Saunders is given in Table 1 [*3*].

In 1966 the friability rating was assessed to A-101 specification covering ferrochromium ferroalloys. The other subcommittee chairmen were advised to evaluate their own ferroalloys under their specification and include a friability rating on those specifications for which they were responsible. This was very difficult because everyone had mixed emotions, or mixed experiences, I should say, with alloys within their own group. At that time I was a member of Subcommittee 2 on manganese alloys and we had very diverse opinions of which alloys were very strong and which were soft. Because of this, and the lack of agreement on friability, not all ferroalloys contain a friability rating.



TENTATIVE SPECIFICATIONS
FOR
FERRO-MANGANESE[1]

Serial Designation: A 99 - 25 T

This is a **Tentative Standard** only, published for the purpose of eliciting criticism and suggestions. It is not a Standard of the Society and is subject to annual revision.

ISSUED, 1925

Grades. 1. These specifications cover ferro-manganese in one grade only.

Basis of Purchase. 2. Ferro-manganese shall be furnished in pigs, lumps, crushed or screened to size, as specified.

Chemical Requirements. 3. The material shall conform to the following requirements as to chemical composition:

Manganese, minimum	78.00 per cent
Phosphorus, maximum	0.35 "
Carbon, maximum	7.5 "
Silicon, maximum	1.00 "
Sulfur, maximum	0.050 "

Sampling. 4. When agreed upon by the purchaser and seller the sampling shall be carried out in accordance with the Tentative Methods of Sampling Ferro-Alloys (Serial Designation: A 103 - 25 T) of the American Society for Testing Materials.[2]

Methods of Chemical Analysis. 5. When agreed upon by the purchaser and seller the chemical analysis shall be carried out in accordance with the Tentative Methods of Chemical Analysis of Ferro-Alloys (Serial Designation: A 104-25 T) of the American Society for Testing Materials.[3]

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[1] Criticisms of these Tentative Specifications are solicited and should be directed to Mr. Charles McKnight, Jr., Secretary of Committee A-9 on Ferro-Alloys, International Nickel Co., 67 Wall St., New York City.

[2] See p. 537. [3] See p. 542.

FIG. 1—*Original ferroalloy specifications.*

TENTATIVE SPECIFICATIONS
FOR
FERRO-SILICON[1]

Serial Designation: A 100 - 25 T

This is a **Tentative Standard** only, published for the purpose of eliciting criticism and suggestions. It is not a Standard of the Society and is subject to annual revision.

ISSUED, 1925

Grades. 1. These specifications cover three grades of ferro-silicon, as follows:

Grade A;
Grade B; and
Grade C.

Basis of Purchase. 2. (*a*) The ferro-silicon shall be furnished in lumps, or crushed or screened to size, as specified.

(*b*) When furnished in lump or granulated form the ferro-silicon shall be free from excessive disintegration.

Chemical Requirements. 3. The material shall conform to the following requirements as to chemical composition:

	GRADE A	GRADE B	GRADE C
Silicon, per cent...........	47.00 to 53.00	72.00 to 78.00	85.00 to 95.00

4. An analysis of each shipment of ferro-silicon shall be furnished the purchaser, showing the percentage of silicon.

Sampling. 5. When agreed upon by the purchaser and seller the sampling shall be carried out in accordance with the Tentative Methods of Sampling Ferro-Alloys (Serial Designation: A 103 - 25 T) of the American Society for Testing Materials.[2]

Methods of Chemical Analysis. 6. When agreed upon by the purchaser and seller the chemical analysis shall be carried out in accordance with the Tentative Methods of Chemical Analysis of Ferro-Alloys (Serial Designation: A 104 - 25 T) of the American Society for Testing Materials.[3]

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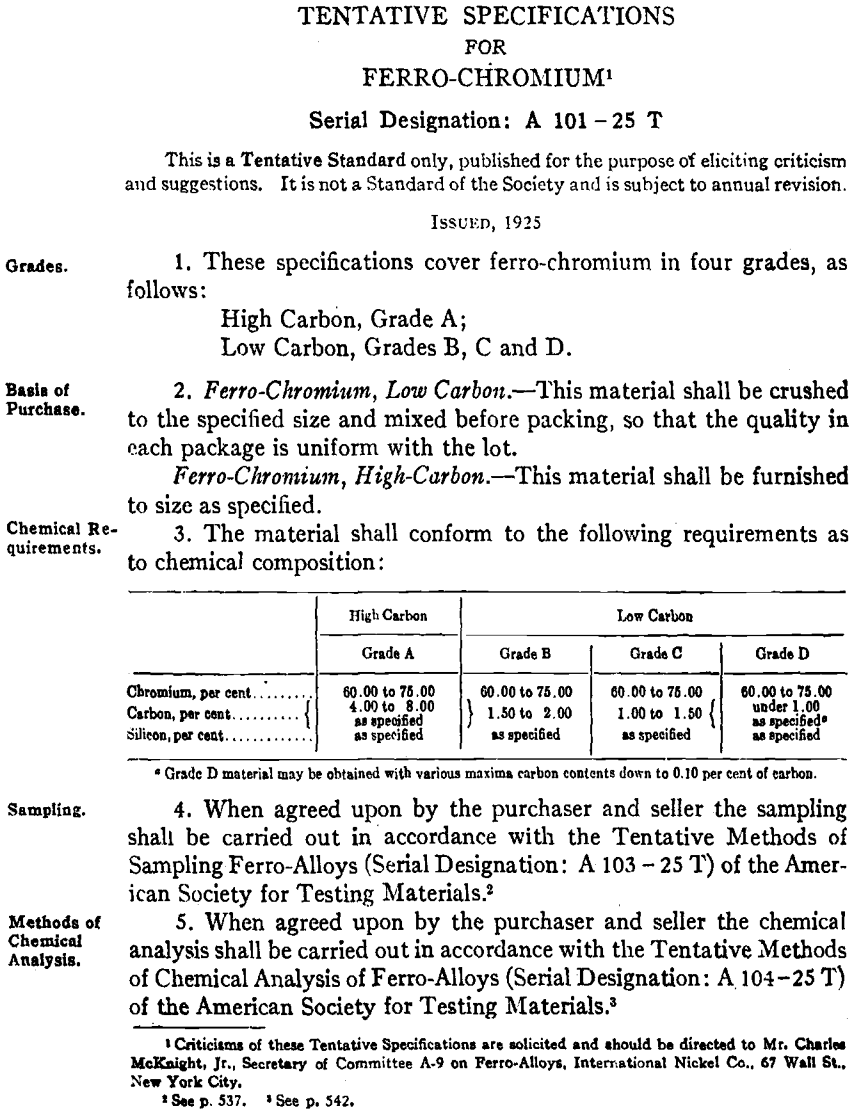
[1] Criticisms of these Tentative Specifications are solicited and should be directed to Mr. Charles McKnight, Jr., Secretary of Committee A-9 on Ferro-Alloys, International Nickel Co., 67 Wall St., New York City.

[2] See p. 537. [3] See p. 542

FIG. 1—*Continued.*



TENTATIVE SPECIFICATIONS
FOR
FERRO-CHROMIUM[1]

Serial Designation: A 101 - 25 T

This is a **Tentative Standard** only, published for the purpose of eliciting criticism and suggestions. It is not a Standard of the Society and is subject to annual revision.

ISSUED, 1925

Grades. 1. These specifications cover ferro-chromium in four grades, as follows:

High Carbon, Grade A;
Low Carbon, Grades B, C and D.

Basis of Purchase. 2. *Ferro-Chromium, Low Carbon.*—This material shall be crushed to the specified size and mixed before packing, so that the quality in each package is uniform with the lot.

Ferro-Chromium, High-Carbon.—This material shall be furnished to size as specified.

Chemical Requirements. 3. The material shall conform to the following requirements as to chemical composition:

	High Carbon	Low Carbon		
	Grade A	Grade B	Grade C	Grade D
Chromium, per cent	60.00 to 75.00	60.00 to 75.00	60.00 to 75.00	60.00 to 75.00
Carbon, per cent	4.00 to 8.00 as specified	1.50 to 2.00	1.00 to 1.50	under 1.00 as specified[a]
Silicon, per cent	as specified	as specified	as specified	as specified

[a] Grade D material may be obtained with various maxima carbon contents down to 0.10 per cent of carbon.

Sampling. 4. When agreed upon by the purchaser and seller the sampling shall be carried out in accordance with the Tentative Methods of Sampling Ferro-Alloys (Serial Designation: A 103 - 25 T) of the American Society for Testing Materials.[2]

Methods of Chemical Analysis. 5. When agreed upon by the purchaser and seller the chemical analysis shall be carried out in accordance with the Tentative Methods of Chemical Analysis of Ferro-Alloys (Serial Designation: A 104-25 T) of the American Society for Testing Materials.[3]

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[1] Criticisms of these Tentative Specifications are solicited and should be directed to Mr. Charles McKnight, Jr., Secretary of Committee A-9 on Ferro-Alloys, International Nickel Co., 67 Wall St., New York City.

[2] See p. 537. [3] See p. 542.

FIG. 1—*Continued.*

TENTATIVE SPECIFICATIONS
FOR
FERRO-VANADIUM[1]

Serial Designation: A 102 - 25 T

This is a **Tentative Standard** only, published for the purpose of eliciting criticism and suggestions. It is not a Standard of the Society and is subject to annual revision.

Issued, 1925

Grades. 1. These specifications cover ferro-vanadium in four grades, as follows:

Grade A;
Grade B;
Grade C; and
Grade D.

Basis of Purchase. 2. The material furnished under this specification shall be crushed to the specified size, and mixed before packing, so that the quality in each package is uniform with the lot. The material shall be packed in sound containers, sufficiently strong to prevent loss in transportation.

Chemical Requirements. 3. The material shall conform to the following requirements as to chemical composition:

	Grade A	Grade B	Grade C	Grade D
Vanadium, per cent	30.00 to 40.00	30.00 to 40.00	35.00 to 45.00	35.00 to 45.00
Carbon, per cent	3.00 to 6.00	1.5 to 3.00	not over 1.5	not over 0.75
Silicon, per cent	*8.00 to 15.00*	*5.00 to 8.00*	*not over 2.00*	*not over 2.00*
Phosphorus, per cent	not over 0.250	not over 0.250	not over 0.150	not over 0.100
Sulfur, per cent	not over 0.300	not over 0.300	not over 0.200	not over 0.100
Aluminum, per cent	not over 2.00	not over 2.00	not over 2.00	not over 1.00

Sampling. 4. When agreed upon by the purchaser and seller the sampling shall be carried out in accordance with the Tentative Methods of Sampling Ferro-Alloys (Serial Designation: A 103 - 25 T) of the American Society for Testing Materials.[2]

Methods of Chemical Analysis. 5. When agreed upon by the purchaser and seller the chemical analysis shall be carried out in accordance with the Tentative Methods of Chemical Analysis of Ferro-Alloys (Serial Designation: A 104-25 T) of the American Society for Testing Materials.[3]

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[1] Criticisms of these Tentative Specifications are solicited and should be directed to Mr. Charles McKnight, Jr., Secretary of Committee A-9 on Ferro-Alloys, International Nickel Co., 67 Wall St., New York City.

[2] See p. 537. [3] See p. 542.

FIG. 1—*Continued.*

TABLE 1—*Friability rating system* [3].

Code No.	Definition
1	Very tough materials which are susceptible to little, if any, breakage during shipment or handling. (Example: low carbon ferrochrome)
2	Some breakage of large pieces probable in shipping and handling. No appreciable fines produced from either lump or crushed sizes. (Example: chromium metal)
3	Appreciable reduction in size of large pieces possible in shipping and handling. No appreciable production of fines in handling of crushed sizes. (Example: ferrovanadium)
4	Appreciable reduction in size of large pieces upon repeated handling. Some fines produced upon repeated handling of crushed sizes. (Example: standard ferromanganese)
5	Appreciable reduction in size in repeated handling of large pieces. Appreciable fines may be produced in the handling of crushed sizes. (Example: 50 percent ferrosilicon)
6	This category represents the most friable alloys. (Example: calcium silicon)

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, is entirely their own responsibility.

Though the process to make electrolytic manganese was developed in the late 1940's and was used by the steel industry, particularly in the melting of stainless steel, the specification was not written until 1967 and not approved until 1969. The same occurred with nickel oxide sinter.

There are reasons for this, as stipulated in the ASTM Bylaws. No proprietary alloys are to be included and there must be at least two suppliers. And then, before a specification is written, there must be a need and more than one consumer of the product. Then too, a history of its use must be acquired before the product can establish itself as a viable, useful tool to steelmaking.

So much for the brief history of what has been done and those specifications now active. Table 2 indicates the specifications now established by A-9 and their approval dates as ASTM Standards [*4*]. The specifications are reviewed every five years to keep them current with changing steel technology.

Current Status of Committee

The present A-9 Committee consists of 41 members of which 12 are consumers, 16 suppliers, 8 general interest, 4 unclassified, and one staff member. We strive to keep a balance between suppliers and consumers, though this does not act to discriminate against an interested prospect for application.

TABLE 2—*Chronology of ASTM ferroalloy standards* [4].

				Present Status		
Standard	Material	Written	No. of Revisions	Active 1976	Withdrawn	Transferred
A 97	W-powder	1925	0	. . .	1934	. . .
A 98	Spiegelelsen	1925	5	X	. . .	. . .
A 99	Fe-Mn	1925	5	X	. . .	. . .
A 100	Fe-Si	1925	5	X	. . .	. . .
A 101	Fe-Cr	1925	6	X	. . .	. . .
A 102	Fe-V	1925	5	X	. . .	. . .
A 103	sampling	1927	0	. . .	. . .	1936
A 104	check analysis	1927	0	. . .	. . .	1936
A 132	Fe-Mo	1932	5	X	. . .	. . .
A 144	Fe-W	1932	6	X	. . .	. . .
A 145	LC-Fe-Mo	1932	5	X	. . .	. . .
A 323	Fe-B	1949	2	X	. . .	. . .
A 324	Fe-Ti	1950	3	X	. . .	. . .
A 481	Cr metal	1963	2	X	. . .	. . .
A 482	Cr-Si	1963	2	X	. . .	. . .
A 483	Si-Mn	1963	1	X	. . .	. . .
A 495	Ca-Si/Ca-Si-Mn	1963	1	X	. . .	. . .
A 550	Fe Cb	1965	2	X	. . .	. . .
A 601	electro Mn	1969	1	X	. . .	. . .
A 610	size sampling	1970	1	X	. . .	. . .
A 636	Ni oxide	1970	1	X	. . .	. . .
A 701	Fe-Mn-Si	1974	0	X	. . .	. . .

There are presently seven subcommittees which have jurisdiction over the specifications. They are separated as follows:

9.01 Chromium additives
9.02 Manganese additives
9.03 Silicon additives
9.04 Boron, columbium additives
9.05 Titanium, tungsten, vanadium additives
9.06 Molybdenum, nickel additives
9.07 Sampling, sizing

How does the A-9 Committee work? I would like to present just a very brief description of how a specification becomes a part of the ASTM Standards. A standard is proposed by a member of ASTM and the specification is undertaken in the appropriate subcommittee. When the tentative standard has been written, it is voted upon in the subcommittee and, if approved, will then be brought to vote by the entire A-9 Committee. Once approved by the entire committee, it is forwarded to ASTM, hereafter called the Society. It again is voted upon and, depending upon the response, if approved by the Society, it becomes a standard of ASTM.

At the present time, A-9 has three liaison representatives to various committees:

E-3—on chemical analysis, which is vital part of the ferroalloy industry. An example of the standard method utilized for many years to obtain samples for chemical analysis is shown in Fig. 2 [5]. This method of sampling has been utilized by the ferroalloy industry to obtain samples for chemical analysis of the major element contained in the ferroalloys.

E-11—We have a representative to E-11 on statistical analysis. This particular committee is related to our sampling techniques, presently contained under Subcommittee 7 as the means of defining sampling techniques. Figure 2 shows also some of the methods used to obtain samples for ferroalloys. These represent methods accepted by both supplier and consumer to obtain a representative sample for both sizing and chemical analysis in case there are differences.

E-34—We have liaison with E-34, which has to do with environmental toxicity—a more or less household word, not only in the steel industry but in our industry as well. This is a newly created committee and, although there have been attempts to establish a separate committee on this, none has yet been formed. The purpose of E-34 is to monitor trends not only in the steelmaking and ferroalloy-making industry, but in the chemical industry as well. It will attempt to correlate all toxic components for the industries and guard against any possible problems that may occur by their generation, either during manufacturing, handling, or use.

ISO—Last but not least, A-9 is represented at the ISO, the International Standards Organization. This is an association of worldwide ferroalloy producers, some of whose products come into the United States. We feel that ISO is significant in establishing worldwide standards on ferroalloys. A representative from the United States must be present at these meetings to insure that our standards on sampling, chemical analysis, and packaging of ferroalloys receive consideration.

The ferroalloy industry does export products such as molybdenum, various manganese products, and vanadium to other markets throughout the world. The industry's exports are very small compared with its imports, but we feel it an integral part of the domestic ferroalloy industry. Although our sizing and sampling techniques as well as our chemical analysis are significant, the need for a worldwide standard for ferroalloys is obvious. The cross-fertilization of the ideas of all worldwide ferroalloy producers has led to some interesting results. Although it took almost three years, we have finally established agreement between all nations on sampling and size determination. However, some of the standard ferroalloys have met with some indifference by other countries.

At the present time, A-9 is considering additional specifications. I stated at the outset that changing steel technology reflects not only on chemical specifications of ferroalloys, but also on which ferroalloys need to be included as specifications.

Interestingly enough, in 1973 our current chairman proposed a standard for ferrophosphorus. This is the first mention of ferrophosphorus since 1934. A specification was never written. Currently, because of pollution, Environmental Protection Agency (EPA) regulations, and the relationship to the environment, the field of ferrophosphorus producers has narrowed down to three. It was felt, therefore, that there was no need for a standard because all products vary only in silicon content and the major problem is obtaining the product rather than meeting a specification. The magnitude of consumption also was considered minimal and, therefore, a specification was not written.

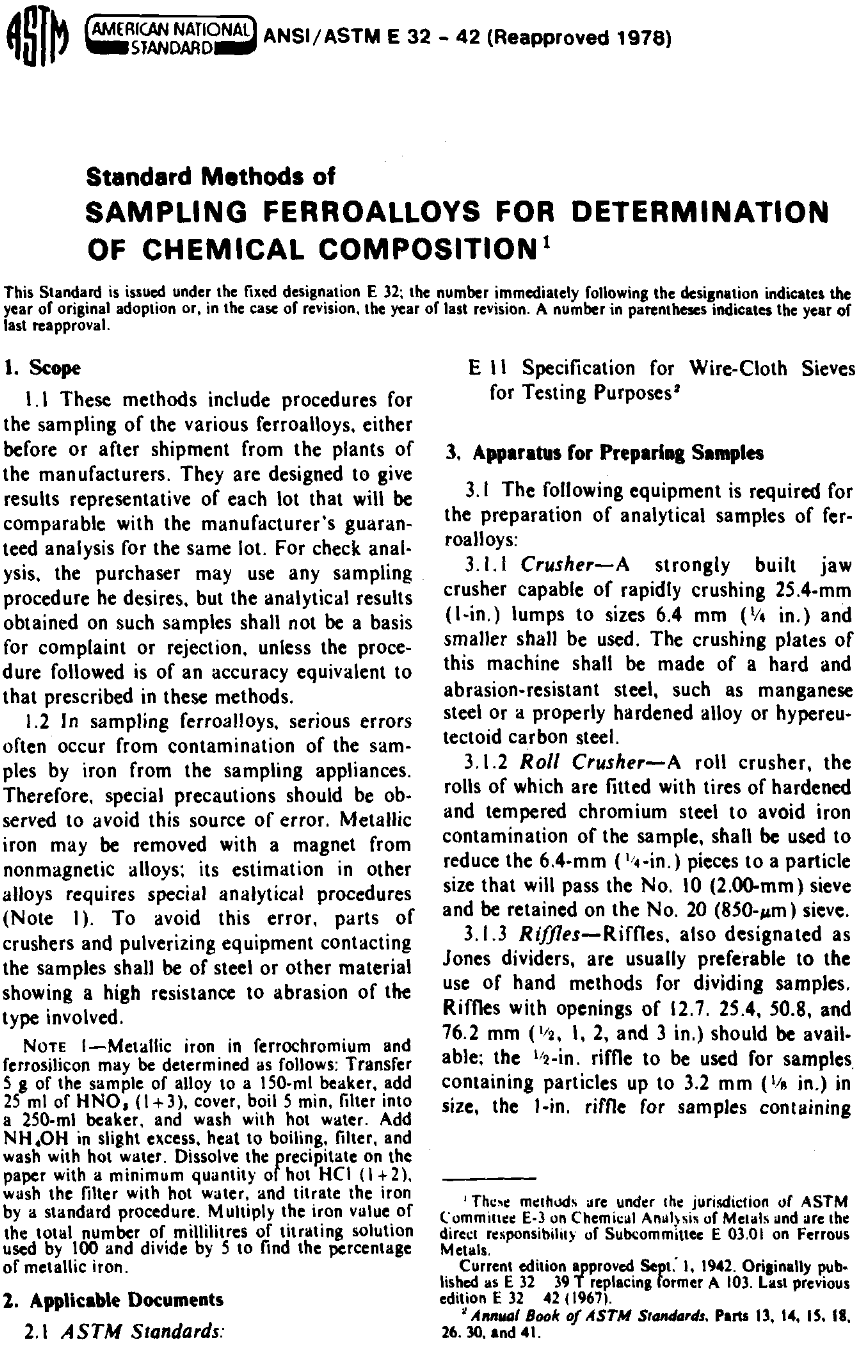
The era of high-strength/low-alloy steels, supermachinability, and stainless steel prompted new developments for nitrogen-containing products. The nitrided portion of medium-carbon ferromanganese was added to the fold and this was done by including another column under ferromanganese specifications. This was a result of examining the current specifications and amending them to reflect the current needs of the industry.

Current Status of Specifications

This brings us to the question, What are the specifications compared with right now? I will cite a few. A portion of the current specification for ferromanganese with the added column for the nitrided-bearing materials is shown in Fig. 3. The specification for ferrochromium is shown in Fig. 4. Note also the nitrided materials, as well as some of the carbon contents. I might point out that the need for low-carbon ferrochromium is declining because of the recent innovation of the Argon Oxygen Decarbonization process (AOD). Major quantities of this material were used by stainless steel producers and it now has deteriorated to very minimal tonnage, probably no more than 36 000 metric tons (t) (40 000 short tons) a year; at one time it was over 180 000 t (200 000 tons). Note, too, that the specification for ferrochromium does include the friability rating associated with the particular chromium alloy.

Table 3 represents all the current specifications under the jurisdiction of A-9. It may be thought that this covers all alloying agents used by the steel industry. It does not. A couple of examples follow of products suggested for standardization that did not make it.

Vanadium carbide, for one, is a viable product but, up until two years ago, was a proprietary alloy of which there was only one supplier. When the specification was proposed, there were two suppliers. The tentative specification was so general because of different manufacturing processes that it was decided that it really was not a specification at all and therefore was held in abeyance.



AMERICAN NATIONAL STANDARD ANSI/ASTM E 32 - 42 (Reapproved 1978)

Standard Methods of

SAMPLING FERROALLOYS FOR DETERMINATION OF CHEMICAL COMPOSITION[1]

This Standard is issued under the fixed designation E 32; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 These methods include procedures for the sampling of the various ferroalloys, either before or after shipment from the plants of the manufacturers. They are designed to give results representative of each lot that will be comparable with the manufacturer's guaranteed analysis for the same lot. For check analysis, the purchaser may use any sampling procedure he desires, but the analytical results obtained on such samples shall not be a basis for complaint or rejection, unless the procedure followed is of an accuracy equivalent to that prescribed in these methods.

1.2 In sampling ferroalloys, serious errors often occur from contamination of the samples by iron from the sampling appliances. Therefore, special precautions should be observed to avoid this source of error. Metallic iron may be removed with a magnet from nonmagnetic alloys; its estimation in other alloys requires special analytical procedures (Note 1). To avoid this error, parts of crushers and pulverizing equipment contacting the samples shall be of steel or other material showing a high resistance to abrasion of the type involved.

NOTE 1—Metallic iron in ferrochromium and ferrosilicon may be determined as follows: Transfer 5 g of the sample of alloy to a 150-ml beaker, add 25 ml of HNO_3 (1+3), cover, boil 5 min, filter into a 250-ml beaker, and wash with hot water. Add NH_4OH in slight excess, heat to boiling, filter, and wash with hot water. Dissolve the precipitate on the paper with a minimum quantity of hot HCl (1+2), wash the filter with hot water, and titrate the iron by a standard procedure. Multiply the iron value of the total number of millilitres of titrating solution used by 100 and divide by 5 to find the percentage of metallic iron.

2. Applicable Documents

2.1 *ASTM Standards:*

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[2]

3. Apparatus for Preparing Samples

3.1 The following equipment is required for the preparation of analytical samples of ferroalloys:

3.1.1 *Crusher*—A strongly built jaw crusher capable of rapidly crushing 25.4-mm (1-in.) lumps to sizes 6.4 mm (¼ in.) and smaller shall be used. The crushing plates of this machine shall be made of a hard and abrasion-resistant steel, such as manganese steel or a properly hardened alloy or hypereutectoid carbon steel.

3.1.2 *Roll Crusher*—A roll crusher, the rolls of which are fitted with tires of hardened and tempered chromium steel to avoid iron contamination of the sample, shall be used to reduce the 6.4-mm (¼-in.) pieces to a particle size that will pass the No. 10 (2.00-mm) sieve and be retained on the No. 20 (850-μm) sieve.

3.1.3 *Riffles*—Riffles, also designated as Jones dividers, are usually preferable to the use of hand methods for dividing samples. Riffles with openings of 12.7, 25.4, 50.8, and 76.2 mm (½, 1, 2, and 3 in.) should be available; the ½-in. riffle to be used for samples containing particles up to 3.2 mm (⅛ in.) in size, the 1-in. riffle for samples containing

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[1] These methods are under the jurisdiction of ASTM Committee E-3 on Chemical Analysis of Metals and are the direct responsibility of Subcommittee E 03.01 on Ferrous Metals.

Current edition approved Sept. 1, 1942. Originally published as E 32 39 T replacing former A 103. Last previous edition E 32 42 (1967).

[2] *Annual Book of ASTM Standards*, Parts 13, 14, 15, 18, 26, 30, and 41.

FIG. 2—*Sampling ferroalloys for chemical analysis.*

particles up to 9.6 mm ($\frac{3}{8}$ in.), the 2-in. for samples containing particles up to 19.1 mm ($\frac{3}{4}$ in.), and the 3-in. for samples containing particles up to 2 in. in size. Riffles should be of the enclosed type to reduce dust losses. The use of multiple riffles is not approved.

3.1.4 *Mortar and Pestle*—The mortar and pestle shall both be made of properly hardened alloy steel of a kind and grade designed to resist severe abrasive forces (Note 2). Suitable dimensions of the mortar are 79.4 mm ($3\frac{1}{8}$ in.) in outside height, 76.2 mm (3 in.) in outside diameter, 39.7 mm ($1\frac{9}{16}$ in.) in inside diameter, and 60.3 mm ($2\frac{3}{8}$ in.) in inside depth, the bottom 12.7 mm ($\frac{1}{2}$ in.) of which shall be rounded. The pestle shall be 152 mm (6 in.) in length, 38.1 mm ($1\frac{1}{2}$ in.) in diameter, and rounded at the bottom. The upper part of the pestle should be slightly softer than the remainder in order to decrease the tendency to shatter. Both the mortar and pestle, after hardening, shall be polished with abrasive paper to remove all scale. The narrow clearance between the pestle and the sides of the mortar reduces the dust loss.

NOTE 2—*For example:* steel mortars and pestles of the following composition, after proper hardening and tempering treatments, have been found satisfactory:

Carbon, percent	0.60
Manganese, percent	0.25
Phosphorus, percent	0.02
Sulfur, percent	0.02
Silicon, percent	0.25
Chromium, percent	1.25
Tungsten, percent	2.20
Vanadium, percent	0.10

After machining annealed steel of this grade to the usual form and dimensions, each part is heated to between 760 and 800 C, quenched in a light, mineral quenching oil and tempered at once. The pestle may be treated by quenching the lower portion only, the upper portion being permitted to air cool, and then tempering the quenched portion.

NOTE 3—Mechanically operated pulverizing equipment may be substituted for the mortar and pestle, provided suitable tests show that the use of such equipment does not affect the composition of a sample of any material obtained by these methods.

3.1.5 *Sieves*—The sieves shall conform to Specification E 11.

4. Unit Quantities for Sampling and Analysis

4.1 Each shipment, except as otherwise agreed upon by the purchaser and the manufacturer, shall constitute a unit for sampling and analysis. It is recommended that shipments of any alloy exceeding 100 tons be divided into smaller lots for sampling according to some plan best adapted to the material and conditions, such as each cast, each carload, each ladleful, or each binful.

4.2 *Division of Samples*—In these methods the term "divide" is used to indicate a division of a sample into two approximately equal parts of similar composition as in riffling.

5. Sampling Spiegeleisen and 15 percent Ferrosilicon

5.1 Spiegeleisen is generally cast in pigs and shipped in bulk. Since this alloy is very hard and somewhat tough, sampling is most accurately and easily accomplished during the tapping of the metal from the furnace or during the pig-casting operation by taking small spoonfuls and pouring the metal quickly into a test mold designed to solidify the metal quickly and give a clean test pig that is easily broken. Sampling of the metal in the solid state is difficult, and is best done during the loading or unloading, except when the material is loaded from bins or unloaded by dumping. The procedure, therefore, may be varied to suit the conditions but shall always conform to the following requirements:

5.1.1 *Sampling at Furnace*—The purchaser may arrange with the manufacturer to have the sampling done at the furnace. If so, each shipment or each cast may constitute a unit sample for analyzing. The sample shall be obtained by collecting portions with a spoon from the runner as the metal flows from the furnace, unless the metal is treated in the runner or ladle to change its composition, in which event the portions shall be taken as the metal flows from the ladle to the pig casting machine. In any case, at least two spoonfuls of metal shall be taken from each ladle, one spoonful while the first third of a ladleful is flowing into or from the ladle and the second while the last third is flowing. Each spoonful shall be taken in a manner to avoid collecting dirt or slag, and the clean metal shall be immediately poured into a clean shallow mold to form a thin chill casting from which small pieces approximately equal in size may be readily broken. When the spiegeleisen is cast in sand beds, the molten metal being run from the furnace directly to the casting floor, the

FIG. 2—*Continued.*

samples shall be taken by dipping skimmed molten metal from the runner trough and pouring it into a small quartered cast-iron button mold. A sample shall be taken in this manner to represent the metal being cast in each pig bed. From the test castings thus obtained to represent a shipment, approximately equal portions shall be taken and combined to form the sample which shall have a gross mass of not less than 200 g. The sample shall then be alternately crushed in a mortar and sieved until it all passes through a No. 80 (180-μm) sieve. If the sample is to be analyzed by more than one laboratory, it shall be mixed, coned, and quartered upon glazed paper (Note 4). The sample or samples thus prepared shall be thoroughly mixed, dried for 1 h at 105 to 110 C, and preserved for analysis in well-stoppered bottles properly labeled for full identification, including the name of the material, the manufacturer, the date, the cast or lot number, etc.

NOTE 4—Finished samples are frequently divided into four portions: one for the purchaser, one for the manufacturer, one for an umpire if necessary, and one held in reserve.

5.1.2 *Sampling Solid Forms*—When the metal is in the solid state a gross sample shall first be collected by selecting random pigs or pieces at regular intervals during the loading or unloading. Surface sampling of piles of the material will not give a representative sample. When piles of the material must be sampled, the pieces shall be selected according to some fixed plan which assures the obtaining of pieces comprising the gross sample from uniformly distributed points throughout, a condition requiring the moving of all or many of the pieces in the pile. For lots of 50 tons or larger, 1 pig or piece shall be taken for each ton, and for small lots the number of pieces shall be proportionately increased to 25 pieces for a 10-ton lot, or 10 pieces for a 1-ton lot. The various pigs thus collected shall be broken approximately in half by any convenient means, and one of the halves of each pig shall be reserved. From the fractured surface of each of these half pigs, an approximately equal portion shall be taken by any suitable means (as by spalling with a heavy hammer), care being taken by the sampler to see that these spalls are not all from the outer edges of the pigs but at least some are obtained from the central portion, and that none contains portions of the outer surface which may be contaminated with sand or other foreign material. The spallings from each half pig as collected shall be placed in separate envelopes and weighed to the nearest 1 g. Each portion so selected shall be of approximately the same mass.

The portions shall then be combined to form the sample and alternately crushed (preferably in a hardened-alloy steel mortar) and sieved until it passes a No. 6 (3.35-mm) sieve. Between 10 and 15 oz shall then be separated from the crushed sample by riffling and this portion shall be pulverized to pass a No. 80 (180-μm) sieve. The pulverizing of over-sizes is best done with the hardened steel mortar and pestle, while sieving frequently to keep the size close to 180-μm and prevent loss of dust. The pulverized sample shall be thoroughly mixed upon glazed paper, divided if necessary, labeled, and dried prior to analysis, in accordance with 5.1.1.

6. Sampling Ferrosilicon, Standard Ferromanganese, Silicomanganese, Ferrophosphorus, and 12 to 15 percent Zirconium Alloy

6.1 Alloys in this group are shipped in both lump and crushed form, in bulk as well as in containers. Carload lots are generally shipped in bulk, except the finely crushed sizes which are usually shipped in containers. Different procedures are required for sampling the lump and the crushed alloy, and the work of sampling is most conveniently done while loading or unloading.

6.2 *Lump Alloy*—In sampling bulk shipments, lumps of average size shall be set aside for the sample at regular intervals in the ratio of one lump from approximately each 300 lb. The sample shall be accumulated throughout the loading or unloading operation so that all parts of the shipment will be equally represented. If the alloy is in containers every fifth container shall be dumped, and one representative lump shall be taken from each 60 lb of alloy which is equivalent to one lump per 300 lb for the lot. The sample shall also include a representative amount of edge metal, small lumps, and any fines that may be present.

FIG. 2—*Continued.*

From each of the lumps in the sample there shall be broken three small pieces each about 19 mm (¾ in.) in size, one from each of two opposite surfaces (top and bottom, if present) and one from the center, the three pieces constituting a partial vertical cross-section of the lump.

The small pieces, together with a representative portion of any fines present, shall be combined and crushed to pass ¼-in. sieve. Not less than 30 lb shall be separated from the crushed sample by riffling and at least a quarter portion of this shall be rolled to pass a No. 10 (2.00-mm) sieve. A 6 to 8-oz portion obtained by riffling (a larger amount when more than one sample is required) of the 2.00-mm sample shall then be pulverized to pass a No. 100 (150-µm) sieve. The pulverizing is best done with the hardened alloy-steel mortar and pestle, while sieving frequently to keep the size close to 150 µm and prevent loss of dust. The pulverized sample shall be poured upon glazed paper, mixed thoroughly, and divided, if necessary (Note 4) by quartering, dried for 1 h at 105 to 110 C, and then preserved in a well-stoppered bottle or bottles.

6.3 *Crushed Alloy*—One container out of every five in the shipment shall be opened and the contents dumped. A sample representative of both lumps and fines shall be taken from each of the dumped containers to give a combined sample of approximately 1 percent of the mass of the lot or shipment, this sample being composed of equal amounts of the samples taken from all containers dumped. If in bulk, a fixed portion of representative material shall be taken with a shovel or scoop at regular intervals during the loading or unloading to accumulate a sample of about 1 percent of the mass of the lot.

The 1 percent sample shall be mixed and divided once if its mass is between 200 and 300 lb or twice if it weighs more than 300 lb. The portion reserved shall be crushed to pass a 1-in. (25.0-mm) sieve (unless its largest pieces are under this size), again divided, and then crushed to pass a ¼-in. (6.3-mm) sieve. Preparation of the sample shall then be completed as described for 6.4-mm (¼-in.) material in 6.2.

7. Sampling High-Carbon Ferrochromium, Medium-Carbon Ferromanganese, Low-Carbon Ferromanganese, Silicon Metal, Calcium-Silicon, and 35 to 40 percent Zirconium Alloy

7.1 These alloys are shipped in both lump and crushed form, usually in containers.

7.2 *Lump Alloy*—One out of every five containers shall be dumped. Pieces 12.7 to 19.1 mm (½ to ¾ in.) in size shall be broken from the lumps, and a fair proportion of any fines that may be present shall be included. The gross sample shall contain approximately one piece for each 50 lb of alloy. The accumulated sample shall be mixed and reduced in size in accordance with 6.2.

7.3 *Crushed Alloy*—Crushed alloy (material 50.8 mm (2 in.) and less in size) shall be sampled as described in 6.3, except that a 10 percent representative sample shall be taken from each container opened to give a 2 percent gross sample. For lots of 10 tons or more, the 2 percent sample shall be mixed and divided once in half. For lots of less than 10 tons, dividing the sample at this stage shall be omitted. The portion retained shall be crushed to pass a 1-in. (25.0-mm) sieve (if above this size) in a heavy crusher provided with smooth plates of manganese steel, and again passed through the riffle to obtain a sample of about 100 lb. This portion shall be crushed to pass a ¼-in. (6.3-mm) sieve, divided twice, and the quarter portion reserved shall be crushed to pass a No. 10 (2.00-mm) sieve. Between 6 and 8 oz shall then be separated from the crushed sample by riffling, and this portion shall be prepared for analysis in accordance with 6.2.

For lots larger than 10 tons, a somewhat smaller percentage of the lump shall be crushed for the sample, while for smaller lots the percentage shall be increased somewhat to provide a suitable amount of sample for mixing and riffling to size.

8. Sampling Low-Carbon Ferrochromium

8.1 Low-carbon ferrochromium is shipped in both crushed and lump form, in bulk and in containers. The alloy usually contains about 70 percent chromium, and has a carbon

FIG. 2—*Continued.*

content ranging from 0.06 to 2.0 percent, according to the maximum specified. The combination of hardness and toughness characteristic of this material, particularly of the lower carbon grades, makes it the most difficult of any of the ferroalloys to sample properly. In view of the great importance of the accurate determination of the carbon content, the utmost care shall be taken to avoid contamination of the sample with fragments of steel from the tools used in preparing the sample. Bucking boards shall not be used.

8.2 When the alloy is in lump form, a piece or pieces representing a full cross section of the original cast shall be taken from points distributed throughout the lot, to give a gross sample amounting to about 1 percent of the mass of the lot. The cross section pieces should be as nearly uniform in size as possible.

8.3 When the alloy is in crushed form in containers, one container out of each five shall be emptied and sufficient representative material taken from each to give a gross sample of about 1 percent of the mass of the lot. For shipments in bulk, representative portions shall be selected with a shovel at regular intervals during the unloading operation to accumulate a 1 percent sample.

8.4 The 1 percent sample shall be crushed to pass a 1-in. (25.0-mm) sieve (if above this size) in a heavy crusher provided with smooth plates of manganese steel, and riffled twice. The resulting quarter shall be crushed to pass a ½-in. (12.5-mm) sieve and riffled once. The sample shall be further crushed to pass a ¼-in. (6.3-mm) sieve and riffled three times. The resulting eighth portion of the sample shall be reduced to pass a No. 6 (3.35-mm) sieve by pounding in a hardened alloy-steel mortar, and riffled to a weight of 6 to 8 oz. This amount shall be pulverized to pass a No. 30 (600-μm) sieve in a hardened alloy-steel mortar, while sieving frequently in order to keep the sample as near to this size as possible, until the entire sample has passed the sieve. The pulverized sample shall be mixed thoroughly upon glazed paper, divided if necessary (Note 4) by quartering, dried for 1 h at 105 to 110 C, and preserved in a well-stoppered bottle or bottles.

9. Sampling Ferrovanadium, Ferromolybdenum, Ferrotungsten, Ferrocolumbium, Ferrotitanium, Ferrozirconium, and Ferroboron

9.1 These alloys are shipped in containers and are all high-priced materials. Therefore, it is important that the sampling be thoroughly representative, irrespective of the amount of material involved.

9.2 *Shipments 20000 lb or Under in Mass*—All the containers of a shipment shall be emptied to form a cone shaped pile. The pile shall be sampled by shoveling, the mass of the gross sample being adjusted to the size of the lumps of the alloy. For lots of more than 8000 lb, one shovelful out of every four shall be reserved for the sample. If the lot weighs less than 8000 lb, one shovelful out of three or out of two, or shovelfuls otherwise adjusted so as to obtain a gross sample larger than the amounts specified below, shall be taken. The gross sample thus collected shall be coned and again divided by shoveling. This procedure shall be repeated, if necessary, until the weight of the gross sample is reduced to 2000 lb for 64-mm (2½-in.) material, 250 lb for 25.4-mm (1-in.) pieces, or 100 lb for alloy crushed to 6.4-mm (¼-in.) size. In the case of ¼-in. material the sample shall then be mixed and riffled once to 50 lb, but larger samples shall be crushed and divided as follows:

9.2.1 *Coarse Material, 64 mm (2½ in.) maximum*—The 2000-lb sample shall be crushed in a heavy crusher provided with smooth plates of manganese steel to pass through a 1-in. (25.0-mm) sieve, mixed thoroughly by coning at least three times, and riffled to 250 lb.

9.2.2 *One-Inch Material*—The 250-lb sample shall be crushed in a heavy crusher provided with plates of manganese steel to pass a ¼-in. (6.3-mm) sieve. After having been mixed thoroughly by coning at least three times, it shall be riffled to about 50 lb.

9.2.3 *One-Fourth-Inch Material*—The 50-lb sample of 6.4-mm (¼-in.) material obtained in mixing and reduction of gross samples of 64 or 25.4-mm (2½ or 1-in.) material or in splitting the gross sample of ¼-in. material shall be further crushed in laboratory rolls to pass a No. 10 (2.00-mm) sieve, again

FIG. 2—*Continued.*

E 32

mixed thoroughly by coning, and riffled to 10 or 15 lb. This sample shall be crushed to pass a No. 20 (850-μm) sieve, mixed thoroughly by coning, and divided with a riffle to 1 lb or 500 g. The 500-g sample shall be mixed thoroughly by coning and divided by riffling into four portions of about 125 g each. Three of these portions shall be held in reserve, and one portion shall be pulverized in the hardened alloy-steel mortar to pass a No. 100 (150-μm) sieve. The pulverized sample shall be dried for 1 h at 105 to 110 C, poured upon glazed paper, mixed thoroughly, divided, if necessary, (Note 4) by quartering and then preserved in a well-stoppered bottle or bottles.

9.3 *Shipments over 20000 lb in mass*—When the shipment exceeds 20000 lb, it shall be divided as nearly as possible into lots of 20000 lb each or fraction thereof, and the resulting 1-lb or 500-g samples taken shall be combined and mixed thoroughly by coning at least three times. This sample shall then be divided by riffling to 1 lb or 500 g which weight shall be further divided and pulverized as in accordance with 9.2.2.

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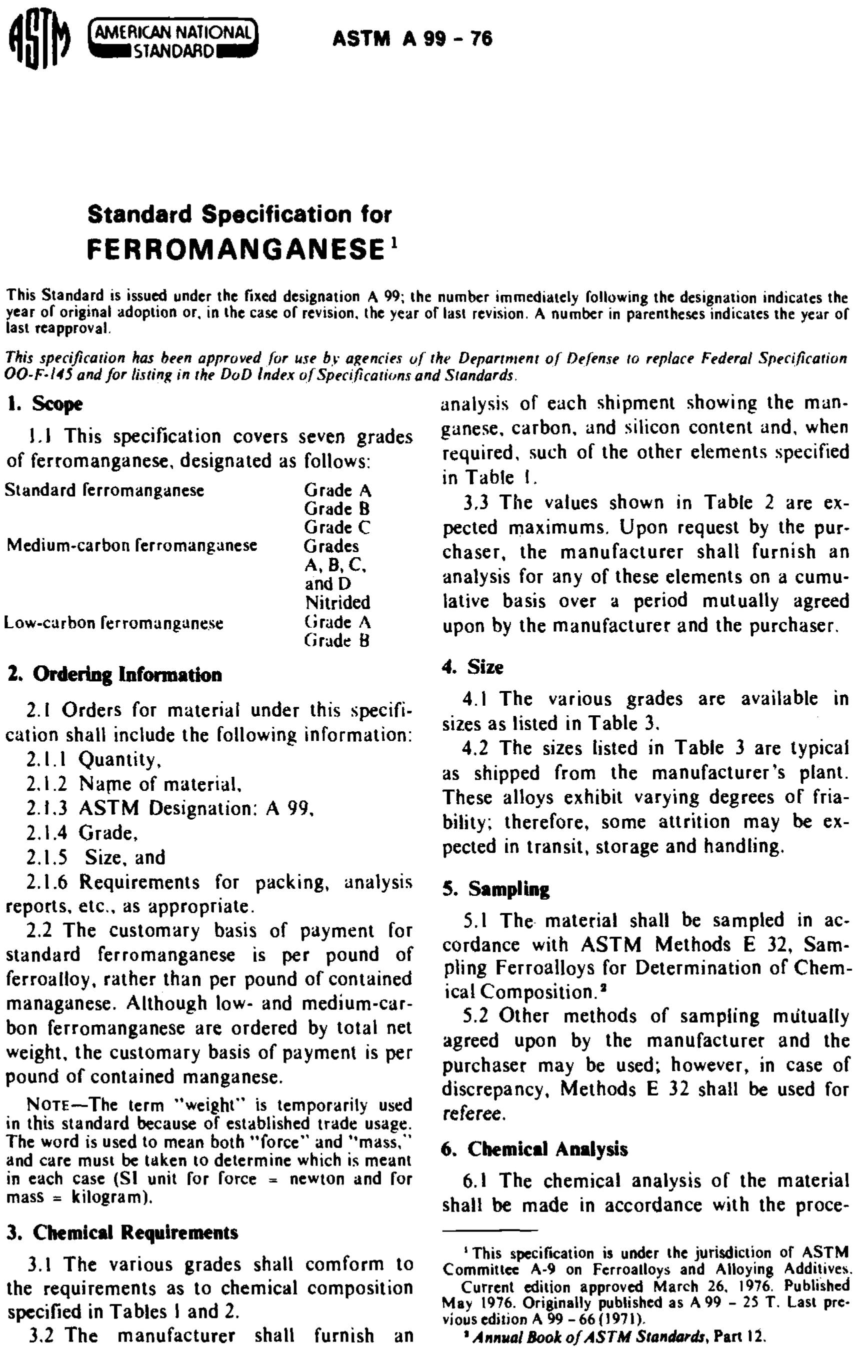
FIG. 2—*Continued.*

Another consideration was vanadium pentoxide, because it could be utilized by the tool steel industry. It was decided that vanadium pentoxide was more a raw material for the ferroalloy industry and that no one in tool steel manufacturing was using it; therefore, no specification was required.

I have discussed the steel industry's needs being reflected in the ferroalloy specifications. There is a reason why I went into this elaborate method of evaluating these ferroalloys and associating them with technology. I would like to describe a few examples. In 1934, tungsten powder, one of the initial specifications, was considered to be obsolete because of the passing of the crucible method of melting steel. It is interesting to note that this should occupy space as a standard specification over a 10-year period, so to speak, before being dropped. The tungsten powder specification was withdrawn because the then need for tungsten powder was for making tungsten carbide. Thus, because a higher-purity product was needed, a new specification had to be devised.

I mentioned that during World War II there were a number of NE steels which came to the foreground because of the shortage of nickel and chrome. Table 4 [*6*] lists several grades of boron alloys. It is interesting to note that out of all those listed, there are only three that are currently active. The rest of them, for one reason or another, have fallen by the wayside. This again indicates the progress made by the steelmakers utilizing ferroalloys, which brings up the next subject: What will the future hold for ferroalloy standards?



AMERICAN NATIONAL STANDARD

ASTM A 99 - 76

Standard Specification for
FERROMANGANESE[1]

This Standard is issued under the fixed designation A 99; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

This specification has been approved for use by agencies of the Department of Defense to replace Federal Specification OO-F-145 and for listing in the DoD Index of Specifications and Standards.

1. Scope

1.1 This specification covers seven grades of ferromanganese, designated as follows:

Standard ferromanganese	Grade A Grade B Grade C
Medium-carbon ferromanganese	Grades A, B, C, and D Nitrided
Low-carbon ferromanganese	Grade A Grade B

2. Ordering Information

2.1 Orders for material under this specification shall include the following information:

2.1.1 Quantity,

2.1.2 Name of material,

2.1.3 ASTM Designation: A 99,

2.1.4 Grade,

2.1.5 Size, and

2.1.6 Requirements for packing, analysis reports, etc., as appropriate.

2.2 The customary basis of payment for standard ferromanganese is per pound of ferroalloy, rather than per pound of contained managanese. Although low- and medium-carbon ferromanganese are ordered by total net weight, the customary basis of payment is per pound of contained manganese.

NOTE—The term "weight" is temporarily used in this standard because of established trade usage. The word is used to mean both "force" and "mass," and care must be taken to determine which is meant in each case (SI unit for force = newton and for mass = kilogram).

3. Chemical Requirements

3.1 The various grades shall comform to the requirements as to chemical composition specified in Tables 1 and 2.

3.2 The manufacturer shall furnish an analysis of each shipment showing the manganese, carbon, and silicon content and, when required, such of the other elements specified in Table 1.

3.3 The values shown in Table 2 are expected maximums. Upon request by the purchaser, the manufacturer shall furnish an analysis for any of these elements on a cumulative basis over a period mutually agreed upon by the manufacturer and the purchaser.

4. Size

4.1 The various grades are available in sizes as listed in Table 3.

4.2 The sizes listed in Table 3 are typical as shipped from the manufacturer's plant. These alloys exhibit varying degrees of friability; therefore, some attrition may be expected in transit, storage and handling.

5. Sampling

5.1 The material shall be sampled in accordance with ASTM Methods E 32, Sampling Ferroalloys for Determination of Chemical Composition.[2]

5.2 Other methods of sampling mutually agreed upon by the manufacturer and the purchaser may be used; however, in case of discrepancy, Methods E 32 shall be used for referee.

6. Chemical Analysis

6.1 The chemical analysis of the material shall be made in accordance with the proce-

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[1] This specification is under the jurisdiction of ASTM Committee A-9 on Ferroalloys and Alloying Additives. Current edition approved March 26, 1976. Published May 1976. Originally published as A 99 - 25 T. Last previous edition A 99 - 66 (1971).

[2] *Annual Book of ASTM Standards*, Part 12.

FIG. 3—*ASTM ferromanganese specification.*

dure for ferromanganese as described in ASTM Methods E 31, Chemical Analysis of Ferroalloys,[2] or alternative methods which will yield equivalent results.

6.2 If alternative methods of analysis are used, in case of discrepancy, methods prescribed in Methods E 31 shall be used for referee.

6.3 Where no method is given in Methods E 31 for the analysis for a particular element, the analysis shall be made in accordance with a procedure agreed upon by the manufacturer and the purchaser.

7. Packaging

7.1 Ferromanganese shall be packaged in sound containers, or shipped in bulk, in such manner that none of the alloy is lost or contaminated in shipment.

8. Inspection

8.1 The manufacturer shall afford the inspector representing the purchaser all reasonable facilities, without charge, to satisfy him that the material is being furnished in accordance with this specification.

9. Rejection

9.1 Any claims or rejections shall be made to the manufacturer within 45 days from receipt of material by the purchaser.

TABLE 1 Chemical Requirements[A]

	Standard Ferromanganese			Medium Carbon Ferromanganese				Nitrided Medium Carbon Ferromanganese	Low Carbon Ferromanganese	
	Grade A	Grade B	Grade C	Grade A	Grade B	Grade C	Grade D		Grade A	Grade B
Manganese,[B] %	78.0 to 82.0	76.0 to 78.0	74.0 to 76.0	80.0 to 85.0	80.0 to 85.0	80.0 to 85.0	80.0 to 85.0	75 to 80[C]	85.0 to 90.0	80.0 to 85.0
Carbon, max %	7.5[D]	7.5[D]	7.5[D]	1.5	1.5	1.5	1.5	1.5[C]	As specified[E]	0.75
Silicon, max %	1.2	1.2	1.2	1.0	1.5	0.70	0.35	1.5[C]	2.0	5.0 to 7.0
Phosphorous, max %	0.35	0.35	0.35	0.30	0.30	0.30	0.30	0.3	0.20	0.30
Sulfur, max %	0.050	0.050	0.050	0.020	0.020	0.020	0.020	0.020	0.020	0.020
Nitrogen %								4% min		

[A] For purposes of determining conformance with this specification, the reported analysis shall be rounded to the nearest unit in the last right-hand place of figures used in expressing the limiting value, in accordance with the rounding method of ASTM Recommended Practice E 29, for Indicating Which Places of Figures Are to Be Considered Significant in Specified Limited Values.[2]

[B] *For purposes of determining the manganese content of any shipment, manganese shall be reported to the nearest 0.01 percent, applying the same rounding procedure as prescribed in Footnote A.*

[C] Based on metallic content.

[D] Carbon values shown are maximum; with normal silicon content, carbon will typically be in the range 6.9 to 7.2 percent.

[E] Grade A low carbon material may be obtained with the following maximum percentage of carbon 0.75, 0.50 and 0.10.

TABLE 2 Supplemental Chemical Requirements[A]

	Composition, max, percent		
	Standard Ferromanganese, All Grades	Medium-Carbon Ferromanganese, All Grades	Low-Carbon Ferromanganese, All Grades
Arsenic	0.30	0.15	0.10
Tin	0.020	0.010	0.010
Lead	0.050	0.050	0.020
Chromium	0.50	0.50	0.50

[A] For purposes of determining conformance with this specification, the reported analysis shall be rounded to the nearest unit in the last right-hand place of figures used in expressing the limiting value, in accordance with the rounding method of Recommended Practice E 29.

FIG. 3—*Continued.*

TABLE 3 **Standard Sizes and Tolerances**

Product	Standard Sizes	Tolerances[A]	
Standard ferromanganese Grades A, B, C	8 by 4 in.	90 lb lump, max	10 % max passing 4-in. sieve
	5 by 2 in.	10 % max retained on 5-in. (125-mm) sieve	10 % max passing 2-in. sieve
	4 by 1 in.	10 % max retained on 4-in. (100-mm) sieve	10 % max passing 1-in. (25-mm) sieve
	2 by ¼ in.	10 % max retained on 2-in. (50-mm) sieve	10 % max passing ¼-in. sieve
	⅜ in. by 12 mesh	5 % max retained on ⅜-in. (9.5-mm) sieve	5 % max passing No. 14 (1.40-mm) sieve
	¼ in. by down	5 % max retained on ¼-in. (6.3-mm) sieve	
	8 mesh by down	5 % max retained on No. 8 (2.36-mm) sieve	
	20 mesh by down	5 % max retained on No. 20 (850-μm) sieve	
Medium-carbon ferromanganese Grades A, B, C, and D	8 by 4 in.	90 lb lump, max	10 % max passing 4-in. sieve
	5 by 2 in.	10 % max retained on 5-in. sieve	10 % max passing 2-in. sieve
	4 in. by down	10 % max retained on 4-in. sieve	12 % max passing ¼-in. sieve
	2 in. by down	10 % max retained on 2-in. sieve	15 % max passing No. 8 sieve
	8 mesh by down	5 % max retained on No. 8 sieve	
Medium-carbon ferromanganese Nitrided grade	briquetted only		
Low-carbon ferromanganese Grades A and B	6 by 2 in.	10 % max retained on 6-in. sieve	10 % max passing 2-in. sieve
	4 by ¼ in.	10 % max retained on 4-in. sieve	5 % max passing ¼-in. sieve
	8 mesh by down	5 % max retained on No. 8 sieve	
	20 mesh by down	5 % max retained on No. 20 sieve	

[A] Specifications of sieve sizes used to define tolerances herein are as listed in ASTM Specification E 11, for Wire-Cloth Sieves for Testing Purposes (*Annual Book of ASTM Standards*, Part 41).

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, Pa. 19103, which will schedule a further hearing regarding your comments. Failing satisfaction there, you may appeal to the ASTM Board of Directors.

FIG. 3—*Continued.*

TABLE 3—*Summary ASTM ferroalloy specifications.*

A-98	Spiegeleisen	A-481	chromium metal
A-99	ferromanganese	A-482	chromium silicide
A-100	ferrosilicon	A-483	silicomanganese
A-101	ferrochromium	A-495	calcium silicide
A-102	ferrovanadium	A-550	ferrocolumbium
A-132	ferromolybdenum	A-601	electrolytic manganese
A-144	ferrotungsten	A-610	sampling and testing ferroalloys for determination of size
A-146	molybdenum oxide		
A-323	ferroboron		
A-324	ferrotitanium	A-636	nickel oxide sinter
		A-701	ferromanganese silicon

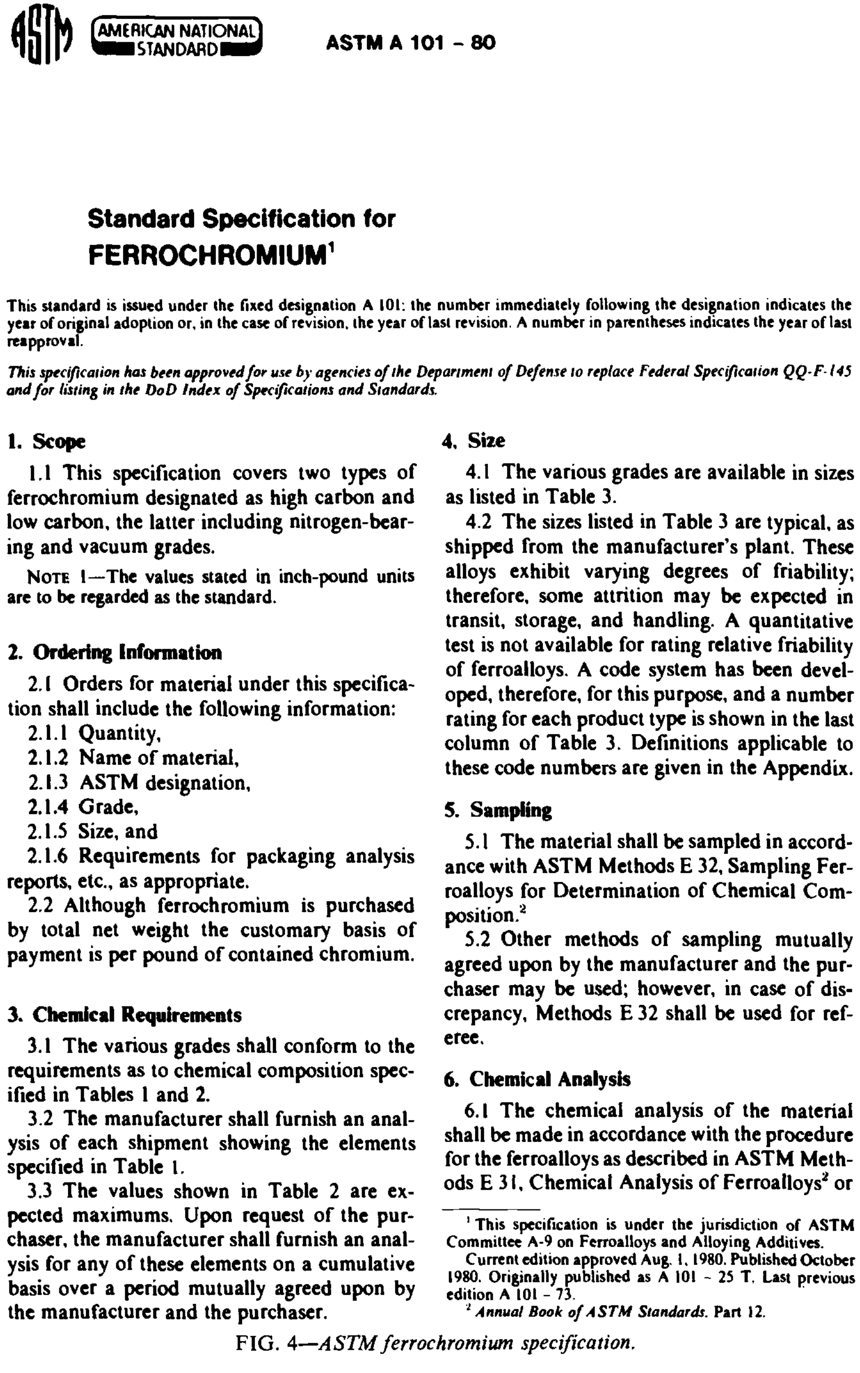
Ferroalloy Standards of the Future

As mentioned previously, not only has the chemistry changed to reflect the needs of the steel industry, but also the other attributes of ferroalloys as well, such as sizing, for example. At one time there were over 400 different sizes of the various ferroalloys. It appears from a supplier's standpoint that some standardization should be initiated. Steel industry consumers prefer lump ferroallloy material for furnace additions, but their ideas of lumps can vary from 20 by 10 to 10 by 2.5 cm (~8 by 4 to 4 by 1 in.), etc. Figure 5 shows one version of a lump. On the other hand, there are fines. No steelmakers want fines in their steelmaking shops. Fines cannot be tolerated. By fines, I mean products under 0.6 cm (1/4 in.) in size, because they get trapped in the slag and get carried away by the pollution-control devices installed in, not only the basic oxygen furnaces (BOF's), but the electric furnaces as well. Size, therefore, becomes an integral part of any standard. Should sizes be standardized?

What will it be? Will it be something like an ASTM austenite grain size chart where 10 by 2.5, 7.5 by 2.5, 7.5 by 1.25 cm (~4 by 1, 3 by 1, 3 by 1/2 in.)—however many that may be had—can reflect a different number?

Decide, What is a fine size? 0.5 cm (1/4 in.) down, 0.3 cm (1/8 in.) down, 8 mesh, 325 mesh, 500 μm? A prime example of fines is shown in Fig. 6. All we, as suppliers, do is reflect the industry preference. Not only the steel industry has preferences, but affiliated industries as well. And I cite, for example, the electrolytic manganese specification where weld rod requirements and their specifications are shown as a standard. They, in fact, really do need such fine material in order to coat weld rods. Will the weld rod industry, as the trend moves from coated rods to cored rods, alter the mesh sizing? It probably will. But how much, and who knows?

An interesting facet of the ferroalloy industry is the friability ratings. How will this rating influence customer's ordering, shipping, and handling? Once again there is no standard test developed, and friability is a property comparable to a machinability test in the steel industry; there is no one standard



AMERICAN NATIONAL STANDARD

ASTM A 101 - 80

Standard Specification for FERROCHROMIUM[1]

This standard is issued under the fixed designation A 101; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

This specification has been approved for use by agencies of the Department of Defense to replace Federal Specification QQ-F-145 and for listing in the DoD Index of Specifications and Standards.

1. Scope

1.1 This specification covers two types of ferrochromium designated as high carbon and low carbon, the latter including nitrogen-bearing and vacuum grades.

NOTE 1—The values stated in inch-pound units are to be regarded as the standard.

2. Ordering Information

2.1 Orders for material under this specification shall include the following information:

2.1.1 Quantity,

2.1.2 Name of material,

2.1.3 ASTM designation,

2.1.4 Grade,

2.1.5 Size, and

2.1.6 Requirements for packaging analysis reports, etc., as appropriate.

2.2 Although ferrochromium is purchased by total net weight the customary basis of payment is per pound of contained chromium.

3. Chemical Requirements

3.1 The various grades shall conform to the requirements as to chemical composition specified in Tables 1 and 2.

3.2 The manufacturer shall furnish an analysis of each shipment showing the elements specified in Table 1.

3.3 The values shown in Table 2 are expected maximums. Upon request of the purchaser, the manufacturer shall furnish an analysis for any of these elements on a cumulative basis over a period mutually agreed upon by the manufacturer and the purchaser.

4. Size

4.1 The various grades are available in sizes as listed in Table 3.

4.2 The sizes listed in Table 3 are typical, as shipped from the manufacturer's plant. These alloys exhibit varying degrees of friability; therefore, some attrition may be expected in transit, storage, and handling. A quantitative test is not available for rating relative friability of ferroalloys. A code system has been developed, therefore, for this purpose, and a number rating for each product type is shown in the last column of Table 3. Definitions applicable to these code numbers are given in the Appendix.

5. Sampling

5.1 The material shall be sampled in accordance with ASTM Methods E 32, Sampling Ferroalloys for Determination of Chemical Composition.[2]

5.2 Other methods of sampling mutually agreed upon by the manufacturer and the purchaser may be used; however, in case of discrepancy, Methods E 32 shall be used for referee.

6. Chemical Analysis

6.1 The chemical analysis of the material shall be made in accordance with the procedure for the ferroalloys as described in ASTM Methods E 31, Chemical Analysis of Ferroalloys[2] or

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[1] This specification is under the jurisdiction of ASTM Committee A-9 on Ferroalloys and Alloying Additives.

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[2] *Annual Book of ASTM Standards*, Part 12.

FIG. 4—*ASTM ferrochromium specification.*

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alternative methods that will yield equivalent results.

6.2 If alternative methods of analysis are used, in case of discrepancy, Methods E 31 shall be used for referee.

6.3 Where no method is given in Methods E 31 for the analysis for a particular element, the analysis shall be made in accordance with a procedure agreed upon by the manufacturer and the purchaser.

7. Packaging

7.1 The material shall be packaged in sound containers, or shapped in bulk, in such a manner that none of the product is lost or contaminated in shipment.

8. Inspection

8.1 The manufacturer shall afford the inspector representing the purchaser all reasonable facilities, without charge, to satisfy him that the material is being furnished in accordance with this specification.

9. Rejection

9.1 Any claims or rejections shall be made to the manufacturer within 45 days from receipt of material by the purchaser.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, Pa. 19103, which will schedule a further hearing regarding your comments. Failing satisfaction there, you may appeal to the ASTM Board of Directors.

FIG. 4—*Continued.*

TABLE 1 Chemical Requirements[A]

Type Ferrochromium	Composition, %						
	Grade	Chromium	Carbon	Silicon	Sulfur, max	Phosphorus, max	Nitrogen
High carbon	A	52.0–58.0	6.0–8.0	6.0 max	0.040	0.030	...
	B	55.0–64.0	4.0–6.0	8.0–14.0	0.040	0.030	...
	C	62.0–72.0	4.0–9.5	3.0 max	0.060	0.030	...
Low carbon	A	60.0–67.0	0.025 max	1.0–8.0	0.025	0.030	...
	B	67.0–75.0	0.025 max	1.0 max	0.025	0.030	...
	C	67.0–75.0	0.050 max	1.0 max	0.025	0.030	...
	D	67.0–75.0	0.75 max	1.0 max	0.025	0.030	...
Vacuum low carbon	E	67.0–72.0	0.020 max	2.0 max	0.030	0.030	...
	F	67.0–72.0	0.010 max	2.0 max	0.030	0.030	...
	G	63.0–68.0	0.050 max	2.0 max	0.030	0.030	5.0–6.0
Nitrogen bearing		62.0–70.0	0.10 max	1.0 max	0.025	0.030	1.0–5.0

[A] For purposes of determining conformance with this specification, the reported analysis shall be rounded to the nearest unit in the last right-hand place of figures used in expressing the limiting value, in accordance with the rounding method of ASTM Recommended Practice E 29, for Indicating Which Places of Figures Are to Be Considered Significant in Specified Limiting Values.[2]

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TABLE 2 Supplementary Chemical Requirements[A]

Type	Composition, max, %					
	High Carbon		Low Carbon	Vacuum Low Carbon[B]		Nitrogen Bearing
Grade	A, B	C	All Grades	E, F	G	–
Nitrogen	0.050	0.050	0.12	0.050	[C]	[C]
Manganese	0.75	0.75	0.75	0.75	0.75	0.75
Nickel	0.50	0.50	0.50	0.50	0.50	0.50
Vanadium	0.50	0.50	0.50	0.50	0.50	0.50
Copper	0.050	0.050	0.050	0.050	0.050	0.050
Molybdenum	0.050	0.050	0.050	0.050	0.050	0.050
Columbium	0.050	0.050	0.050	0.050	0.050	0.050
Tantalum	0.050	0.050	0.050	0.050	0.050	0.050
Cobalt	0.10	0.10	0.10	0.10	0.10	0.10
Aluminum	0.25	0.25	0.10	0.10	0.10	0.10
Titanium	0.50	0.10	0.050	0.050	0.050	0.050
Zirconium	0.050	0.050	0.01	0.01	0.01	0.01
Antimony	0.01	0.01	0.01	0.01	0.01	0.01
Arsenic	0.005	0.005	0.005	0.005	0.005	0.005
Lead	0.005	0.005	0.005	0.005	0.005	0.005
Tin	0.005	0.005	0.005	0.005	0.005	0.005
Zinc	0.005	0.005	0.005	0.005	0.005	0.005
Boron	0.005	0.005	0.005	0.005	0.005	0.005
Silver	0.005	0.005	0.005	0.005	0.005	0.005
Bismuth	0.005	0.005	0.005	0.005	0.005	0.005

[A] For purposes of determining conformance with this specification, the reported analysis shall be rounded to the nearest unit in the last right-hand place of figures used in expressing the limiting value, in accordance with the rounding method of Recommended Practice E 29.

[B] The inert oxide (SiO_2 + CaO + MgO + Al_2O_3) content of vacuum low-carbon ferrochromium shall be specified as 3.50% max.

[C] See Table 1.

FIG. 4—*Continued.*

TABLE 3 Standard Sizes and Tolerances

Product	*Standard Sizes*	*Tolerances*		Friability Ratings
Ferrochromium:				
High-carbon	8 in. (200 mm) by 4 in. (100 mm)	10 in. (250 mm), max	10 %, max, passing 4-in. (100-mm) sieve	4
	6 in. (150 mm) by down	10 %, max, retained on 6-in. (150-mm) sieve		
	5 in. (125 mm) by 2 in. (50 mm)	10 %, max, retained on 5-in. (125-mm) sieve	10 %, max, passing 2-in. (50-mm) sieve	
	4 in. (100 mm) by ½ in. (12.5 mm)	10 %, max, retained on 4-in. (100-mm) sieve	10 %, max, passing ½-in. (12.5-mm) sieve	
	3 in. (75 mm) by 1 in. (25 mm)	10 %, max, retained on 3-in. (75-mm) sieve	10 %, max, passing 1-in. (25-mm) sieve	
	3 in. (75 mm) by ¼ in. (6.3 mm)	10 %, max, retained on 3-in. (75-mm) sieve	10 %, max, passing ¼-in. (6.3-mm) sieve	
	¼ in. (6.3 mm) by down	5 %, max, retained on ¼-in. (6.3-mm) sieve		
	8 mesh (2.36 mm) by down	5 %, max, retained on U.S. No. 8 (2.36-mm) sieve		
Low-carbon	8 in. (200 mm) by down	10 in. (250 mm), max		1
	8 in. (200 mm) by 4 in. (100 mm)	10 %, max, retained on 8-in. (200-mm) sieve	5 %, max, passing 4-in. (100-mm) sieve	
	4 in. (100 mm) by down	10 %, max, retained on 4-in. (100-mm) sieve		
	3 in. (75 mm) by 1 in. (25 mm)	10 %, max, retained on 3-in. (75-mm) sieve	10 %, max, passing 1-in. (25-mm) sieve	
	8 mesh (2.36 mm) by down	5 %, max, retained on U.S. No. 8 (2.36-mm) sieve		
Vacuum low carbon	brick or pellet	designated by manufacturer		

FIG. 4—*Continued.*

to evaluate it and everybody seems to have his own. The specifications as we have them now were shown as developed by Earl Saunders. Efforts will be made to standardize such a test so that all ferroalloys can be included.

Packaging has also changed, although it is generalized in the ASTM specification. Every supplier of ferroalloys has specific packaging standards. Will this also reflect the need for ferroalloys? It appears that not only sizing but packaging as well will reflect some of those technological advances. In the current days of the BOF where tonnage items such as ferromanganese and ferrosilicon are handled in bulk quantities, sizing becomes a specific, and a very critical, attribute. Will packaging change to protect sizing? In many instances, it already has.

Other requirements for the future are the alloys themselves, for which there are no standards; for example, the desulfurizing agents. As people in the steel industry realize, sulfur level is of very critical importance. It affects not only ductility and machinability, but also tensile properties, hardenability, and inclusion distribution. The trend, of course, is for lower and lower sulfur because of the metallurgical improvements one can obtain, if not through total elimination, through inclusion control. Whether a company desulfurizes the hot metal or whether they desulfurize the steel made therefrom, it is an important facet of the iron and steelmaking process.

TABLE 4—*Boron-bearing ferroalloys.*

Name	Typical Composition, Weight %										Recommended Addition, lb per Ton			Producer[b]
												Open Hearth		
	B	Ti	V	Zr	Al	Si	Mn	C	Fe	Other	Electric Furnace	<0.30 C	>0.30	
Silvaz No. 3	0.55 to 0.75	9 to 11	9 to 11	5 to 7	5 to 7	35 to 40	. . .	. . .	balance	. . .	6	6	4	1
Silcaz No. 3	0.55 to 0.75	9 to 11	. . .	3 to 5	6 to 8	35 to 40	. . .	. . .	balance	9 to 11 Ca	6	6	4	1
Bortam	1.5 to 1.9	16 to 18	. . .	. . .	13 to 15	20 to 22	21 to 24	<1	balance	. . .	4.5	4.5	3	2
Carbortam	0.9 to 1.15	14 to 17	. . .	. . .	1 to 2	2.5 to 3	0.1 to 0.2	6.5 to 7.5	balance	0.1 to 0.2 Cr	4.5	4.5	3	2
Borosil	3 to 4	. . .	. . .	. . .	. . .	40	. . .	. . .	balance	. . .	3	3	2	3
Manganese-boron	15 to 20	. . .	. . .	. . .	. . .	<1.5	balance	<3	<5	. . .	[a]	[a]	[a]	1
Nickel-boron	15 to 18	. . .	. . .	. . .	<1	<1.5	. . .	<0.5	<3	balance Ni	[a]	[a]	[a]	1
Grainal No. 79	0.5	20	. . .	4	13	. . .	8	. . .	balance	. . .	6	6	4	4
Grainal No. 1	0.2	15	25	. . .	10	. . .	. . .	. . .	balance	. . .	6	6	4	4
Grainal No. 6	0.2	20	13	. . .	12	. . .	. . .	. . .	balance	. . .	6	6	4	4
Ferroboron	17.5	. . .	. . .	. . .	0.5	1.5	. . .	. . .	balance	. . .	0.75	0.75	0.5	1
Ferroboron	12	. . .	. . .	. . .	. . .	4	. . .	<3	balance	. . .	1.2	1.2	0.8	5
Fused boron trioxide glass	31	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	99B_2O_3	[a]	[a]	[a]	. . .
Pyrobor	22	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	100 $Na_2B_4O_7$	[a]	[a]	[a]	. . .
Boron carbide	80	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	100 B_4C	[a]	[a]	[a]	6

[a] Not normally recommended for adding boron to steel.

[b] 1. Electrometallurgical Co.
2. Titanium Alloy Manufacturing Co.
3. Ohio Ferro Alloys Co.
4. Vanadium Corp. of America.
5. Molybdenum Corp. of America.
6. Norton Co.

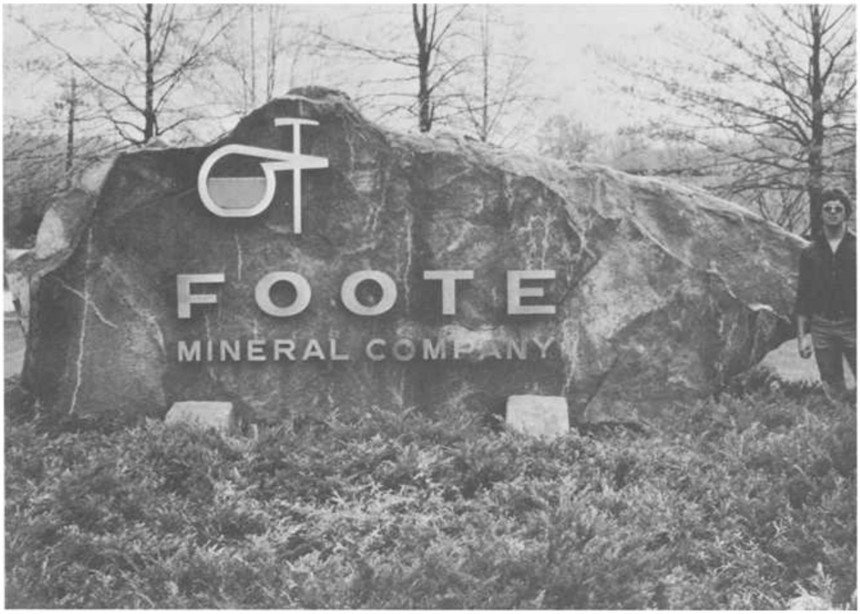

FIG. 5—*Lump product example.*

Another alloy is the magnesium-containing ferrosilicon. At present, A-9 is working on just such a specification via its Subcommittee A-9.03. These alloys have become very prominent because of the industry's need for lower and lower sulfur levels. Ferrozirconium and ferrozirconium-silicon have also come into use and, as yet, we have no specification for them. They are being studied by the same subcommittee.

Metallurgical practices have also influenced the types of alloys required. We have now entered into the period where rare earth compounds are used to control inclusion shapes and distribution. There are certainly several suppliers of these products, and one wonders if they could be combined into a single specification. Should they?

Now for future work. We feel that the chilling factor of ferroalloys could be significant. This varies from alloy to alloy and there is no particular agreement on the chill effect of the various ferroalloys, particularly when comparing lumps versus fines versus intermediate sizing. We feel that extensive work could be done in this area.

We are unsure which ferroalloys will be in effect by the year 2000. We feel that the present alloys are adaptable to steel technology and can be altered to reflect changing steel technology. What this may be will depend upon the requirements of the steel industry in the upcoming years. Committee A-9 is ready to serve the steel industry by updating through systematic review of

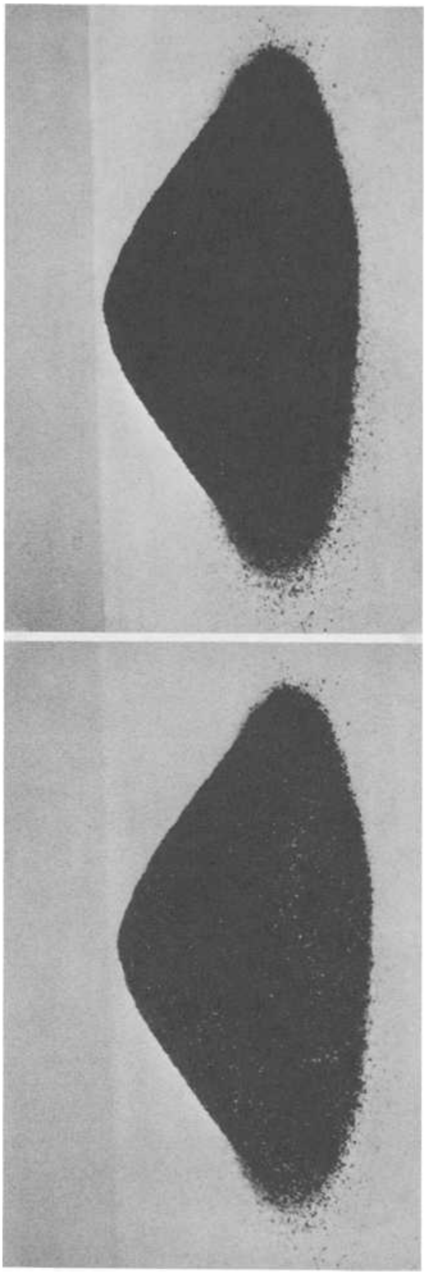

FIG. 6—*Fines* (left) *and finer fines* (right) *product examples.*

specifications and untried new ones, including those of current interest, and thereby protect not only the consumer, but the supplier as well.

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[*1*] *Proceedings*, American Society for Testing and Materials, 1925.
[*2*] *Transactions*, American Institute of Mining, Metallurgical, and Petroleum Engineers, Vol. 62, 1925.
[*3*] *1980 Annual Book of Standards—Part 2*, American Society for Testing and Materials.
[*4*] Cook, A. G., "Work of the ASTM A-9 Committee on Ferroalloys," *Proceedings*, Electric Furnace Conference, American Institute of Mining, Metallurgical and Petroleum Engineers, 1976.
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[*6*] Udy, M. C., "Boron and Steel—Principles and Practice" in *Proceedings*, Electric Furnace Conference, American Institute of Mining, Metallurgical and Petroleum Engineers, 1951.

P. L. Weston[1]

International Activities of Committee A-9

REFERENCE: Weston, P. L., "**International Activities of Committee A-9,**" *Ferroalloys and Other Additives to Liquid Iron and Steel, ASTM STP 739,* J. R. Lampman and A. T. Peters, Eds., American Society for Testing and Materials, 1981, pp. 32–39.

ABSTRACT: The International Organization for Standards (ISO) was formed in 1949 to establish organizational working procedure and working groups to formulate international test standards for materials. In this work national government agencies have contributed largely to the ISO program (one notable exception being the United States.) Recent expansion has been in product performance, air quality, and reference materials. The ISO is organized via a council formed by three elected officers and 14 member organizations. An executive committee handles administrative duties and a general assembly of all member organizations is the working body. An appointed Secretary-General is the chief executive of ISO. A plenary meeting held every three years constitutes the ISO working meeting.

ISO standards are originated as working documents from a small working group or task group. Upon approval by a subcommittee the document becomes a draft proposal and is given an identification number. After approval by the technical committee, the proposal becomes a draft international standard (DIS). This document is published as an international standard after ratification by 75 percent of the general assembly voters. At present there are 160 active ISO technical committees, 550 subcommittees and over 1000 working groups or task groups. The ferroalloys technical committee (TC 132) functions in three subcommittee areas: SC-1 Sampling, SC-2 Chemical Analyses, and SC-3 Specifications. As of 1980, twenty-seven proposed standards for ferroalloys are in various stages of development.

KEY WORDS: standards, international standards, ASTM A-9, technical advisory group, secretariat, ferroalloys

Since World War II the United States has been the dominant industrial and economic force in the world. Besides being directly involved in the industrial rebuilding of Germany and Japan, the United States concurrently established her own supremacy in new technology industries such as computers, space travel, medicine, and rare metals.

Now after three decades or so, we are harassed by a variety of powerful irritants—the energy/liquid fuel problem, often times encouraged by an eth-

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nic control group called the Oil Producing and Exporting Countries (OPEC), raging double-digit inflation, environmentalist pressure to preserve and conserve, stronger organizational efforts in the political arenas, Office of Safety and Health Administration (OSHA) edicts, Equal Employment Opportunity Commission (EEOC) demands, Equal Rights Amendment, and a host of other government regulations, interventions, and hard face controls. Third-World developments using our support of cheap currency loans, and enjoying the obvious economic advantages of lower-cost raw materials, power, and labor, are fast becoming real competition in the marketplace. But surely as we look around us in our affluence—it comes as no new shock—the great United States of America can no longer dictate world economy with her technological advantage. Now we must learn "real quick-like" that cooperation with the rest of the industrial world becomes a necessity for our economic survival. In the past, as the world industrial leader, the United States had little, if any, incentive to spend time and energy getting involved in international standards on a global basis. In 1949 when the International Organization for Standardization (ISO) was being formed, the United States was represented by the American National Standards Institute (ANSI). The initial work of ISO concentrated on the dull tasks of (1) formating the ISO organizational arrangement and working procedures and (2) establishment of working groups to formulate internationally acceptable test standards. After 30 years the organization is well established and a number of technical groups have been active in the traditional subjects of standardization. The expansion of technical standardization may be shown by the more recent developments. For example, the ISO has expanded into product performance in the Committee on Mechanical Testing, TC 164. U.S. representation in this sector is via the Metals Property Council formed by a coalition of engineering and metals societies. The Council also assumes financial obligations of membership and involvement in Committee TC 164.

Just released in February 1980, the U.S. Environmental Protection Agency (EPA) is supporting the ASTM Subcommittee D-22.09 work on ISO/TC 146—Air Quality Measurement Methods. ASTM Subcommittee D-22.09 will administer the Secretariat of TC 146's Subcommittee 2 on Work Place Atmospheres. A number of technical organizations (government, industry, and professional societies) agreed to provide technical support on this topical issue. Also, recently, the ISO has established a Council Committee on Reference Materials (REMCO) in order to develop guidelines for certification and availability of reference materials in international standards. It is encouraging to note that concerned governmental agencies are involved in these new ISO ventures. However, the United States remains the only country which does not supply direct tangible government support for ISO activities. So far, U.S. industries have given some limited financial support but have supplied much of the technical expertise in ISO committee work.

Now I do not advocate government involvement in international standards for political motivation. There is plenty of activity in the technico-political arena by a number of agressive nations. Virtually all the participants (notable exceptions are the United States and Great Britain) in the ISO program are backed by the facilities and personnel of national governmental bodies or technical agencies. I feel quite confident in our present posture of representation by technical societies or organizations most competent and most interested in that particular field. Similarly, the technical publications recognize our involvement and the results of our work in international standards.

I do suggest that some form of formalized backing be indicated by our government. A coordinated approach by industry and government appears to be inevitable if we are to exercise much influence on the international standards program. Other countries are beginning to use international standards to develop economic and commercial policy, that is, certification standards or product standards that will affect international trade. Even the General Agreement on Tariffs and Trade (GATT) code allows nonuse of an international standard as a criterion for filing a complaint. A clear explicit expression of U.S. Government support for our representation in international standards would really increase our stature and bargaining strength at the technical sessions.

Standardizations in itself can exert control over the economic use of natural resources and materials in accordance with national policies. The control of raw material economics and manufactured goods can affect both export or internal consumption. Emerging nations can benefit from international standards, making use of published expertise on specifications and methodology for their own industrial development. International standards are fast becoming a necessity for equitable trade relationships between countries of varied cultures or business philosophy. Apart from commercial items, the development of prescribed clean air standards, water pollution, worker safety, and product liability are rapidly accelerating toward more effective controls, especially via governmental agencies, throughout the world.

The development of all these disciplines into a common workable relationship will undoubtedly use a bit of the worlds' technical energies in the future. No culture or community will knowingly maintain a direct road to death or destruction. On the other hand, overenthusiastic environmentalists can stifle an industry—even a nation—to its capitulation. One common basis for mankind to resolve these problems is the consensus standards agreed upon by the world communities. To be knowledgeable is to be forearmed in the technological conflicts of the future. A common knowledge that can bind the participants into a singular purpose will most assuredly develop the strength necessary to hammer out the survival and growth guidelines for our technological society of the 20th century.

ISO Organizational History

The first meeting of the International Standards Organization took place in Paris, France, 1949. It was established that the executive structure of ISO maintain the offices of president, vice president, treasurer, and secretary-general and that business be conducted by groups of member bodies called the Council, the Executive Committee, and the General Assembly.

The Council is formed by the president, vice president, treasurer, and fourteen member bodies. The Council has the responsibility of the operation and administration of the ISO. Meetings are scheduled at least once a year.

The Executive Committee is composed of the vice president and three to seven representatives of member bodies. This committee assists the council in matters of administration, organization, and finance.

The General Assembly is the policy working body of the ISO comprising member body delegates. Meetings are convened at least once every three years (normally every three years since the initial Paris meeting in 1949).

The Council appoints a secretary-general, who may be likened to a chief operating officer (COE). The secretary-general is in charge of the Central Secretariat office, which in turn coordinates the work of the ISO technical committees. The secretary-general also represents the ISO in relationship with other international organizations, applies the constitution, rules of procedure, and directives in the technical work of ISO.

Executive Administration Groups

Council	Administrative committee composed of the president and fourteen member body representatives
Executive Committee	A task group composed of the vice president and three to seven member body representatives
General Assembly	All the member body representatives with elected president, vice president, secretariat-general, executive committee, and advisory committees
Technical Meeting	A meeting of a Technical Subcommittee to develop standards relating to the subcommittee assignment
Plenary Meeting	A meeting of all members of a technical committee (for example, TC 132—Ferroalloys) concurrent with meetings of all subcommittees
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
ANSI	American National Standards Institute
ISO	International Organization for Standardization

IEC	International Electrotechnical Commission (similar to ISO)
O	Observing members of a committee
P	Participating (voting) members of a committee
C	Corresponding members
Secretariat	Participating member designated or elected as leader of a technical committee
Secretariat-General	Secretariat of the ISO

Abbreviations

TC	Technical Committee (approximately 160)
SC	Subcommittee; subgroups of the technical committees composed of five or more members with a secretariat (approximately 550)
WG	Working Group: set up by a TC or SC to work on a particular problem (approximately 750)
TG	Task Group: subgroup of a working group to develop particular working documents (approximately 250)
TAG	Technical Advisory Group represents a member body in a technical committee; the chairman of the TAG is usually the voting delegate at technical committee meetings
WD	Working Document: presented by a member body for consideration as a draft proposal (often a national standard)
PDP	Preliminary Draft Proposal: an original document submitted to subcommittee from a working group
DP	Draft Proposal: document developed from a preliminary draft proposal incorporating comments from committee members. There may be any number of draft proposals identified as first, second, third, etc.
DIS	Draft International Standard: a draft proposal that has been approved by a majority vote. A DIS draft is submitted by the Technical Committee Secretariat to the ISO General Secretariat for distribution and final approval by the Council. The DIS is submitted to the Council for letter ballot or comments or both. It must be approved by 75 percent of the ballots cast. Upon approval by Council and Editorial Committee (EDCO) approval of the printer's proofs, the document is published as an international standard.

Technical Committee Structure

The Secretariat convenes all the meetings of the technical committees and subcommittees, sets voting procedures, and distributes documents to the member bodies. Membership status in the technical committees may be "P" participating member, "O" observer member, or "C" correspondent member (normally an organization from developing countries that do not have a national standards body). A technical committee is formed to carry on the standards work within one natural area of expertise (usually defined by an industry or technology). International standard work is performed through the action of over 150 ISO technical committees (TC's). Most technical committees divide specific elements of their responsibility into subcommittees (SC's) or working groups (WG's). Today there are over 500 subcommittees, 700 working groups, and over 250 special study groups working under the direction of ISO. To illustrate this type of organization, let us examine the ferroalloys under the responsibility of Technical Committee 132, with three subcommittees:

Ferroalloys Subcommittees—

TC 132/SC 1	Ferroalloys—Sampling Secretariat: Mr. W. C. Mizin—deputy director of the Institute of Research in Metallurgy, Tcheliabinsk, U.S.S.R.
TC 132/SC 2	Ferroalloys—Chemical Analysis Secretariat: Mr. L. Danielson—director of Swedish Institute for Metals Research, Stockholm. References to X-ray fluorescence and atomic absorption methods to be considered after the wet methods are agreed upon (includes titration, gravimetric or photoelectric measurements).
TC 132/SC 3	Ferroalloys—Specifications (Physical and Chemical). Dr. Frank from DIN, Deutsches Institut fur Normung, e.V., Zweigstelle, Koln, West Germany.

Each member body of the ISO assembly designates a technical advisory group (TAG) on the respective technical committees. ASTM Committee A-9 on Ferroalloys has the TAG for TC 132 (Ferroalloys) from ANSI, the United States member body of ISO. The role of the technical society (that is, ASTM, AISI, ASME, etc.) within the TAG group/or technical committee or both has really defied definition. This presence of inferred jurisdiction as compared with conferred authority to act on behalf of the national industry quite often inhibits decisive action by the delegation at technical committee meetings.

Current Activities

As of this date, there are twenty-seven proposed standards at various stages of development in Ferroalloys Technical Committee 132. Five standards deal with sampling:

DRS 3713	General rules of sampling and sample preparation; initiated 1971; did not pass TC 132 DIS vote.

DP 4551	Sampling for size and analysis; initiated 1972; did not pass TC 132 DIS vote.
DP 4552.1	Sampling and sample preparation for chemical analysis: Part 1—FeCr, FeCrSi, FeSi, SiMn, and FeMn; initiated 1975; second draft vote in 1980.
DP 4552.2	Sampling and sample prep for chemical analysis: Part 2—FeTi, FeMo, FeW, FeNb (FeCb); initiated 1976, first draft being written.
DP 7087	Experimental methods in sampling for evaluation of quality variation and precision; initiated 1977; first draft composed and distributed for comments.

Twelve standards concern chemical analysis.

DIS 4139	FeSi; determination of aluminum by atomic absorption; initiated 1974; sent to Central Secretariat for Council vote.
DIS 4173	FeMo; determination of molybdenum gravimetrically; initiated 1974; approved by TC 132 members.
DIS 6467	FeV; determination of vanadium potentiometrically; initiated 1974; approved by TC 132 members.

Nine proposals are being submitted to the Central Secretariat to be registered as draft proposals:

1 Ti in FeTi
2 Nb in FeNb (chemical)
3 Nb in FeNb (X-ray)
4 W in FeW (chemical)
5 W in FeW (X-ray)
6 Carbon in ferroalloys
7 Sulfur in ferroalloys
8 Phosphorus in ferroalloys
9 General X-ray methods of ferroalloy analysis

Ten specifications standards have been completed for presentation to the Council:

DIS 5445	FeSi
DIS 5446	FeMn
DIS 5448	FeCr, March 1980
DIS 5447	SiMn
DIS 5449	FeCrSi
DIS 5450	FeW
DIS 5451	FeV
DIS 5452	FeMo

DIS 5453	FeNb (FeCb)
DIS 5454	FeTi

The first four specification standards on the foregoing list were previously rejected by the Council vote. As of this date, I am not aware of any international standard published from TC 132—Ferroalloys. (Since this symposium five specification standards have been published in 1980.)

As may be realized, this work on international standards for ferroalloys is becoming quite active since many of the standards are approaching publication. Those of us who have attended the sessions can only re-emphasize the fact: International standards will become more and more important in the future and unless the United States maintains active participation (being present) at the technical sessions, the results will be established without our input. I for one strongly advocate that ASTM Committee A-9, with all the assistance we can generate, increase our presence in ISO TC 132 activities, at least for the next four years.

R. E. Corder[1]

Stockpile Focus on Ferroalloys

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ABSTRACT: This paper deals with stockpiling of various ferroalloys in the National Defense Stockpile. The purpose and philosophy of stockpiling various forms of strategic and critical materials for national defense emergencies are discussed in addition to a historical review of the background and history of stockpiling various ferroalloys.

The methodology and econometric computer modeling used to calculate the overall stockpile quantities are described as well as the method used for calculating specific quantities of each ferroalloy. The potential pitfalls and problems associated with changes in specifications, industry usage patterns, and geographical shifts in production centers are included in the discussion.

The results of the use of the new methods and the effects on future stockpiling plans are presented.

KEY WORDS: goals, annual materials plan, supply, requirements, inventory mix

Why do we stockpile ferroalloys? What are our goals? As Table 1 indicates, the ferroalloys in the National Defense Stockpile represent a significant amount of money and material.

Goals also represent much more. They represent the vulnerability of the United States to a shortage or loss of production during a supply interruption or a wartime emergency.

Inventories represent readily available material for immediate use during an emergency surge period while the U.S. ferroalloy industry is gearing up to handle increased requirements.

Inventories also represent material to be used in emergency situations where sudden increased demand exceeds the capacities of domestic production facilities.

And, more recently, inventories represent a stockpiling of energy, transportation services, and labor, all of which would be in short supply in the event of an emergency.

How did all of this start? Where do we stand now and where are we going?

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TABLE 1—*National Defense Stockpile.*

Material	Desired Inventory Mix	Inventory (ST)[a]	Value ($ millions)
FeCr HC[b]	185 000	402 000	278
FeCr LC[c]	75 000	300 000	394
FeCr Silicon	90 000	57 000	42
FeCb	0	598 000 (LB[e] Cb)	3
FeMn HC	439 000	600 000	273
FeMn MC[d]	0	29 000	22
FeMn silicon	0	24 000	12
FeW	0	841 000 (LB W)	10
FeV	1 000	0	0
			total 1034
Nickel	200 000	0	0
Cobalt	85 400 000	40 802 000 (lb Co)	1020

[a] Short tons (2000 lb).
[b] High carbon.
[c] Low carbon
[d] Medium carbon.
[e] Low boron.

History and Background

A brief history of stockpiling should begin with the creation of the Army-Navy Munitions Board in 1922 as the planning and policy office to provide for military needs only. Next came the Strategic Materials Act of 1939. However, this Act became virtually inoperable by 1940, when it was superceded by broader and more urgent mobilization programs.

The Strategic and Critical Materials Stock Piling Act of 1946, which amended the 1939 Act, was the basic legislation under which most of the stockpile material was acquired. Acquisition was at a low level from 1946–1950, sharply accelerating during the Korean War and tapering off during the middle and late fifties. There has been very little acquisition since then.

During the period of heavy acquisition, the Defense Production Act of 1950 and the Agricultural Trade Development and Assistance Act (1954) helped to provide a significant amount of material for the stockpile.

In July of 1979 the Congress passed the Strategic and Critical Materials Stock Piling Act Revision of 1979 (PL 96-41), which sets out specific guidance for stockpile activities. Some of the more important features are listed in the following.

1979 Strategic and Critical Materials Stock Piling Act

1. This is a *National Defense* stockpile and is not to be used for economic or budgetary purposes.
2. The stockpile is to cover the "military, industrial and essential civilian" needs of the nation for at least three years of an emergency.
3. Authorizations are required for both disposals and appropriations for acquisitions.
4. All moneys from the sale of stockpile commodities go into the "National Defense Stockpile Transaction Fund."

The act contains additional guidance and direction by encouraging barter arrangements for strategic materials and the development of domestic resources. Also required by the Act is the use, whenever possible, of competitive procedures and the avoidance of undue disruption of usual markets.

Another look at Table 1 shows the column marked "Desired Inventory Mix." Some of the ferroalloys in the stockpile inventory are higher than the targets while some are lower.

What are the goals? What do they stand for? How are they calculated or set and what causes them to change?

Goals are the successors to the old "objectives," but they are quite different. Goals are targets, they are not fixed as objectives were. Goals can and will change as new developments in data, technology, and domestic and international events occur. They are measures of the size of the nation's vulnerability to shortage in an emergency; they are points toward which progress will be made over a period of time. They definitely are not planned commitments to buy a specific quantity of material. We have three methods of achieving these goals: outright purchase, encouragement of increased domestic capacity, and barter. Each of the methods has several degrees of latitude that give the overall program more flexibility.

What brought about these new goals? What influences them and what do they include? Let us step back to 1975 and take a look.

Because there was general belief in 1975 that the existing configuration of the stockpile was substantially different from the ideal, and because of the inability to get disposal authorization from Congress, the Administration decided to conduct a study of every aspect of stockpiling: data, methods, basic assumptions about the type and length of emergency the nation should stockpile for, and also the sensitivity of the stockpile program to budgetary considerations, international conditions, and changes in commodities markets.

In August 1975 the National Security Council instructed the Administrator of General Services to chair the study, which included representatives from eight other federal agencies with stockpile responsibilities or interests. These agencies were State, Defense, Interior, Treasury, Office of Management and Budget (OMB), Council on International Economic Policy

(CIEP), Central Intelligence Agency (CIA), and General Services Administration (GSA). The Administrator delegated the chairmanship to the Director of the Federal Preparedness Agency. Numerous study groups prepared the technical analyses and an Interagency Steering Committee composed of high-level representatives from all eight agencies reviewed and monitored these activities on a frequent, often daily basis.

The most up-to-date modeling techniques available were used. These techniques made it possible to project what the economy would be in a wartime situation several years hence, what the resulting levels of industrial production would need to be, and what strategic and critical materials would be needed to support this production. That stage of activity has come to be known as "Phase I."

In February 1976 the National Security Council directed a follow-on study (Phase II). During the course of the study, a number of issues arose that could only be satisfactorily resolved by a Presidential decision.

In August 1976 President Ford approved the proposed new stockpile planning process.

In October of 1977 President Carter reaffirmed the 1976 Policy and Planning Process and specified that initial acquisitions provide a strong readiness posture for the first year of an emergency.

Highlights of the New Policy and Procedures

The stockpile study, therefore, resulted in the issuance of a new Presidential policy guidance providing for a stockpile capable of supporting U.S. defense requirements during a major war, over a three-year period, and assuming a prior large-scale industrial and defense mobilization. The new policy also provided for a broad range of basic civilian needs to ensure the health, welfare, morale, and productivity of the civilian population, and to maintain the vitality of the wartime economy.

Although in the 1976 study the Federal Emergency Preparedness Agency (FEMA) had developed a "new" methodology for estimating stockpile goals (formerly known as objectives), much of the traditional approach remained. For example:

1. Goals are still based on the shortfall of supplies compared to requirements.
2. Adjustments for "belt-tightening" of the civilian population are still made.
3. The reduced needs of the civilian population are still provided for.
4. Discounts of the supplies of foreign nations are still applied.

What has changed basically are the methods utilized to estimate the goals. More specifically, Figure 1 shows a simplified flow chart of the goal calculation procedure.

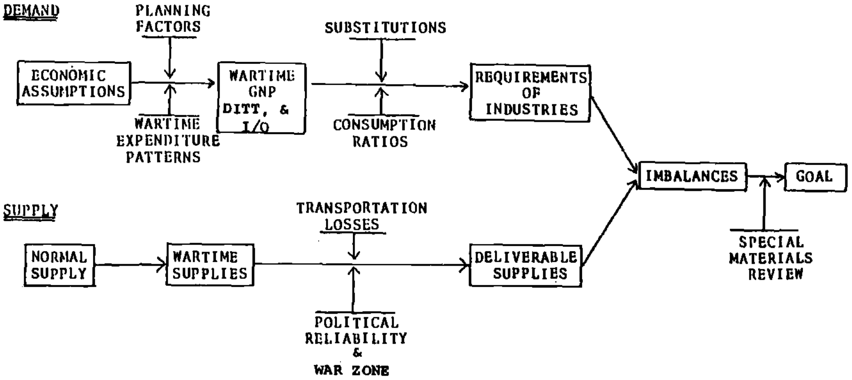

FIG. 1—*Stockpile estimation methodology.*

Goals (Fig. 1)

Instead of estimating goals by including defense requirements with the rest of civilian requirements, the following measures are taken:

1. The economy is divided into three separate sectors (defense, essential civilian, and basic industrial) and separate sets of requirements are estimated for each sector in each war planning year.
2. Separate supply estimates also are developed for each sector for each year.
3. Wherever the requirements exceed the supplies (in any sector in any year), the amount, an "imbalance," is recorded.
4. All the imbalances are added up for a material, and, for practical purposes, that total becomes the stockpile goal.

Requirements

Requirements estimates begin with estimates of wartime GNP for each year, then

1. The gross national product (GNP) is divided into the three sectors just mentioned, (defense, essential civilian, and basic industrial) and these in turn are separately converted to estimates of industrial production necessary to support the sectors.
2. The industrial production is related to trends in materials consumption rates for each industry to obtain quantity estimates of materials needed by American industries to support the war economy.
3. The materials quantities are reduced slightly to account for feasible substitution possibilities.

Supply

Supply estimates begin with data based on projections of expanded production possibilities from over 100 countries.

Each country is assigned wartime economic and political reliability rating and its supplies of stockpile materials are discounted based on that rating.

Transportation losses are applied to the remaining supplies of stockpile materials assumed to be available from each country.

Rationale for Sectors (Table 2)

A major reason for dividing the economy into three sectors is to be able to take national security priorities into account better than was done in the past. Older methods, by lumping all requirements together, could not distinguish that a pound of aluminum for a fighter plane is more important than a pound of aluminum for pots and pans in a home kitchen. The sectors were specified to include the following concepts:

Defense—All production necessary to obtain weapons, manpower and support, including the production necessary to support suppliers of Department of Defense (DOD) contractors.

Essential Civilian—Those expenditures necessary to maintain the health, safety, morale, and productivity of that segment of the population in support of the war or emergency.

Basic Industrial—Those expenditures which, after belt-tightening, are necessary to support the population and maintain a viable industrial base.

Through the use of different stockpile "planning factors" (such as rates of production and materials consumption), the confidence of meeting the requirements for each sector is varied in a way that provides very low risk in

TABLE 2—*Developing the stockpile matrix (one hypothetical material).*

Sector	Year 1	Year 2	Year 3
Defense	0	5	5
Essential civilian	5	10	15
Basic industrial	10	10	15
	15	25	35

total: 75
special review: 0
goal: 75

the defense sector, provides only moderate risk in the essential civilian sector, and provides a more optimistic outlook for the basic industrial sector.

After the goal for the basic element has been established, the next step is to determine which forms are most appropriate to stockpile. Materials such as chromium, columbium, manganese, tungsten, and vanadium are used in various forms by industry. The need for some forms will grow much faster than for others during an emergency. At this point, the domestic capacity to produce each form must be considered. This consideration is essentially a time-phased material balance of supply, form, and capacity.

Process for Calculating Goals for Upgraded Forms

1(*a*) Determine requirements by form for each tier, that is, high-carbon ferromanganese, low-carbon ferromanganese, pure metal.

(*b*) Start with defense tier. Subtract calculated supply, by form, from requirement; result is the adjusted requirement.

(*c*) Compare adjusted requirement with annual domestic capacity, by form. If capacity exceeds requirement, hold entire requirement in basic ore form and set open or unused capacity down to next tier. If requirement exceeds capacity, hold sufficient raw material (ore) to fill domestic capacity and hold quantity in excess of capacity in the upgraded form.

2. Repeat for each tier and each year. If capacity exceeds requirement, continue to subtract requirement from unused capacity and hold as basic raw material (ore). At the point when requirement exceeds open capacity, hold all additional requirements in the upgraded form. Total all nine years and tiers for amount in desired inventory mix.

Why do we stockpile ferroalloys? What is the inventory mix?

After the goals are calculated and the magnitude of our vulnerability to material shortages is known, a comparison can be made between the goal and our stockpile inventory for specific materials. The difference between our requirements and our inventory can be used as a relative measure of the need to restructure our stockpile inventory. A method of restructuring the stockpile in an incremental fashion has been devised. It is called the Annual Materials Plan.

The Annual Materials Plan (AMP) is a management device for implementing stockpile goals in a controllable and affordable manner. It contains a list of disposals and acquisitions proposed for a specific fiscal year. It is designed to reflect all factors that affect stockpile goals, as well as energy, environmental, and budgetary considerations, and that are to be integrated with the President's budget. Another important characteristic of the Plan is that it presents proposed acquisitions and disposals in one package. Sales and acquisitions in the next few years can be approximately balanced. The Plan gives a coherent picture of both sides of the stockpile program to the Congressional committees that approve appropriations or authorize disposals.

The AMP represents a major effort on the part of several agencies to develop each year a list of materials for stockpile acquisition or disposal. National security requirements must be balanced against market and budget constraints. The process is designed to encourage maximum interagency participation. All of the agencies represented on the Annual Materials Plan Steering Committee review and may recommend revisions to the proposed list of material in the light of their respective areas of interest.

The National Defense Stockpile Policy Division of FEMA provides a list of goals, shortfalls, excesses, and priorities to the Market and Technical Services Division, Federal Property Resources Service, GSA. After an evaluation of the market outlook, the Market and Technical Services Division proposes quantities of commodities for acquisition or disposal. These proposals are provided to the four AMP subcommittees, which furnish to the full committee their suggested revisions. Differences in these proposals and revisions are then resolved by the Steering Committee and submitted to the Director of FEMA for approval.

The four AMP subcommittees are:

1. Strategic Implications
2. International Economic & Political Impacts
3. Market Impact
4. Economic & Budgetary Impact

All of the foregoing information has been interesting, comprehensive, and general. What does all of this mean for the ferroalloy industry and what effect will stockpile policy have on the industry's future?

In the overall policy view, a manganese unit is a manganese unit and a chromium unit is a chromium unit, whatever the form, with reservations for domestic capacity to produce each form. The ideal mix in the stockpile inventory would be an exact duplicate of the most recent industry usage pattern form by form with added material for the producing sectors expected to surge during a wartime emergency. However, it would also be very expensive to restructure the inventory each time a major technological trend appeared. The change in low-carbon ferrochromium usage brought on by the argon oxygen decarburization (AOD) process and the current change in ferrochrome silicon usage are two examples of changes that could have an effect on the stockpile inventory mix.

An initial comparison of the low-carbon ferrochromium goal and inventory might indicate that there is some excess material that should or could be disposed of to raise revenue. However, a closer appraisal will show that those chromium units are eminently usable over a wide range of applications. They are also endowed with some very real cost-saving benefits. Energy, transportation, labor, and raw materials costs invested in that material have appreciated greatly over the years.

While the excess material may not be in the ideal form desired, its use as an alternative will provide a degree of flexibility in establishing industry priorities during an emergency. Additionally, the energy, labor, and transportation incorporated into these materials will ease the demand on those resources during an emergency.

One question arises: What about the conversion of some of the stockpile ore into upgraded forms? The answer is, a possibility yes, but the near-term probability is very low. The reasons for the low near-term probability are economic. The philosophy is that with a limited budget it is more prudent to acquire materials for which we have large goals and little or no inventory than to convert materials presently in the stockpile to a more desirable form. Also, with the changing usage patterns the risk of any technological obsolescence is much less if the material is held in the basic raw-material form. The latter reason holds only as long as the domestic capacity does not diminish.

The future of ferroalloys in the stockpile? They are an integral and important part of our materials preparedness posture. For the Stockpile Division, we shall continue to work at determining their production, supply, usage patterns, and specification changes in cooperation with industry and other government agencies. We intend to keep the stockpile as current and up to date as funds and market conditions permit. In this way we will be able to carry out our mandate "to prevent a dangerous and costly dependence upon foreign sources . . . during a period of national emergency."

DISCUSSION

P. L. Weston[1] (*written discussion*)—In reference to strategic raw materials stockpiles, I was privileged to visit virtually all of the alloy stockpiles in the United States. Most of the raw materials and in-process material are stocked relatively close to the usage center. But regarding material quality, do you have a formal ongoing program to replenish that material that has degradated to a nonusable condition, that is, ferromanganese stockpiles hydrated and oxidized to dust?

R. E. Corder (*author's closure*)—The structure and mechanism are in place for the rotation of stockpile materials subject to degradation. In most cases, this has been applied to agricultural and medicinal materials. Funding for this type of program has had a very low priority in the past. When the new stockpile program is funded and operational, it is hoped that more attention and resources can be devoted to upgrading the quality of some materials that have been degraded by time and the elements.

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Present State of U.S. Ferroalloy Industry

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ABSTRACT: This paper describes the major ferroalloys of chromium, manganese, and silicon, and examines the ferroalloy industry, its special needs, and its problems. The major producers and the market they serve are listed, and the manufacturing procedure and the materials required are illustrated. Sources of materials and their changing availability are reviewed along with geopolitical influences and their effects on domestic industry. Trends, short and long term, and what we can expect in the future conclude the presentation.

KEY WORDS: ferroalloys, chromium, manganese, silicon, geopolitics, steel, iron

Ferroalloys are masteralloys, originally intended to serve the iron and steel industry. These iron-based alloys supply the reactive elements necessary to process and alloy ferrous metals. Since the manufacturing techniques are similar, the industry has expanded to provide iron-free products to the nonferrous and chemical areas.

While many critical elements such as vanadium, columbium, molybdenum, and tungsten are found as ferroalloys, we are restricting this discussion to the major alloys, that is, those of silicon, manganese, and chromium. These are the tonnage metals of the industry, and are essential to nearly all phases of ferrous metallurgy.

A recent joint survey by the Environmental Protection Agency (EPA) and the Ferroalloy Association reported 20 companies, 44 plants, and 145 furnaces in 14 states. Actually, there are 14 different companies today that make one or more of these three ferroalloy products.

The industry is power-intensive. It had its roots in the French Alps, and Norway, and in this country at Niagara Falls, all areas where early hydropower was available. Since that time it has spread to other low-cost industrial power areas, such as the Ohio Valley, Tennessee Valley Authority, and as far west as the Bonneville power system.

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Process

The major alloys of silicon, manganese, and chromium are made by the endothermic reduction of an oxide ore with carbon in an electric furnace. This type of unit is called a submerged-arc furnace, since the electrodes are immersed in the charge and a substantial portion of the electrical heating is by resistance through the burden. Figure 1 shows an open furnace of this type. The electrodes are of large diameter, measuring from 0.9 to 1.5 m (3 to 5 ft). The larger units usually use a self-baking electrode rather than the sectioned baked carbon shown here, as long as the product specification can accept the additional iron content inherent in the self-baking design. Figure 1 also shows a turntable base to permit continuous rotation of the shell, desirable to maintain open crucible conditions. A small furnace will consume about 10 000 to 12 000 kW per hour, while modern large units are rated at 20 000 to 50 000 kW per hour.

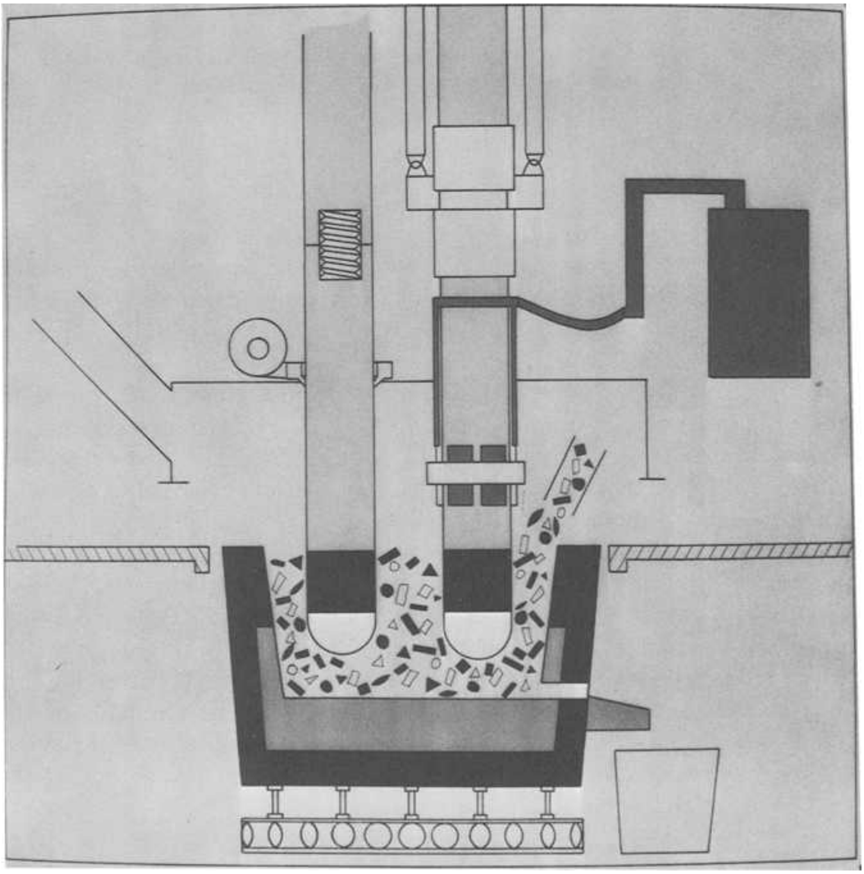

FIG. 1—*Submerged arc furnace.*

While carbon reduction is the primary process utilized, both silicon and aluminum reduction processes are employed where metallurgy or economics indicate their use. The raw materials used can be cataloged as follows:

Ores	Reducers	Fluxes
quartzite	low-ash coal	. . .
chromite ore	by-product coke	burnt lime
manganese ore	petroleum coke	alumina (drosses ores, clays)
steel turnings	wood chips	olivine

These materials are blended in the proper stoichiometric proportions, and fed steadily to the furnace top. The furnaces operate continuously, being offline only for repairs or economic outages. The metal is tapped at intervals and usually cast in shallow molds or beds to form a slab. It is broken to the size required, ranging from head-size lump for open-hearth additions to the fine rice size used in foundry ladles.

Silicon alloys are essentially slag-free since the ore, quartzite, is nearly pure silica. In contrast, manganese and chromium ores contain gangue materials which must be fluxed to a slag. This is usually tapped with the metal and separated to the ladle.

Products

The primary finished products are listed in Tables 1, 2, and 3. The silicon alloys range from 14 percent silvery iron to the nearly pure 98.5 percent silicon metal. The 50 and 75 percent ferrosilicon grades are primarily used by the iron and steel industry. Silvery iron is a high-silicon form of pig iron which has foundry applications, and silicon metal finds its market in the aluminum and chemical industries. In the latter it is the source material for silicone chemicals and for the high-purity silicon used in the semiconductor industry.

TABLE 1—*Silicon alloys.*

Silvery iron	14 to 22% Si
50% ferrosilicon	46 to 49% Si
75% ferrosilicon	73 to 77% Si
Magnesium ferrosilicon	45% Si 6% Mg 0.3 to 0.5% Ce
Calcium silicon	62 to 67% Si 28 to 32% Ca 3% Fe max
Silicon metal	98 to 99% Si 0.35 to 0.50 to 1.00% Fe max 0.03 to 0.07 to 0.40% Ca max (0.20 to 0.50% Al max)

TABLE 2—*Manganese alloys.*

Standard ferromanganese	75 to 80% Mn
	7% C
	1% Si max
	0.35% P max
Medium-carbon ferromanganese	80 to 85% Mn
	1.50% C max
	1.50% Si max
	0.30% P max
Low-carbon ferromanganese	80 to 85% Mn
	0.10 to 0.30 to 0.75% C max
	2% Si max
	0.15 to 0.20 to 0.30% P max
Silicomanganese	65 to 68% Mn
	2 to 3% C max
	17 to 14% Si
	0.20 P max
Manganese metal	99% Mn

The manganese alloys are used almost entirely by the ferrous area. The high-carbon "standard" ferromanganese is over 70 percent of the domestic market, with the premium-priced lower-carbon materials used as process requirements dictate. The purer manganese metal finds application in both ferrous and nonferrous processes where iron levels must be controlled.

The chromium alloys listed in Table 3 have an interesting history. The ferrochromium silicon with approximately equal parts of chromium, silicon, and iron is a low-carbon product made by direct carbon reduction. It was developed as an economical silicon reducing agent for the manufacture of low-carbon ferrochromium. With the advent of in-furnace oxygen blowing of stainless steel in the 1940's, this interprocess alloy found a comparable use as a slag deoxidizer in the steel industry and became a standard commodity. Ten years ago, the advent of the Argon-Oxygen-Decarburization (AOD)

TABLE 3—*Chromium alloys.*

High-carbon ferrochromium	65 to 70% Cr
	2.00% Si max
	5 to 6.5% C
Charge-grade ferrochromium	55 to 65% Cr
	3.00% Si max
	6 to 8% C
Low-carbon ferrochromium	65 to 70% Cr
	1.00% Si max
	0.02 and 0.05% C
	(0.02 to 0.05% N_2)
Ferrochromium silicon (chromium silicide)	35 to 40% Cr
	40 to 50% Si
	0.02 and 0.05% C

TABLE 4—*Electrometallurgical industry, Dept. of Commerce SIC 3313.*

	1970	1977
Net tons[a] produced	2 364 000	1 618 000
Total employees	10 400	8 900
Production man-hours	17 600 000	14 300 000
Sales	$519 000 000	$930 600 000
Annual capital investment	$ 28 800 000	$ 46 100 000

[a] 1 U.S. (short) ton = 0.9 metric ton.

process enabled the stainless steel maker to utilize the less-expensive high-carbon grades of ferrochromium. The low-carbon grade, which had been dominant in stainless manufacture, has dropped to a fraction of its former volume.

Industry

The electrometallurgical industry as covered by the Department of Commerce's Standard Industrial Code (SIC) No. 3313 applies to ferroalloy production. Table 4 compares production, employees, and dollars involved in 1970 versus 1977. The sales and capital expenditures show increases due to inflationary effects. The unit figures show that the industry has shrunk during the period. This has been due solely to import penetration.

Table 5 lists total major alloy consumption annualized for recent 10-year periods, and breaks down production as domestic or imported. While usage has increased at a steady rate, production has declined at the expense of imports, which show a growth from 5.0 to 33.5 percent. For the actual year 1978, this penetration has risen to 51.3 percent.

Breaking this down into products, Table 6 shows the 1978 figures of tons consumed, both domestic and imported. Ferrochromium and ferromanganese, which rely completely on imported ores, show the greatest import penetration. The offshore countries which have supplied these ores are now nearly all involved in converting the raw ore to finished product or planning

TABLE 5—*Major ferroalloys (annual net tons of alloy).*

Year	Tons[a] Consumed	Tons Domestic	Tons Imported	% as Imports
1940 to 1960	1 859 000	1 767 000	92 000	5.0%
1960 to 1970	2 362 000	2 000 000	362 000	25.3%
1970 to 1978	2 480 000	1 646 000	833 000	33.5%

[a] 1 U.S. (short) ton = 0.9 metric ton.

TABLE 6—*Major ferroalloys, annual net tons*[a] *of contained element. Year: 1978.*

Product	Tons[a] Consumed	Tons Domestic	Tons Imported	% as Imports
Ferrochromium	298 000	112 000	186 000	62.4%
Ferromanganese	896 000	297 000	599 000	66.9%
Ferrosilicon and silicon metal	486 000	366 000	120 000	24.6%

[a] 1 U.S. (short) ton = 0.9 metric ton.

to do so. Silicon alloys are less affected, since the United States has good supplies of raw materials for silicon alloys, and reasonably competitive power rates.

Market Distribution

A perspective of these alloys is gained by looking at the market distribution of the various grades. Tables 7, 8, and 9 show how the tonnages of the types of alloy discussed earlier compared in 1978.

Silicon alloys service the most diversified market. Fifty and 75 percent ferrosilicon combined provide about 60 percent of the silicon units, and all of that goes to the iron and steel industry. Thirty percent of the units are as silicon metal, with about two-thirds going to the primary and secondary aluminum industry, and the remaining third to the chemical industry.

Manganese is mostly used in the ferrous area, with the lower-cost high-carbon ferromanganese making up the bulk of the sales. It accounts for over 70 percent of contained manganese usage, in contrast to 15 percent for the lower-carbon grades, 10 percent for silicomanganese, and 5 percent for the metal.

As earlier stated, the recent introduction of the AOD process into stainless manufacture has made the high-carbon grades of ferrochromium dominant. In 1978 it supplied over 80 percent of chrome units used domestically, with low-carbon ferrochromium reduced to 15 percent and ferrochromium silicon to 5 percent.

TABLE 7—*Silicon, annual net tons*[a] *of ferroalloy. Year: 1978.*

Ferrosilicon: 50%	440 000
Ferrosilicon: 75%	160 000
Silicon metal	150 000
Other	100 000
Total net tons	850 000

[a] 1 U.S. (short) ton = 0.9 metric ton.

TABLE 8—*Ferromanganese annual net tons*[a] *of ferroalloy. Year: 1978.*

High-carbon ferromanganese	850 000
Medium low-carbon Fe Mn	150 000
Silicomanganese	150 000
Manganese metal	30 000
Total net tons	1 180 000

[a] 1 U.S. (short) ton = 0.9 metric ton.

Sources

Of the majors, the silicon alloys alone have adequate supplies of raw materials in the continental United States. Excellent-quality quartzite (99.4 percent silica) is found as large gravel in both the Carolina's and Alabama and supplies most of the industry. Local deposits of both gravel and massive quartzite are exploited to supplement these primary sources. The low-ash (2 to 5 percent) semi-bituminous coals of West Virginia and Alabama are world-renowned for the production of alloys, and the cokes, steel scrap, wood, and fluxes are plentiful commodities from many sources. Imports are making inroads, but the domestic industry can be economically competitive.

Manganese and chromium offer a different story. The key ores for these materials lie overseas and the shipment of finished alloy rather than ore is becoming of increasing interest to the countries which control these ore reserves.

Dealing with manganese first, Table 10 lists the production of manganese ore in 1977. In the Western Hemisphere, only Brazil and Mexico are significant, and they contribute just 6 percent of the world production and have only 2.5 percent of the confirmed reserves. In contrast, the six significant producers of the Eastern Hemisphere mined 84 percent of the world production and have 96.5 percent of the reserves. Twenty-two other countries supplied minor amounts.

Today, over 60 percent of the manganese alloys used in the United States are imported. As is reasonable to expect, most of the simpler alloys such as the direct reduced higher-carbon grades come from the less-developed coun-

TABLE 9—*Ferrochromium, annual net tons*[a] *of ferroalloy. Year: 1978.*

High-carbon ferrochromium and charge-grade Fe Cr	400 000
Low-carbon ferrochromium	60 000
Ferrochromium silicon	40 000
Total net tons	500 000

[a] 1 U.S. (short) ton = 0.9 metric ton.

TABLE 10—*Manganese ore sources, net tons for 1977.*

Country	Production	Reserves
Brazil	999 000	43 700 000
Mexico	536 000	2 200 000
Australia	1 529 000	160 000 000
China, People's Republic	1 100 000	17 000 000
Gabon	2 040 000	85 000 000
India	1 955 000	28 000 000
Republic of South Africa	5 564 000	790 000 000
U.S.S.R.	9 370 000	700 000 000
	23 093 000	1 825 900 000
22 other countries	1 174 000	18 100 000
30 total	24 267 000	1 844 000 000

NOTE: Excludes sea-floor deposits.

tries with new industries, and the more sophisticated lower-carbon products come mostly from the old-line industrial countries with a long tradition of making such alloys. The exception is South Africa, which has equipped itself to make nearly all the alloy products for export to the world.

Forty-six percent of the standard ferromanganese imported in 1978 was from South Africa, 21 percent was from France, which relies on the large ore deposits in its former colony, Gabon, and 33 percent was from 11 other countries, none exceeding 5 percent.

Low- and medium-carbon ferromanganese came from seven countries, with France, South Africa, Spain, and Norway contributing 93 percent in roughly equal proportion.

Manganese metal was 85 percent from South Africa, and most of the balance from Japan.

In the face of this import penetration, the domestic manganese industry is 40 percent of what it was 10 years ago. Blast furnace capacity, which used to provide over half of the production, is gone. The electric furnace producers are shipping 60 percent of their 1970 levels.

In the ferrochromium area, the situation is similar. Table 11 lists chromite sources worldwide and again the Western Hemisphere is seriously lacking. Brazil is the only country with significant production, and it contributed 2 percent of the world total from 0.4 percent of the world reserves. The great bulk of the earth's chromite is found in a sector running north from South Africa through Rhodesia, the Sudan, Turkey, Iran, Albania, and into the Urals in Russia. Lesser quantities are found along the Pacific Basin in India, Madagascar, and the Philippines.

The ores are of two types: "metallurgical" or lower iron grades with a chromium/iron ratio of 2.5 to 3.5, and the high-iron ores with a chromium/

TABLE 11—*Chromite ore sources, net tons for 1977.*

Country	Production	Reserves
Brazil	210 000	6 800 000
Albania	970 000	not available
Finland	655 000	11 000 000
India	387 000	7 800 000
Iran	180 000	1 700 000
Madagascar	198 000	5 600 000
Philippines	592 000	5 300 000
Republic of South Africa	3 656 000	1 156 000 000
Turkey	700 000	5 600 000
U.S.S.R.	2 400 000	23 000 000
Zimbabwe/Rhodesia	660 000	620 000 000
	10 608 000	1 842 800 000
13 other countries	196 000	23 200 000
24 total	10 804 000	1 866 000 000

iron ratio of 1.5 to 2.0. The largest production and reserves are found in South Africa, which essentially are all of the high-iron type. Finland also supplies the high-iron material, but, aside from these two major sources, most of the other countries have the metallurgical grade in a wide assortment of analyses and physical forms.

With a few exceptions such as the Bushveld Complex in the Transvaal, or the Great Dyke of Rhodesia, most chromite is found in pods or lenses which can vary from uncommercial deposits a few feet in dimension to the great Guleman find in Eastern Turkey which contained 1 1/2 million tons.[2] Most production comes from deposits containing 100 000 tons or more.

Domestically produced ferrochromium alloys are also supplanted by foreign, as indicated by the 62.4 percent import penetration in 1978. Again, this is strongest in the lower-cost, low-chromium and higher-carbon grades of charge ferrochromium. These cheap chromium units find their major market in supplying the AOD units of the large stainless steel maker.

South Africa has about 75 percent of the world's known chromite reserves. Their high-iron-type ore yields only 55 percent charge chrome and they have pioneered the production and application of this lower-cost grade in the international steel trade. Pursuing this program, they have developed a very large capacity of 700 000 to 800 000 tons, sufficient to supply over half the world's requirements for all types of ferrochromium.

Other countries following suit on a lesser scale are Turkey, Brazil, Finland, India, and the Philippines. Some of their output is destined for their own needs, but the majority is for export to the industrialized nations.

[2] 1 U.S. (short ton) = 0.9 metric ton.

Remarks

In all of these product areas, the original growth was as part of an industrialized economy. Ferroalloy capacity grew in North America, Europe, and Japan to meet local demands of their iron and steel facilities. In the last few years, this balance has been changed by the development of new producing facilities without matching domestic need—these plants are primarily for export.

The only large market still lies in the three industrial areas of the free world, and these new offshore facilities are competing with the home industries for the market available. This market is finite, based on the volume and type of metals and chemicals produced. Price variations will not increase or decrease the quantity of alloys needed—the market is not elastic in this regard.

The foreign producer, with the advantage of lower-cost materials, labor, and power can underprice our domestic industry, and, with the aid of government subsidies and export support, will sell at whatever it takes to keep his furnaces operating. Since the market is not elastic, the domestic producer, not only in the United States, but in the other key areas of Europe and Japan, is being squeezed out.

Our own domestic industry has objected strongly to the "unfair" aspects of our free trade posture and in compliance with U.S. regulations have brought complaints under Section 201, dumping, Generalized System of Preferences (GSP) extension, and countervailing duty statutes. Some of these actions have been successful, and some have not.

Even if we do achieve a fair market balance, the economic advantage of the offshore producer is real, and will exert a constant pressure on all industrial area producers. Japan is moving to curtail their alloy industry and rely on imports, and the United States and Europe are part way there.

There is no doubt that the penetration of imports will continue to grow in the United States, certainly in the tonnage chromium and manganese alloys. This is a growing market area, and the domestic producer is not expanding, but contracting, in these products. Recent expansions have been limited to silicon products, where there is a chance to compete.

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Ferroalloys in the 80's

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ABSTRACT: The paper presents a review of recent user requirements for ferroalloys, and of our understanding of their metallurgical properties. Particular attention is given to alloy density, solution processes, and thermal effects. Alloy addition processes are reviewed, with major emphasis on ladle injection technology. Future developments are analyzed in light of recent and current trends.

KEY WORDS: ferroalloys, metallurgical properties, technology, steelmaking, injections, deoxidizers, desulfurizers, steelmaking

There is a strong temptation, when addressing the subject of ferroalloys, to dwell on factors other than technological. Indeed, subjects such as materials availability, economics, and geopolitics have received considerable attention in recent years, and are addressed in the present volume as well. Such attention is certainly justified in view of the changing nature of the U.S. ferroalloy industry [*1*].[2] This is linked unavoidably with the even more critical question of our minerals self-sufficiency, or rather the lack of it [*2*].

Perhaps it has been the emergence of these concerns along with the major changes in steelmaking technology and, of course, the continuing criticality in energy and raw materials cost that has prompted some significant developments in both the use of ferroalloys and our understanding of them. While the title of the paper implies a look into the future, we cannot avoid reviewing the events of the past few years, especially since these developments will have a bearing on the directions we are likely to see in the coming decade.

Choice of Addition Agents

The use of ferroalloys has a traditional aspect that is part of the art of steelmaking. With the current increased emphasis on cost control and efficiency, steelmakers are taking more critical looks at their raw materials, as several excellent reviews demonstrate. Thornton of the British Steel Corp. observed, for example, that it is a *combination* of technical, economic, and

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

commercial factors that determines the most suitable alloying addition [*3*]. Developments in process technology have broadened the variety of ferroalloys and allowed steelmakers a much wider choice; selection must always be based on total cost, not simply initial price. Purity, or the level of tramp elements, provides a good case in point.

As a general rule, higher residual levels are to be expected in the lower-cost ferroalloys. While "impurities" such as carbon or silicon can occasionally be used to metallurgical advantage—as fuels, for example—most tramps exact penalties in terms of higher energy usage, increased flux and scavenger consumption and, because of larger slag volumes, reduced furnace output. Steelmakers are therefore advised to make certain that their mass and energy balances are complete, lest what appeared to be a cost savings actually becomes an increased expenditure at a decrease in productivity [*4*].

The important metallurgical properties of ferroalloys and other addition agents were discussed in considerable detail by Peters [*5*]. The co-chairman of this symposium considered the reasons why addition agents behave as they do and, in so doing, laid to rest a few misconceptions. He pointed out, for example, that contrary to popular belief, it is an alloy's solubility, rather than its melting range, that determines how quickly an addition dissolves. Lead, the most obvious example, has a very low melting point but is virtually insoluble in steel. Titanium alloys, melting above 1700°C, dissolve readily without ever actually melting. Still, we ferroalloy producers continue to provide melting range information with all our products.

Other factors cited as influencing the solution rate, and perhaps the choice of ferroalloys, include the composition and structure of the alloy, its thermal conductivity and heat capacity at steelmaking temperatures, and the physical form and size in which it is to be added. Composition, or alloy richness, can be a two-sided coin, of course. In some cases, for example, boron additives, lean addition agents are known to give higher, more uniform, and consistent recoveries. Concentrated additions can be more economical, however, and rich alloys present less of a materials handling problem than those which are highly diluted. The problem may seem a minor one until melt shop personnel object to lifting large bags of a dilute alloy when smaller bags of a more concentrated addition can be used instead.

I should mention the related problems of friability and sizing, especially because of the efforts of our ASTM A-09 Committee to develop and agree on a reliable and reproducible test. The current system of six qualitative friability ratings is probably at least as good as the empirical knowledge most steelmakers gain quite quickly. If additional work is to be done in this area in the future, perhaps it will be linked to areas where the generation of excessive fines is a particular problem. Injection lance clogging may be a case in point. Again, sizing is another of those two-sided coins; small particles are known to dissolve in liquid steel faster (which should lead to higher recoveries) but they must also be sufficiently dense. If not, they will have difficulty penetrating thick or viscous slags, where they can become mechanically entrapped and oxidized. Large lump additions will penetrate slags easily, but being slower to dissolve, may have to be added earlier, thus making them more susceptible to oxidation.

The Importance of Density

I have touched on the importance of density for two reasons. First, it is becoming recognized as a critical factor in alloy recovery in some cases, and second, its relationship to at least one system has been rather extensively studied, as described in the following.

In his review, Peters emphasized the importance of an alloy's density as a determining factor for high and consistent recoveries, choosing several common vanadium additions to illustrate his point: Standard grades (60 to 70 percent vanadium) of ferrovanadium have densities around 6.5 g/cm^3. These compare quite favorably with the density of liquid steel at steelmaking temperatures, usually given as 7.15 g/cm^3. Vanadium carbide-type addition agents, on the other hand, have densities nearer to 4.5 g/cm^3 and therefore tend to float on the bath, at the slag-metal interface, or even remain trapped in the slag itself. Thus, despite the fact that vanadium carbide is highly soluble in steel, its recovery is impaired unless special techniques are employed to keep it submerged until dissolved.

The question of density and dissolution time has been covered extensively by Guthrie and his co-workers at McGill University [*6–10*]. Their work centered around another light and erratic addition agent, aluminum. They looked at the general question of what happens when cold additions are made to the liquid steel bath. It was shown conclusively that the initial action is the formation of a solid steel shell around the addition particle (Fig. 1). What happens next depends on the particle's size, melting range, thermal conductivity and specific heat plus the degree of superheat in the steel. Four possible paths of action are postulated, as shown in Fig. 2. The first three assume that the melting range of the addition is below the freezing "point" of the bath; the fourth has the situation reversed. In all cases, however, immersion is immediately followed by the formation of a steel shell.

Small lumps of relatively low-melting additions such as ferromanganese, silicomanganese, aluminum, and lead will likely melt completely inside this shell before it remelts and allows its contents to escape to the bath as in Path 1. The addition's density dictates whether melting occurs at or below the bath surface and therefore becomes a major factor in determining the alloy's recovery.

High degrees of superheat and large particle diameters, combined with low thermal conductivities, lead to Path 2 situations, wherein the steel shell melts back before the addition has itself melted. In some cases, a second shell can in fact form, but this requires that the superheat be minimal, as in Path 3.

FIG. 1—*Cross section of a ferromanganese cylinder (2.54 cm diameter) following immersion for 30 s in a steel bath having an initial superheat of 30°C. (Note the steel shell, the melting zone, and the unmelted core.)* [38]

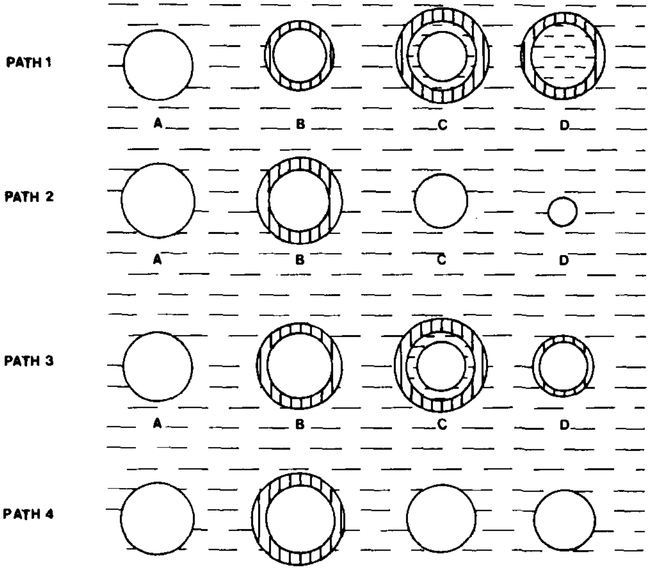

FIG. 2—*Four kinetic paths for alloy additions melting or dissolving in molten steel or both* [38].

Path 4 is simply the case of dissolution of the high melting addition in the bath, after the shell has melted back. The shell can melt from the *inside,* given an exothermic heat of solution for the addition. This can occur, for example, with some rich grades of ferrosilicon.

Hydrodynamic and buoyancy effects have been the subject of a number of studies [*6,10,11*]. A controversy has developed out of this that apparently has not yet been resolved. The case in point is the viability of the Sumitomo "bullet shooting technique" for aluminum additions. In this process, finned bullet-shaped aluminum projectiles are fired into the steel bath at quite high velocities. The hope is that they will penetrate deep enough so that steel shell formation and remelting can occur before the bullet has surfaced. It appears that the technique does lead to a decrease in aluminum consumption, and perhaps an improvement in consistency of recovery by as much as a factor of three. However, the aspect ratio, length/diameter, of the bullets is extremely important. This has been shown by shooting wooden bullets into a water tank. (The density ratios for wood and water are quite similar to those for aluminum and steel.) A 5-cm wooden "bullet" shot 1 m deep into a stillwater bath remains submerged for 2.4 s, while an equivalent 5-cm sphere resurfaces after only 1.4 s. About the same time should result for aluminum bullets in a steel bath. Doubt remains, however, whether even bullet shooting can result in complete subsurface melting for an addition as light as aluminum [*12*]. It should be noted that under entry velocity conditions comparable to normal hand- or chute-charging, aluminum will remain submerged for well less than 1 s, having penetrated the bath by at most 1 m, Fig. 3. Under these conditions, subsurface melting is impossible.

There are alternative solutions to the aluminum problem: submerged stationary aluminum doughnuts similar in principle to plunged stars can improve recovery rates by 10 percentage points [*13*]. Computer studies [*6*] predict that feeding aluminum wire can produce subsurface melting under proper conditions. The question of subsurface melting can be avoided entirely by injecting liquid aluminum, as has been done for U.S. Steel's "MA-RK" steels for a number of years [*14*]. Also, a number of steelmakers have reported [*15–19*] that ferroaluminum, which is more than twice as dense as aluminum itself, gives better recoveries and more predictable and reproducible results. These findings are completely consistent with the predictions of Guthrie and the McGill University researchers. It has been reported that the rapid dissolution rate and consistent behavior of ferroaluminum is gaining it favor as a furnace-blocking addition for use in conjunction with high-speed oxygen probes [*15,17*], as well as for conventional ladle additions.

Thermal Effects

Another important development over the past 10 years has been the increased attention given to chill factors. The original (1962) work by Chip-

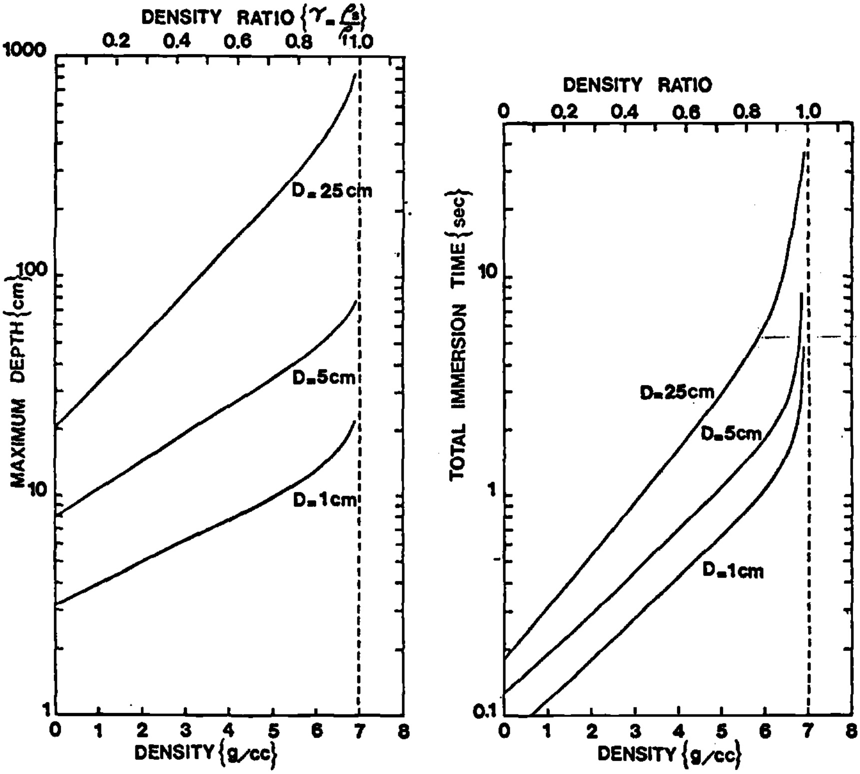

FIG. 3—*Effect of addition density on maximum depth of penetration beneath the liquid surface and total immersion time before resurfacing. Light additions such as aluminum metal resurface almost immediately; denser ferroaluminum* ($\gamma = 0.72$) *remains submerged considerably longer* [6].

man and Elliott [*20*] was applied to the solution of commercially pure metals, as well as for ferromanganese and ferrochromium, Table 1. It did not include consideration of thermal effects of deoxidation attending such solution. This was also not included in later work by Chart and Kubaschewski [*21*] for 53 ferroalloys, except in the case of aluminum and silicon alloys reacting with oxygen dissolved in the steel, Tables 2 and 3. Finally, however, King and Chilcott [*22*] classified the most commonly used ferroalloys into 16 groups, arranged the phases expected to be present in the order of decreasing stability (based primarily on free energies of formation), and estimated the chilling effect of the ferroalloys from the heat of formation of each phase, the sensible heats of the elements concerned, and the heats of solution of these elements in liquid steel. The results, given in Table 4, are about as complete a collection of chill factors as one could wish for.

Should any new ferroalloy compositions be encountered, there is a relatively straightforward calculation to derive the needed chill factors from the alloy's composition.

TABLE 1—*Solution chill factors calculated from Chipman and Elliott's graphs.*

Element or Ferroalloy	Solution Chill Factor for One Pound of Ferroalloy per Net Ton of Steel[a] °C	°F
50% ferrochromium	0.9 to 0.95	1.6 to 1.7
75% ferrochromium	0.9 to 0.95	1.6 to 1.7
100% chromium	0.9 to 0.95	1.6 to 1.7
Cobalt	0.9 to 0.95	1.6 to 1.7
Columbium	0.36	0.65
50% ferromanganese	0.9 to 0.95	1.6 to 1.7
75% ferromanganese	0.9 to 0.95	1.6 to 1.7
100% manganese	0.9 to 0.95	1.6 to 1.7
Molybdenum	0.36	0.65
Nickel	0.51	0.91
50% ferrosilicon	0.67	1.20
75% ferrosilicon	−0.12	−0.22
98% ferrosilicon	−0.82	−1.47
Steel scrap	0.9 to 0.95	1.6 to 1.7
Tungsten	0.24	0.44

[a] 1 lb = 0.45 kg; 1 ton = 0.9 metric tons.

From Ref *22:* Solution chill factors as calculated by J. F. Elliott and M. Gleiser in *Thermochemistry for Steelmaking,* Addison-Wesley, Reading, Mass., 1960, based on graphical values given in Ref *20.*

Addition Methods

Thus far, we have considered the ways in which steelmakers select alloy additions, and a few of the recent basic investigations into their physical properties and the way they behave in steel. I could have added as well the considerable amount of thermochemistry that has been developed during the 1970's, but this applies more to an understanding of steelmaking practices rather than to the ferroalloys themselves.

I would now like to look at a few new ways in which ferroalloys are used, especially since this can give us a better view of how they will be used in the next decade. We have already considered the bullet shooting technique. With its dependence on mechanical devices (of which U.S. steelmakers are traditionally suspicious) and probably somewhat higher raw materials costs, bullet shooting will likely not gain wide acceptance outside Japan. The same may be said for impeller-type stirring devices such as that also offered by Nippon Steel [*23*]. Overseas there may be some additional interest regarding the injection of liquid ferroalloys. Recent Russian work [*24*] claims the technique is feasible, although its application outside the U.S.S.R. is highly un-

TABLE 2—*Solution chill factors calculated from chart and Kubaschewski's results.*[a]

		Solution Chill Factor for One Pound of Ferroalloy per Net Ton of Steel	
Ferroalloy	Chemical Composition, Weight %	°C	°F
Aluminum	100Al	−0.09	−0.16
Ferroaluminum	35Al-65Fe	+0.865	+1.56
Ferroaluminum	40Al-60Fe	+0.845	+1.52
Ferroaluminum	45Al-55Fe	+0.815	+1.47
Ferroaluminum	50Al-50Fe	+0.795	+1.43
Ferroaluminum-silicon	50Al-37Si-13Fe	−0.105	−0.189
Ferroboron	15B-2Al-1Si-82Fe	+0.81	+1.46
Ferroboron	20B-2Al-1Si-77Fe	+0.595	+1.07
Chromium	100Cr	+1.075	+1.94
Chromium-carbon	95Cr-5C	+1.345	+2.42
Chromium-carbon	90Cr-10C	+1.535	+2.76
Ferrochromium	75Cr-0.5Si-24.5Fe	+0.970	+1.75
Ferrochromium	73Cr-1Si-0.5C-25.5Fe	+0.985	+1.77
Ferrochromium	64Cr-1Si-5C-30Fe	+1.245	+2.24
Ferrochromium-silicon	42Cr-42Si-16Fe	+0.845	+1.52
Ferrochromium-silicon	61Cr-23Si-16Fe	+1.135	+2.04
Cobalt	100Co	+0.70	+1.26
Ferrocolumbium	40Cb-1Al-59Fe	+0.72	+1.30
Ferrocolumbium	60Cb-1Al-39Fe	+0.57	+1.03
Ferrocolumbium	65Cb-1Al-1Si-33Fe	+0.53	+0.95
Ferrocolumbium	70Cb-1Al-1Si-28Fe	+0.495	+0.89
Ferrocolumbium	62Cb-3Ta-1.5Al-1.5Si-32Fe	+0.535	+0.96
Manganese	100Mn	+0.915	+1.65
Manganese	97Mn-3Fe	+0.915	+1.65
Manganese-boron	21B-1Al-1Si-2Fe-75Mn	+0.61	+1.10
Ferromanganese	85Mn-1.5Si-13.5Fe	+0.915	+1.65
Ferromanganese	80Mn-1.5Si-1.5C-17Fe	+0.935	+1.68
Ferromanganese	78Mn-1Si-7C-14Fe	+1.05	+1.89
Silicomanganese	63Mn-33Si-4Fe	+0.845	+1.52
Silicomanganese	70Mn-20Si-1C-9Fe	+0.92	+1.66
Ferromolybdenum	62Mo-1Si-37Fe	+0.54	+0.97
Ferromolybdenum	70Mo-0.5Si-29.5Fe	+0.54	+0.97
Nickel	100Ni	+0.65	+1.17
Silicon	100Si	−0.85	−1.53
Ferrosilicon	45Si-1Al-54Fe	+0.50	+0.90
Ferrosilicon	75Si-1Al-24Fe	−0.245	−0.44
Ferrosilicon	90Si-1Al-9Fe	−0.62	−1.12
Ferrotantalum	55Ta-9Nb-1Si-1Al-34Fe	+0.465	+0.84
Ferrotitanium	25Ti-2Al-1Si-72Fe	+0.865	+1.56
Ferrotitanium	30Ti-3Al-67Fe	+0.82	+1.48
Ferrotitanium	30Ti-4.5Al-4Si-61.5Fe	+0.835	+1.50
Ferrotitanium	40Ti-3Al-0.5Si-56.5Fe	+0.815	+1.47
Ferrotitanium	70Ti-4Al-26Fe	+0.615	+1.11
Titanium-aluminum	60Ti-40Al	+0.785	+1.41
Ferrotungsten	30W-1C-2Cr-67Fe	+0.69	+1.24
Ferrotungsten	70W-30Fe	+0.405	+0.73
Ferrotungsten	80W-20Fe	+0.325	+0.58

TABLE 2—(*Continued*).

Ferrovanadium	40V-5Si-0.5C-54.5Fe	+0.905	+1.63
Ferrovanadium	60V-0.5Si-1.5Al-38Fe	+0.905	+1.63
Ferrovanadium	75V-0.5Si-1.5Al-23Fe	+0.90	+1.62
Ferrovanadium	80V-0.5Si-1.5Al-18Fe	+0.885	+1.59
Zirconium-aluminum	52.3Zr-47.2Al-0.5Fe	+0.715	+1.29
Zirconium-silicon	40Zr-50Si-10Fe	+0.36	+0.65

Taken from King and Chilcott [*22*] values calculated from data given by Chart and Kubaschewski [*21*].

likely. One doubts that the overall economics of the process will prove attractive.

Pneumatic injection techniques have received a great deal of attention since their commercialization in the mid-1970's [*25*], and we will consider them in somewhat more detail.

It is interesting to note that a process which was viewed with considerable skepticism only six years ago is now becoming so widely accepted. A review of the subject published in late 1978 [*26*] listed 56 installations of injection equipment worldwide: by the end of 1979, the list had grown to over 75 [*27*]. Thyssen-Niederrhein (T-N), Clesid-Irsid, Scandinavian Lancers, and Max Peters are major suppliers of this type of equipment, but there are numerous home-brew variations in steel mills throughout the world. While differing in some technological details, they all basically consist of a system for using an inert carrier gas (usually argon, available in quantity and at relatively low cost as a by-product of the steel mill's tonnage oxygen plant) to convey a powdered addition agent through a refractory sheathed steel lance immersed in the ladle to a depth of about 3 m, as shown in Fig. 4.

TABLE 3—*Deoxidation chill factors of Chart and Kubaschewski.*

	Deoxidation Chill Factor for Reaction With 0.01% Oxygen	
Ferroalloy	°C	°F
100Al	−3.05	−5.49
35Al-65Fe	−2.48	−4.46
40Al-60Fe	−2.55	−4.59
45Al-55Fe	−2.60	−4.68
50Al-50Fe	−2.65	−4.77
100Si	−2.35	−4.23
45Si-55Fe	−2.00	−3.60
75Si-25Fe	−2.26	−4.07
90Si-10Fe	−2.32	−4.18

Taken from Ref *22*, as quoted from Ref *21*.

TABLE 4—*Solution chill values for a one-pound-per-ton addition of various ferroalloys.*[a]

Name	Chemical Composition, Weight %	Solution Chill Factor,[a] for One Pound per Ton	
		°C	°F
Aluminum, Grade No. 1	95Al-2Cu-1Fe-1Mn-1Si	−0.06	−0.11
Aluminum, Grade No. 4	87Al-4Zn-3Si-3Cu-2Fe-1Mn	+0.02	+0.04
Ferroboron	80Fe-18B-1Mn-1Si	+0.75	+1.35
Carbon (graphite)	100C	+2.98	+5.36
Low-carbon ferrochrome	70Cr-29Fe-1Si	+0.98	+1.77
High-carbon ferrochrome	68Cr-25Fe-5C-1.5Si-0.5Mn	+1.25	+2.24
Blocking chrome	60Cr-25Fe-10Si-5C	+1.18	+2.13
Charge chrome	70Cr-23Fe-5C-2Si	+1.21	+2.19
Cobalt	100Co	+0.70	+1.26
Medium-carbon ferromanganese	81Mn-16Fe-1.5C-1.5Si	+0.95	+1.70
High-carbon ferromanganese	76Mn-16Fe-7C-1Si	+1.14	+2.05
Electrolytic manganese	100Mn	+0.91	+1.64
Nickel	100Ni	+0.65	+1.17
Silicomanganese	61Mn-17Si-14Fe-2C	+0.89	+1.59
Ferrophosphorus	71.5Fe-24P-3Mn-1.5Si	+1.30	+2.34
10% ferrosilicon	88Fe-10Si-2C	+0.85	+1.53
50% ferrosilicon	50Si-48Fe-2Al	+0.37	+0.67
75% ferrosilicon	75Si-23Fe-2Al	−0.26	−0.48
Steel scrap	100Fe	+0.82	+1.47
Sulfur	100S	−0.73	−1.31

[a] A positive solution chill factor indicates that the liquid steel temperature decreases when the ferroalloy is added.

The process is quite simple. Well-deoxidized steel is tapped into the treatment ladle, taking care to hold back all or most of the oxidizing furnace slag. A synthetic basic lime/spar slag may then be built up, and the ladle covered for reasons of heat retention, safety, fume control, and avoidance of reoxidation. The lance is then inserted and injection begun. Preliminary argon bubbling, without addition agents, is helpful in sweeping suspended oxides to the slag, thereby increasing the efficiency and consistency of the treatment. The process may end with a final argon stir for inclusion removal, homogenization, and temperature control.

The major functions of ladle injection, as it has been applied to date, are final deoxidation and desulfurization, often to extremely low levels (oxygen below 10 ppm and sulfur less than 0.002 percent). An added benefit, depending on the type of addition agent used, is inclusion shape control. All these reactions tend to improve the cleanliness and mechanical properties of the steel. Transverse and through-thickness (Z-direction) ductility and impact toughness are especially increased, an important factor in pipeline steels,

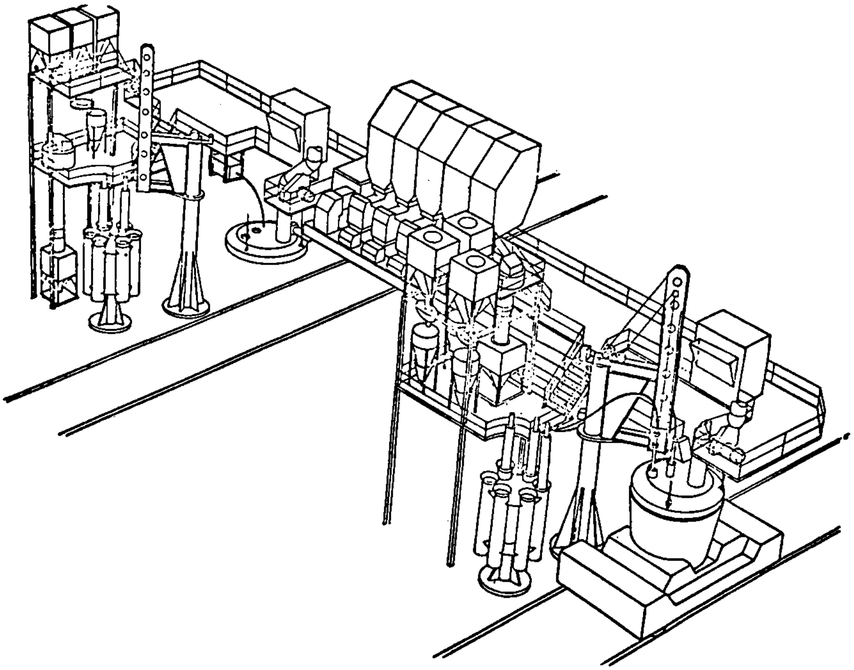

FIG. 4—*Scandinavian Lancers injection system* [35].

heavy plates, and structurals for welded fabrication [*28*]. By reducing the volume fraction of inclusions, and controlling the morphology of those remaining, it is now possible to produce plate with virtually identical impact toughness in the longitudinal and transverse directions, as shown in Fig. 5.

Calcium silicide is the most widely used reagent in injection systems [*27*], although lime, magnesium powder, aluminum, and calcium carbide are also used. To be sure, calcium silicide is a very effective deoxidizer and desulfurizer. It dissociates rapidly on contact with liquid steel. The calcium vapor thus formed has a vapor pressure of 1.8 atm at 1600°C [*26*], sufficient to form bubbles in all but the deepest ladles with high ferrostatic heads. Besides being reactive, these bubbles augment the stirring action. The calcium vapor reacts with dissolved sulfur and oxygen in the bath as well as with entrained sulfides and oxides. Products of the reactions range from calcium sulfides and oxysulfides to a variety of calcium aluminates. The aim, when forming these latter compounds, is to adjust the stoichiometry so as to form low-melting aluminates such as $3CaO \cdot Al_2O_3$ and $CaO \cdot Al_2O_3$, as shown in Fig. 6 [*29,39*]. These readily levitate to the slag. High-melting aluminates, for example, $CaO \cdot 6AL_2O_3$ and $CaO \cdot 2Al_2O_3$, can be worse than the alumina clusters they were supposed to eliminate [*30*]. For one thing, they cause rapid tundish blockage in continuous casters.

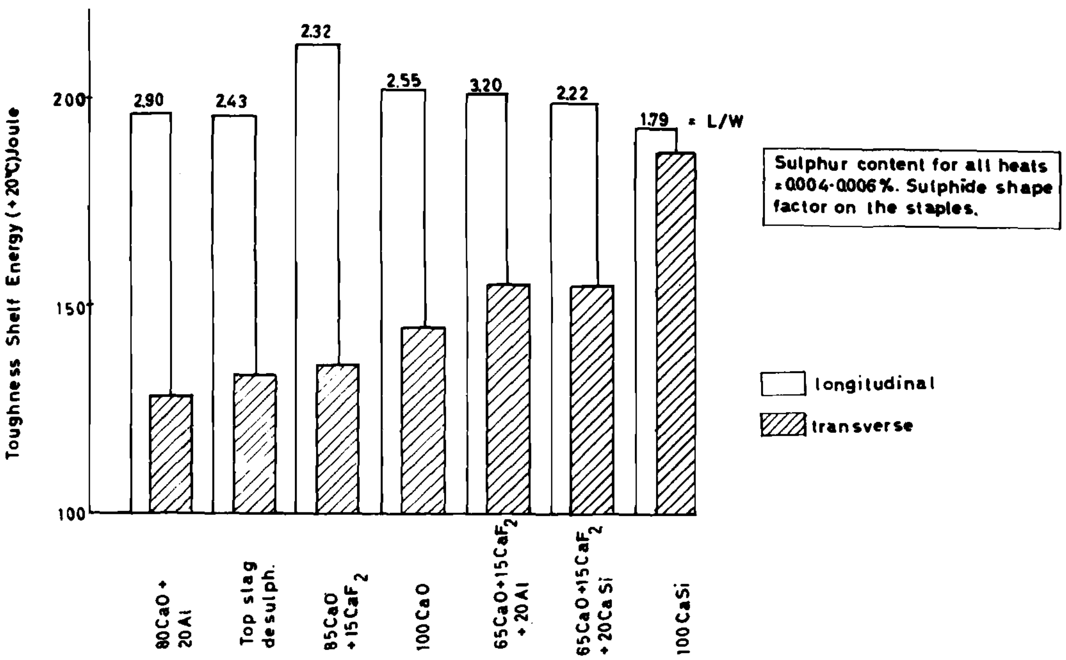

FIG. 5—*A comparison of toughness in longitudinal and transverse direction for the different desulfurization variants. Plate thickness 20 to 30 mm (10 by 10-mm International Standards Organization V-notch test specimens)* [28].

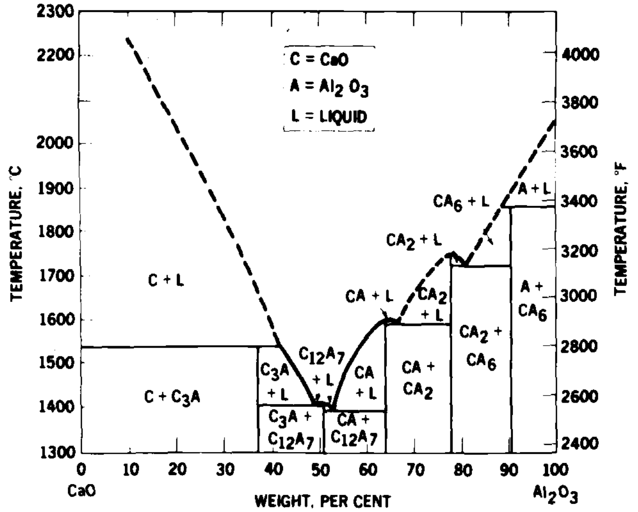

FIG. 6—$CaO\text{-}Al_2O_3$ *system* [29,39].

While the original T-N process was designed for use with calcium silicide, other desulfurizers, usually based on combinations of lime, spar, calcium carbide, magnesium, and aluminum, are also used. Their effectiveness ranges from equivalent to calcium silicide to somewhat less, depending on the benchmark chosen [*22*]. In general, lime-based additions are somewhat more difficult to handle and tend to clog injection lances more frequently than calcium silicide. They therefore require higher gas flow rates. Their deoxidizing power tends to be less sensitive to initial melt oxygen levels. As desulfurizers, they are less efficient than calcium silicide, as shown in Fig. 7, but the well-known fact that the performance of any desulfurizer depends on the degree of deoxidation should not be overlooked.

Injected desulfurizers-deoxidizers do tend to increase steel gas contents slightly. Both hydrogen and nitrogen levels can be expected to rise. This can be important since some ferroalloy additions will be made after ladle injection and these additions can themselves be rich sources of gaseous impurities. Just how important this factor can be was demonstrated in a recent Czech paper [*31*]. Manganese, for example, can be a carrier for a variety of gaseous contaminants, as shown in Table 5. Electrolytic manganese has a high hydrogen content, while aluminothermic manganese can be a rich source of nitrogen. Chromium addition agents can likewise be a source of impurities. Here, gas content appears to be strongly related to the method of manufacture, at least for the U.S., German, and Russian ferrochromes analyzed for the Czech study, Table 6. Gases are found in silicon alloys, particularly if calcium is present as well. Finally, ferrovanadium can be a source of oxygen or nitrogen, depending on its means of production, Table 7.

It should be noted that a number of processes [*28,32,33*] use injected

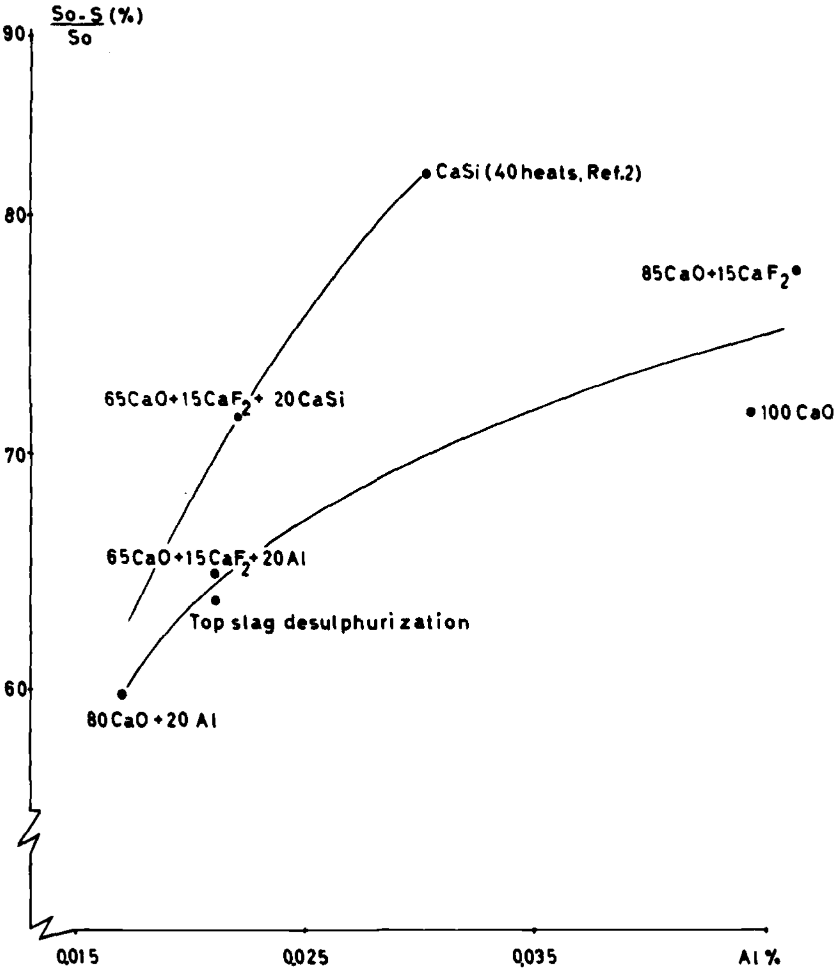

FIG. 7—*Desulfurization as a function of Aluminum content before treatment* [29].

TABLE 5—*Content of gases in manganese manufactured by various technological procedures* [*31*].

	Content of Gases		
Manganese Type	O ppm	N ppm	H $cm^2/100$ g
Electrolytical	300 to 500	100	100 to 150
Aluminothermic	100 to 500	800	30
Silicothermic	max 300	300 to 500	40
Blast furnace	200 to 1000	200 to 500	20 to 40

TABLE 6—*Content of gases in chrome ferroalloys made by various technological procedures* [*31*].

Chrome Type	Content of Gases O ppm	 N ppm	 H $cm^2/100$ g
Aluminothermic	900 to 1200	400	5 to 20
Electrolytical	to 2400	500	570
Silicothermic	...	...	...
Carbon silicothermic	1700 to 3000	300	50
Low-carbon silicothermic	900 to 1200	540 to 1100	16 to 40

TABLE 7—*Content of gases in ferrovanadium made by various technological procedures* [*31*].

Ferrovanadium Manufacturing Process	Content of Gases O %	 N %	 H $cm^3/100$ g
Aluminothermic (80% FeV)	0.2 to 0.5	max 0.2	30 to 90
Silicothermic (40 to 55% FeV)	0.07 to 0.1	max 0.06	20 to 40

argon alone, simply as a stirring agent. The aim is to effect intimate contact between all of the liquid steel and a basic, desulfurizing slag. While the process is effective and may have cost advantages over magnesium or calcium silicide injection for certain product requirements, it does fall outside the topic of this paper.

A novel "injection" process that should be considered is the use of steel-clad calcium wire (and recently calcium silicide cored wire) as a desulfurizer. Several processes have been demonstrated, and seem to work. However, results to date indicate that care must be taken to optimize the process [*34*].

Future Trends

Where can we expect ferroalloy technology to go in the 1980's? From my previous remarks, you can imagine that I believe injection processes will become much more widely applied. Already, there have been reports of the injection addition of alloys other than deoxidizers and desulfurizers [*32,35*]. This trend will certainly continue, especially since new bottom- and top-blown processes such as Oxygen Boden Maximilianshuette and Klöchner Maxhuette Scrap have demonstrated their potential. Because injection can be controlled, from a metallurgical standpoint, much more reliably than traditional addition methods, it offers the means to higher and more reliable alloy recoveries. For our part, ferroalloy suppliers will have to concentrate on developing lower-cost processes for producing ferroalloys in finer sizes, suitable for injection. (I might add that our company is already supplying ferroaluminum in sizes 8 mesh by down for just this purpose.) Granulated or shot-cast ferroalloys carry a spinoff benefit to steelmakers in that they are less prone to the front-to-back and heat-to-heat compositional variations occasionally encountered with bulk ferroalloys.

Injection equipment suppliers will build into their equipment, as some already are, the ability to charge a variety of addition agents, beginning with aluminum or ferrosilicon, on through the final deoxidizers and desulfurizers, to the trim alloy additions themselves (see Fig. 4).

The increased use of duplexing processes, such as Argon Oxygen Decarburization, Finkl-Mohr, Cruesot Loire Uddeholm, and others, has already had a marked effect on ferroalloy usage patterns, particularly in the ratio of low-carbon to high-carbon alloys consumed [*37*]. My personal feeling, however, is that such processes, particularly those based on vacuum, will find increasing use only for those grades where low hydrogen contents are mandatory. Improved quality "tonnage" grades will be produced in atmospheric-pressure ladle processes, especially as these become more flexible.

One thing is certain: The quality of steel produced in 1980 has been far higher than ever produced before. There will undoubtedly be more quality improvements, commensurate with reasonable product requirements, during the next decade. As more steelmakers demand more versatile, more efficient, and more reliable alloy additions to follow this trend, the ferroalloy industry will work to supply them.

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J. P. Balash[1]

Market Position of Ferroalloys Produced from Ocean Nodules

REFERENCE: Balash, J. P., "**Market Position of Ferroalloys Produced from Ocean Nodules,**" *Ferroalloys and Other Additives to Liquid Iron and Steel, ASTM STP 739,* J. R. Lampman and A. T. Peters, Eds., American Society for Testing and Materials, 1981, pp. 76–83.

ABSTRACT: There has been little discussion in most technical circles about the commercial importance of ocean-mined minerals. This paper outlines the market position in the United States and the free world of ferroalloys of manganese, nickel, and cobalt which can be produced from this new source of minerals. The national security value for the United States and the free world of these metals which can be produced from nodules is significant. In contrast, the market share impact under normal circumstances of material produced from nodules is likely to be moderate to small on a world scale, except in the case of cobalt. The market impact was determined by a study of publicly available information on the size and nature of the market for the subject ferroalloys. The results of these studies and other information indicate that the timing of market entry of those consortia now doing exploration and development depends on the resolution of political, technical, and economic barriers. Past investments in ocean mining activity of several consortia are substantial. The capital needs of the existing consortia to commercialize these ventures are large. The development of this embryonic industry is at a critical stage and its long-range potential depends on favorable political support in the United States and the rest of the free world.

KEY WORDS: ferroalloys, ocean mining, nodules, steel geopolitics, minerals

It has been my job over the past years to assist in the marketing planning and research in cooperation with our partners to determine the commercial opportunities for ocean mining. I hope to offer some appreciation of this complex venture, and I ask that the reader recognize these views as my own and not necessarily those of the consortium.

Looking to the 21st century—just 20 years away—we, as a society of nations, must be concerned with resource availability, whether it be oil or minerals or many other resources. Minerals for ferroalloy use are of major and continuing importance.

In addressing this concern, I shall deal with the subject of whether we can find love and happiness on the ocean floor. The fact is, ocean mining of min-

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eral nodules brings a totally new dimension to the availability of manganese, cobalt, nickel, and many other mineral elements.

But we have to get the potential of the ocean floor into perspective, for there are several major pluses and minuses. Ocean mining will not, in all probability, ever solve all of the problems of mineral availability; and it will not, in all probability, have too much effect on price—at least for many years.

However, it is an exciting new aspect of resource development in the minerals field which must be exploited in a world hungry for the elements available. It is a frontier where new methods of exploration, new technologies of mining, and the most efficient methods of mineral extraction are all being pursued, and are being pursued vigorously.

This paper is confined largely to the market aspects of an ocean nodule mining venture, because this is the area of the author's professional concern. But first, the history of this project from its inception to the outfitting and the preparations for deepwater tests is reviewed. This will provide an appreciation of ocean mining, of what are generically called manganese nodules but which, in fact, also contain cobalt, copper, nickel, iron, aluminum, and many other mineral elements. The point is, of course, that ocean manganese nodules contain elements which are key ingredients of ferroalloy products.

Ocean Mining Technique

Nodules grow and replenish themselves; thus there is a popular notion that the supply will be never ending. This is a fallacy, because the time element, which covers hundreds of thousands or millions of years, precludes replenishment of a given mine site in any meaningful time period. But the truth is, presently minable nodules—nodules which already exist from ages past—are in sufficient quantity and are recoverable by known technology so that they offer an exciting new potential which can now be added to the major mineral resources of the world.

In the spring of 1977, a converted ore carrier in the Pacific (Fig. 1) tested a mining system which used compressed air to pump up, through a 15 000-ft[2] pipeline, tons of mineral-rich lumps of material from the seabed. This material is in the form of nodules (Fig. 2). The richest deposits of nodules are found in the North Pacific Ocean and at depths of about 3 to 3 1/2 miles.[3]

U.S. Steel has had a major stake in the success of the undertaking. In 1974 we joined forces with Union Miniere of Belgium in a joint venture called Ocean Mining Associates (OMA). In April of 1977 the Sun Co. joined as a third partner in OMA. The marine operating arm of OMA is Deepsea Ventures, Inc., located on the coast of Virginia.

Union Miniere of Belgium is a multinational mining and metallurgical company. The Sun Co. brings to the project wide experience in offshore oil

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[2] 1 ft = 0.3048 m.

[3] 1 mile = 1.6 km.

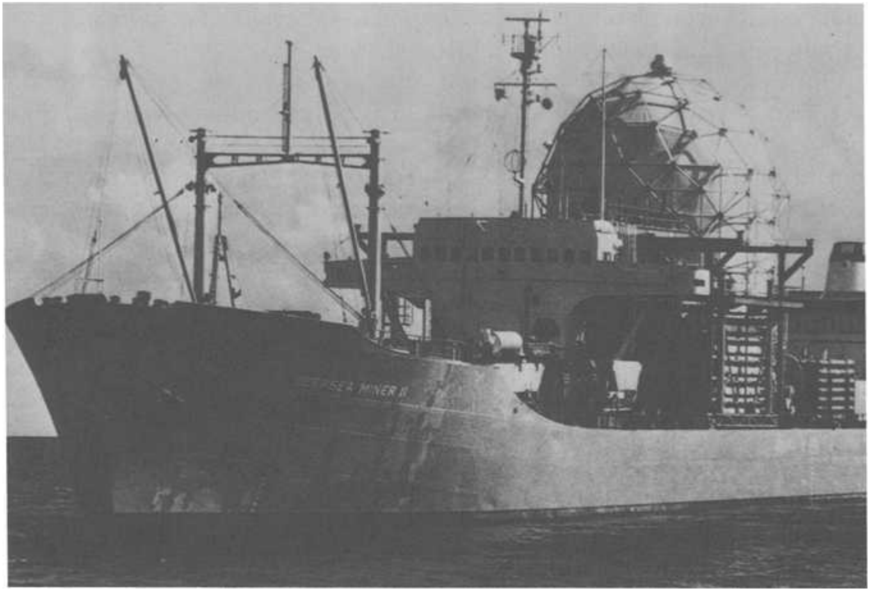

FIG. 1—*Converted ore carrier.*

FIG. 2—*Nodules on ocean bottom.*

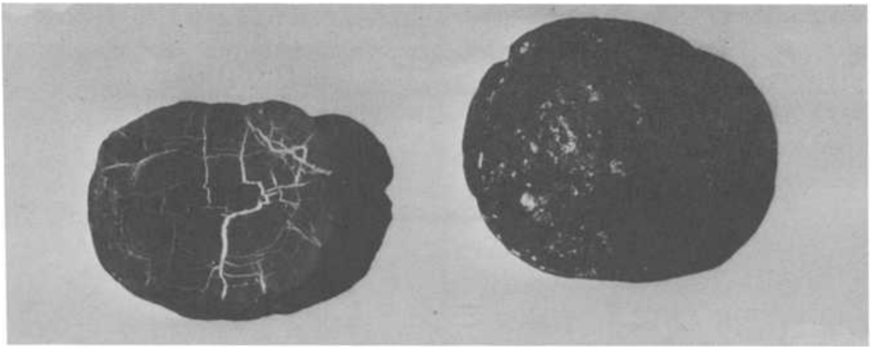

FIG. 3—*Cross section of ocean nodule.*

exploration, drilling, shipbuilding, and integrated petroleum operations. U.S. Steel, of course, has worldwide mining and mineral processing experience and is a major consumer of manganese and other selected nodule elements.

Deepsea Ventures has been particularly successful in pioneering a mining system for raising nodules from the ocean floor. These nodule deposits occur as black potato-shaped lumps averaging 1 to 3 in.[4] in diameter (Fig. 3).

Nodule Concentration and General Analysis

So-called manganese nodules have been found in almost every large body of water in the world, mainly in the oceans, where they are sprinkled over vast areas, in some places as densely as the paving in a cobblestone street. Very importantly, these high-concentration areas of nodules are mostly found outside the presently established limits of any nation's sovereignty.

Thus, most ocean mining ultimately will come under the jurisdiction of an international law of the sea or domestic legislation. Multilateral agreement in this needed area of decision has yet to be completely negotiated and accepted by members of the United Nations. It is hoped that the U.S. Congress will soon pass domestic legislation to provide some economic protection for U.S. ocean miners in order to minimize the impact of this uncertainty, which magnifies the potential commercial risk. All of these jurisdictional problems are not to be taken lightly. Meanwhile, however, the major industrial nations are pursuing nodule mining projects in several multinational consortia.

As a source of minerals, nodule mining and processing is unique. The components of nodules include many, actually well over a dozen, important elements. There generally are no equal cost-performance substitutes for manganese, nickel, and cobalt in most of their end uses. Manganese is a major constituent of nodules, typically 25 to 30 percent of the material.

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[4] 1 in. = 2.54 cm.

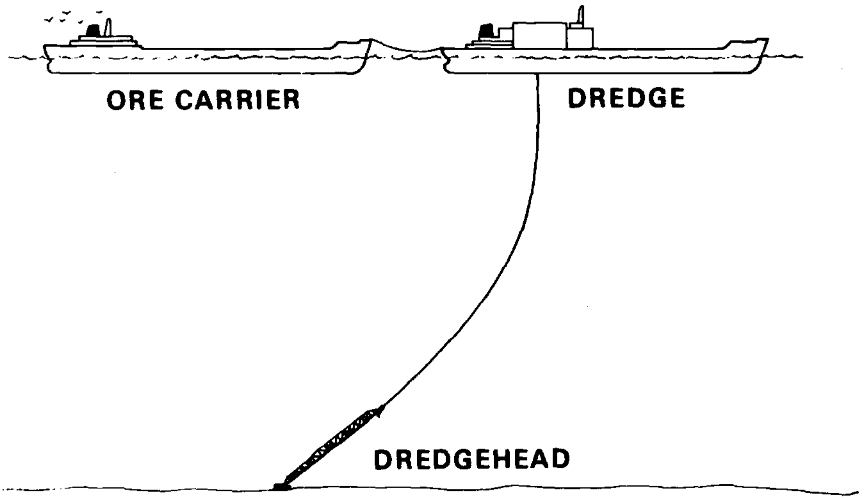

FIG. 4—*Dredge system used for mining ocean nodules.*

Of course, U.S. Steel is interested in manganese because it is critical to the production of steel, and all manganese ore has to be imported. There is a growing market for manganese additions to high- and low-alloy steels in the never-ending effort to get better strength with thinner sections. In Western Europe and Japan, also, steel producers are dependent upon imports of manganese for their entire needs.

Nickel and cobalt are also included in the area of interest. Concentrations in typical nodules are expected to be 1.30 percent nickel and 0.25 percent cobalt.

Assuming a one-million-ton nodule project by the late 1980's, then the output of nodule manganese would be 250 000 net tons[5]; nickel would be about 13 000 net tons, plus about 2500 net tons of cobalt. In addition, several other metallic elements of interest can be mined from the ocean depths.

Experts in metals may wonder why nodule-derived products—with their great abundance—have not yet found their way into the market. The reason is that in a development situation there are unsolved political questions, as well as problems of technology and economics. The latter include the mechanics of ocean mining itself, as well as the winning of metallic elements from the recovered nodules.

Our mining system has been proven at 3000 ft in the Atlantic and has been tested at 15 000 feet in the Pacific (Fig. 4). The techniques and economics must be proven in practice, as we are doing now in our joint venture.

At the same time, efforts are also under way in all other phases of the project—processing, marketing, financing, and other business areas. As to

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[5] 1 U.S. (short) ton = 0.9 metric ton.

timing, as I alluded to earlier, by the late 1980's ocean mining should be an important, viable factor in mineral recovery. In that time framework, let us look at some market data—concentrating on manganese, nickel, and cobalt, which are of special interest. These data are from published sources plus our own judgments as to the most likely probabilities.

Nodule World Market

In 1975, the last year for which fairly complete historical data are available, the situation with regard to metallurgical uses for manganese, nickel, and cobalt was as shown in Table 1. In the free world, manganese demand on a contained basis was 3.5 million net tons, with about 90 percent used in the metallurgical industries. Nickel demand in the free world was about 611 000 net tons, with about 80 percent used for metallurgical applications. Cobalt demand in the free world was about 24 000 net tons, with about 55 percent going into what might be classified as metallurgical uses (superalloys, magnets, carbides, and steels). The metallurgical industries are a big outlet for these critical materials, and the major free world users depend heavily on imports of the ores.

Now let us look at 1985 projections of demand and at the impact of ocean nodules as a source (Table 2). In the short run, total manganese consumption will parallel raw steel projections, assuming little change in the average quantity of manganese use per ton of steel. For 1985, we expect the demand for manganese on a contained basis to be about 5 million net tons for the free world and 1 million net tons for the United States. Manganese output from the processing of 1.0 million dry tons of nodules would be at least 250 000 net tons or 25 percent of the demand in the United States and 5 percent for the free world. The U.S. market could not support the output of too many "economic"-size nodule operations without some price reactions. However, the free world market could absorb more material than the domestic market and would welcome an additional source, unlike the major land-based deposits, which have been a cause for some concern. Total nickel demand is at some 1 million tons for the free world and 260 000 tons for the United States.

TABLE 1—*Free world 1975 demand for manganese, nickel, and cobalt.*

	Thousand Net Tons[a]	Percent Metallurgical Applications
Manganese	3500	90
Nickel	611	80
Cobalt	24	55

[a] 1 U.S. (short) ton = 0.9 metric ton.

TABLE 2—*Projected 1985 demand for manganese, nickel, and cobalt.*

	Thousand Net Tons[a]	% from Ocean Mining
Manganese		
free world	5000	5
United States	1000	25
Nickel		
free world	1000	1.3
United States	260	5
Cobalt		
free world	38	6.5
United States	14	18

[a] 1 U.S. (short) ton = 0.9 metric ton.

Nickel production from the ocean mining of 1 million dry tons of nodules would approach 13 000 net tons—5 percent of the demand for the United States and 1.3 percent for the free world. On this basis, nodule-derived nickel would have a minimal impact on world prices—even as additional ocean nodule projects come on stream.

Here, on the same basis, is the cobalt picture. Demand in 1985 is projected to be 38 000 net tons for the free world and 14 000 for the United States. In this case the result of the first ocean mining project would be more important. Production of 2500 tons would be equivalent to 18 percent of the demand for the United States and 6.5 percent for the free world.

Over the past two decades both nickel and cobalt have experienced periods of tight supply and rising prices. A new source from the ocean depths will surely be most welcome in this situation—additional availability not subject to the same disruptions of supply as present sources. The significance of this prospect is quickly apparent to users of cobalt, because nearly two thirds of the entire world production comes from just one African country.

The projected volume of cobalt from this first project is not likely to have any substantial effect on world prices. In the longer run, added nodule supplies of cobalt are likely to have a moderating effect on prices, which will encourage broader use.

Conclusion

Nodules are a new source for making manganese-based ferroalloys. This situation could be a special case that merits the attention of the whole industry. Plant location, process design, and hardware for processing nodules into metals have a certain amount of flexibility, suggesting some new options. One option of importance is the type and analysis of manganese ferroalloys that might be produced from nodules. Will nodule-based products be a higher analysis than the generally accepted standards? Part of the answer to this question depends on the feedback from the users. How can the nodule processor serve industry's needs better? At this early stage of development, much can be gained by all parties concerned from exchanging information on product needs and available options with nodule-derived ferroalloys.

To summarize the major points of this presentation:

1. Ocean mining opens a much-needed new source of minerals to help counter the global problems of availability and escalating costs.
2. Manganese available from nodules will bring an added measure of security to the steel industry in the United States—and to other countries now lacking their own supply.
3. Cobalt availability still depends upon the mining of its parent metals, nickel and copper. Demand for cobalt, however, grows at a greater pace than supply, resulting in a gap which in the United States has been filled by releases from the government stockpile. The limit of stockpile releases has probably been reached, and a new source such as nodule cobalt is badly needed to fill the gap.
4. Ocean mining of minerals is a new frontier which has a high probability of technical and, hence, economic success. This growing world needs access to this plentiful and rich resource.

A. T. Peters[1]

Control of Ferroalloys in a Large Integrated Steel Mill

REFERENCE: Peters, A. T., "**Control of Ferroalloys in a Large Integrated Steel Mill,**" *Ferroalloys and Other Additives to Liquid Iron and Steel, ASTM STP 739,* J. R. Lampman and A. T. Peters, Eds., American Society for Testing and Materials, 1981, pp. 84–92.

ABSTRACT: The development of alloy purchasing specifications is reviewed along with the control of incoming materials for their chemistry and sizing, and the disposition of marginal shipments. Minimum alloy input is determined and an actual calculation of alloy requirement of a heat of steel is made using a simplified formula. Computerized input calculations for lowest-cost alloy mix are made, as well as computerized and manual checks of actual versus planned alloy input and performance. Finally, new alloy practices and their dependence on required steel quality are determined, and examples given of minimizing the cost/benefit ratio regardless of alloy cost.

KEY WORDS: ferroalloys, steel production, steel, control of chemical composition, alloy recovery

Inland Steel Company produces annually over 8 million tons of raw steel at its Indiana Harbor Works. Most of the output is plain carbon grades with the balance being high-strength and traditional low-alloy steels. No high-alloy grades are produced. Nevertheless, the yearly cost of ferroalloys and other steel additives exceeds $50 million. Consequently, rather strict controls are in use.

Purchasing is centralized, with all requirements being channeled through the Purchasing Department. The purchasing agent obtains any technological guidance required from a raw materials metallurgist, who is in close contact with the steelmaking shops and chemists.

There are three stages of control:

1. Product specification—we have at present over 100 specifications for ferroalloys and other steel additives.
2. Incoming materials control

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[1] Staff metallurgist, Inland Steel Co., East Chicago, Ind. 46312.

3. Input and performance control:
   (*a*) selecting an additive of the lowest overall cost possible that is usable for the given purpose, and
   (*b*) determining the amounts to be added via determination and frequent check of alloy recovery and other factors affecting alloy yield.

These activities aim at minimizing the cost/benefit ratio, not only the cost itself.

The last group of checks is the background for development, be it caused by a new alloy or a new steel grade, or a significant alloy cost change; this may require writing a new specification.

The preceding aspects are considered in turn in the following sections.

Product Specification

It is our philosophy that specifying products by nationally recognized standards is beneficial to both the buyer and seller. Hence the wide use of ASTM standards, for chemical contents, sizing of materials, or methods of analysis. In some cases the standards may be relaxed from those published, in which case the notation "ASTM XYZ Modified" is used and the modification clearly spelled out on the purchase order.

A specification starts when a potential material is presented by a supplier to the buyer and metallurgist. If its description, examination of a small sample, and commercial considerations warrant further experimentation, the performance of production sample lots is determined. If the material is accepted for use, the metallurgist writes a draft of a specification (including sampling and testing required) and sends it to the buyer. The latter adds all commercial information needed and returns the finished form to the metallurgist. He then passes it on to the chemists, who will check the material, and then to the steelmaking shops which are to use the material. Finally, the specification is approved by the manager of steel production. Then it is issued as a sheet in the *Purchasing Specifications Book* and entered into the computer memory.

The specification sheet shows the ASTM or other specification, chemistry, sizing, packaging, shipping, special instructions, etc.

Fluxes are handled similarly, as are other materials such as coating metals.

Changes are handled similarly, a page being issued as "Revision No. . ." and undergoing the same approval process. A change of an ASTM standard may be the reason for issuing a revision. The year designation of the standard is not used, it being understood that the latest revision is applicable.

We may respond to the available supply position by making variants in our specifications for nominally identical materials, such as recognizing two size ranges, but usually with restrictions on oversize or undersize. For instance, we may order some alloy as "4 by 1, no piece over 5 in.[2] in any dimension," on account of limitations of the alloy chute throats, but another lot as "3 by 1/2, maximum 10 percent under 1/8 in.," to prevent large amounts of fines, even if such restrictions are not recognized in ASTM standards. Metric dimensions are acceptable, with the applicable tolerances.

While the procedure may appear complex, it works in practice very well. The Stores Department or the steelmaking shop sends a requisition to Purchasing. Experimental alloys are requisitioned by the raw materials metallurgist through the steelmaking shop that will evaluate them.

The purchasing agent issues to the producer a purchase order showing the entire set of data or a routine release. He may issue his own purchase order or release according to the stock position with respect to the reorder point; this is established yearly by consultation between the manager of steel production, purchasing agent, and the metallurgist, using sales forecasts, past-usage patterns, market conditions, and expected new metallurgical trends.

Material Control

The producer sends the usual shipping notice(s) to the receiving point, but also sends copies with certification of chemistry and sizing to the Chemical and Metallurgical Departments. Most expensive alloys are channeled through the Stores Department, where they are sampled. All shipments, regardless of point of delivery, are inspected for size and most of them are also sampled. When expensive alloys are purchased bagged, with a guaranteed weight of the element per bag, sample bags are also weighed and the amount of contained alloy is calculated after chemical analysis. In briquetted materials, broken briquettes and fines are separated by hand and weighed, rather than by screening.

Apart from formal screen analysis, we use a little tool that gives a fairly good idea of the material size distribution. This is a series of wooden cubes in 1-in.-size increments, threaded on a string. Throwing this gadget on a pile gives, by comparison, a good clue to the distribution of size in the shipment or, even more important, in a part of it, and is often used to decide whether to take a formal screen analysis sample, perhaps even from different parts of the shipment. Occasionally a photograph is taken of the string on the pile and it may be used when undesirable sizes are encountered. One such photograph is shown in Fig. 1.

The results of a chemical analysis, size estimate, or formal screen analysis are circulated to all concerned. If a result does not agree with the specification, it is immediately telephoned to everyone involved and a red flyer, "Danger—Out of Spec," is attached to the report sheet.

The rejection decision, a rather uncommon occurrence, is usually made by the raw materials metallurgist or occasionally by the steelmaking shop and

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[2] Metric conversion factor: 1 in. = 25.4 mm.

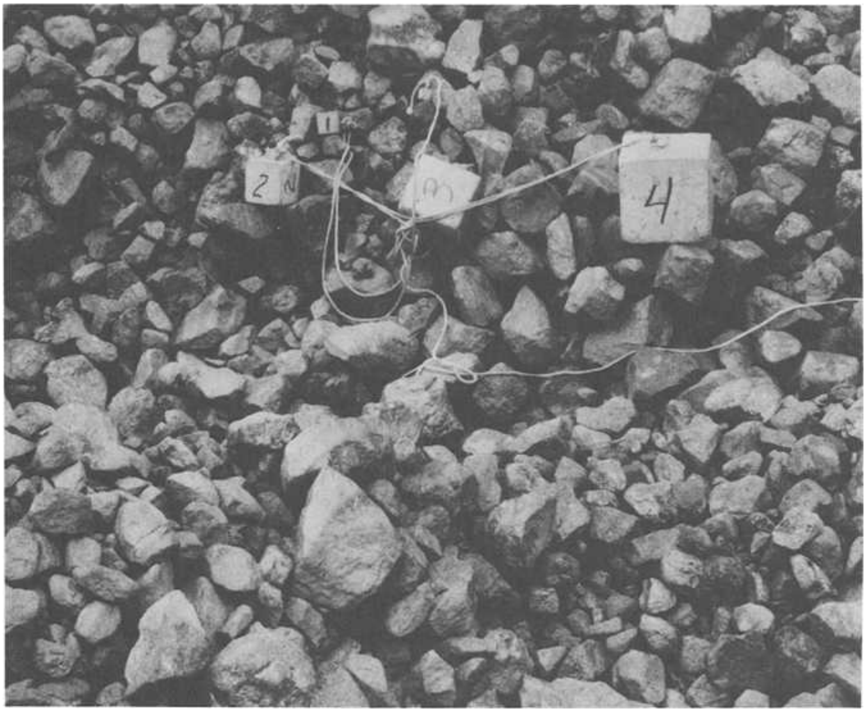

FIG. 1—*Material sizing string.*

transmitted to the purchasing agent. The purchasing agent, along with the metallurgist, takes up the matter with the supplier.

A material may be acceptable for chemistry but off-ordered quality for sizing, in which case screening out the undersize or oversize makes it universally applicable. However, we do not have screening facilities available.

Often a marginal material may be used for specific application or at an increased input rate, or in one specific steelmaking shop only. If this results in increased costs, a suitable credit is requested from the supplier. While these credits do not cover the cost of sampling and checking the shipments, the frequency of missed steel chemistry is very low, with the check system probably contributing to the good performance.

The metallurgist carries all the information from the producers and Inland's checks and once a year runs off a complete summary of ferroalloy quality by material and, within the material, by supplier. Average chemistries and particularly spreads of chemistries are determined and compared with our checks. Sizing abnormalities are noted.

There is an aspect of chemical control that may lead to arguments between the producer and Inland. Some producers tend to bill for many shipments an average pile chemistry. However, since the pile is composed of many casts, even the best cross-bedding and reclaiming may give a check sample that is outside the specification. If such a result is encountered, the Sampling Section of the Chemical Department immediately resamples the shipment and the samples are run individually. If a recheck is outside the specification, the shipment is rejected or renegotiated if the material is usable with limitations.

Input Control

The input of a ferroalloy into a heat depends on the metallic weight charged and steel yielded that varies with the ordered specification. This varies with the carbon level, but also with steelmaking practice and the aim and residual content of the element. Furthermore, it depends on the nominal or average content of the element or elements in the alloy and its recovery, including that of the side elements.

We developed at Inland a shortcut to these complex calculations that saves the melter two calculations, thus two possible sources of error, and is very suitable for control purposes, especially when a heat log which shows the furnace yield is available. It requires the knowledge of average furnace yield for each carbon level, average element content for each alloy or other additive used, and average element recovery—none too difficult to get from files of heat cards and alloy analyses.

The background of this development is

*T*otal *M*etallic *C*harge × *F*urnace *Y*ield = *L*iquid *S*teel *W*eight

$$TMC \times FY = LSW$$

*I*ncrement *R*equired, *IR* = (Aim − Residual) Analysis

then

LSW × *IR* = *G*ross *A*lloy *W*eight × *E*lement *C*ontent × *E*lement *R*ecovery

or

$$LSW \times IR = GAW \times EC \times ER$$

Replacing the unknown to the melter, *LSW* with the known *TMC* × *FY*

$$TMC \times FY \times IR = GAW \times EC \times ER$$

and thus the required

$$GAW = (TMC \times FY \times IR)/(EC \times ER)$$

If we express *FY*/(*EC* × *ER*) with one expression, melter's factor, *MF*, then the amount of the alloy to be added becomes simply

$$GAW = (TMC \times IR)/MF$$

The *TMC* is known to the melter as soon as the heat is charged, the *IR* as soon as the melt or pretap analysis is obtained. The melter looks up the *MF* or has the computer look it up for him for the given specification and either uses his pocket calculator or the computer itself.

A very modern system of alloy control has been described in detail by Arethas and Spangler.[3] This refers to our No. 2 Basic Oxygen Furnace (BOF) Shop. Its benefits are particularly apparent with respect to the very wide range of product mix, from 0.03 to 0.95 percent carbon, with numerous alloy steels made, a total of about 260 grades. There are eight ferroalloy bins and numerous bagged alloys are used as well.

The computer carries up to 294 specifications with up to 16 elements for each specification and up to three alloy practices for each element. Each ferroalloy has its composition, including that of secondary elements and impurities and their recoveries for the given specification entered into the memory, *de facto* a set of melter's factors in three versions for each steel specification.

The reason for the three alternate practices are the varying market conditions, cost, and availability. Shop management may instruct the melters to use preferably Practice A, then shift to B or C, as required.

The melter enters the melt and aim chemistry and out come the recommended alloy practices. These take into account such items as carbon and silicon limits. For instance, the computer will utilize Regular FeMn up to nearly the aim carbon analysis and then supply the balance with the more expensive medium-carbon grade. Or combine Regular FeMn with SiMn to the silicon aim. Or replace the SiMn with FeSi, FeMn, and a recarburizer. A maximum permissible liquid steel chill is another limit built into the calculations.

Once the melter makes his practice selection, he dials in the amounts of the alloys required from the bins. Once he approves, by pushing respective buttons on the scale display from each bin scale (recommended), the amount weighed out is recorded by the computer and both the calculated and actually weighed-out amounts are listed on the heat card printout. Other materials are entered manually, since almost all are bagged and inventory management is quite reliable.

A melter is entitled to modify the alloy inputs according to his judgment of the heat condition, but he must justify his decision on the card. Corrections for reblows, bath overoxidation, etc. are shown in the printed Practice Sheet for each steelmaking specification. Shop management takes up any cases of waste with the individual involved—not a common occurrence.

The net result of the system is consistency of practice from melter to melter, good chemical control in light of the wide product mix, and good cost control.

Each melter is rated monthly for his performance in meeting the ordered steel chemistry and its temperature. The rating sheets are distributed to each man involved. We are planning to spend considerable money on improving

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[3] Arethas, S. P. and Spangler, R., *Iron and Steelmaker*, American Institute of Mining, Metallurgical and petroleum Engineers, June 1976, p. 41.

our system of analyzing each ladle of hot metal to include all elements significant to BOF operations. Once this is introduced, it should become possible to rate each operator also as to his charging and turndown performance, his improved hot metal control contributing to avoidance of heats that must be reblown before tap, which, in general, leads to increased ferroalloy consumption.

It is easy for control purposes to obtain a tabulation of all realized melter's factors by specification, including the heat yield. Of course, a heat with an exceptionally low steel yield from the total metallic charge weight will concentrate the additive in a smaller liquid steel weight, thus giving a higher than aimed for chemistry and a misleadingly high melter's factor, while a high yield may miss the aim on the low side. The printout will highlight this by showing the heat yield next to the factor for each element.

Of course, in the older shops calculations and reporting are done manually and the metallurgists back-calculate the actually realized factors whenever needed, again paying attention to heat yields and other unusual occurrences, such as a slow tap in an open hearth. The calculation is, of course simple from the previous equations

$$MF = (TMC \times IR)/GAW$$

all data available from heat cards.

In these shops, melters are guided in their alloy additives by the Practice Sheet for each specification, which has sliding scales or notes about the expected carbon or other elements recovery, more additions to overoxidized heats or their diversion, etc. In any case, rearranging the equations allows the calculation of the metallic recovery, if desired, as

$$ER = (MF \times FY)/EC$$

Such control calculations pinpoint the average performance of the additive and also its spread. The cost must include the material cost, including handling and credits for other values with the main element, but also penalties due to any steel quality problems.

It may happen, and it has happened in the past, that while the average recovery of an element from the alloy was higher than that obtained from the material in current use, the wide spread of values makes the new alloy unattractive for use.

Development

The existence of good controls leads, of course, to work toward minimizing the cost/benefit ratio. The very first one is lowering the steel chemistry, that is, the input of alloying elements, to the lowest level which insures obtaining the desired properties; this depends on the consistency of alloy performance and thus is easy if the alloy recovery is close to 100 percent independently of the degree of steel oxidation at tap. Saving of molybdenum inputs following its rapid price increase comes immediately to mind. In this case a significant part of the molybdenum input was obtained from segregation and purchases of molybdenum-bearing scrap.

The next is replacement of higher-priced with lower-cost versions of an alloy. Obviously, maximizing the use of regular high-carbon ferro-manganese over the medium-carbon version will result in significant cost savings. Also, secondary savings due to reduction of usage of recarburizer will be realized. In turn, maximizing the use of the medium-carbon grade to replace extra-low-carbon ferromanganese would give significant benefits, and this has been achieved both by increased maximum carbon content of some intermediate-manganese, low-carbon steels, a job which required about two years of metallurgical development work and by some changes in the finishing steelmaking practices. As a result, the usage of the expensive extra-low-carbon grade was cut by about 80 percent.

Sometimes the trend is in the other direction: stricter demands of steel quality may require the use of a more expensive or less available alloy. For instance, steel cast by open-stream continuous casting suffers from aluminum contents exceeding about 0.01 percent. Thus we use only low-aluminum alloy versions for our billet caster. While this introduces stocking and moving costs, it is highly beneficial for cast steel quality.

Similarly, we used our control system to evaluate the performance of steel made with a pressed mix of aluminum with regular high-carbon ferromanganese and came to the conclusion that replacing this mix with a more expensive one, based on medium-carbon FeMn, gives a more consistent carbon recovery, leading to improved steel finishing practices and to better steel quality. Thus the switch was made from a cheaper to a more expensive alloy with significant overall savings.

Two cases which required prolonged metallurgical footwork deserve special mention: the development of vanadium carbide pellets against ferrovanadium and later extensive replacement of vanadium with columbium.

The first[4] required determining why additions of the relatively light pellets resulted in erratic vanadium recovery. Since the material appeared otherwise attractive, we spent significant time on this problem and finally achieved good utilization of the vanadium carbide by changing the traditional manner of sequencing the ladle additions and educating the melters in the new practice, which requires precise timing of the additive and its sequencing in the ladle despite the rather fast BOF taps.

No sooner was this job completed when it becomes obvious that in many high-strength low-alloy steels, vanadium can be successfully replaced by columbium. Since recoveries of columbium and vanadium were similar but the

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[4] Peters, A. T., *Iron and Steelmaker,* American Institute of Mining, Metallurgical and Petroleum Engineers, Jan. 1977, p. 26.

price of the former was a little less than that of vanadium, and the desired metallurgical effects required less than one half columbium in comparison with vanadium, a whole new area of investigation was opened up. However, no large-scale substitution could be carried out until the effects of the switch from vanadium to columbium on virtually each product individually could be determined.

Actually, after more than a year of work, by product and customer metallurgist, it turned out that not all section sizes and not all applications could be converted to the much cheaper columbium practice, but the net effect of the changes made were savings of about one-half million dollars per year. In the meantime, the steelmakers and steelmaking metallurgists had to cool their heels, but product quality was at stake and alloy costs were of secondary importance.

Thus it is not the price, as often presumed, but the cost/benefit ratio that controls alloy practices. Inland spends significant sums every year for their control, but savings in control costs would in all possibility actually increase the alloy costs due to increased missed chemistry heats. This could detrimentally affect the steel performance at the customer's plants, wiping out any savings in cost control of ferroalloys.

R. S. Stryker[1]

Controlling Quality of Ferroalloys and Alloying Additives in the Manufacture of Nickel Alloys for Nuclear Applications

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REFERENCE: Stryker, R. S., "**Controlling Quality of Ferroalloys and Alloying Additives in the Manufacture of Nickel Alloys for Nuclear Applications,**" *Ferroalloys and Other Additives to Liquid Iron and Steel, ASTM STP 739,* J. R. Lampman and A. T. Peters, Eds., American Society for Testing and Materials, 1980, pp. 93-98.

ABSTRACT: Nickel alloys supplied to the nuclear industry must meet strict requirements for quality and traceability of constituents. Ensuring that end products meet those requirements involves careful control of the raw materials used in melting the alloys. Especially important is an effective system of quality control for purchasing and consuming ferroalloys and alloying additives. Development and operation of such a system requires (1) adequate specifications, (2) good relations with suppliers, (3) an approved-suppliers list, (4) formal receiving inspection, and (5) backup surveillance during processing.

KEY WORDS: ferroalloys, alloying, quality control, nickel alloys, raw materials, nuclear applications

Manufacturers of the nickel alloys used in the nuclear industry must meet stringent quality requirements and comply with strict specifications. A comprehensive program of quality assurance must be carefully applied throughout the production sequence from melting and processing to final inspection, testing, and shipment of the finished product. An important aspect of ensuring that the end product is acceptable is determining that the incoming raw materials are of suitable quality.

The elemental metals such as nickel, copper, and chromium that are used in melting are normally of high purity as a result of the methods by which they are produced. Such basic raw materials, received in bulk by the manufacturer of wrought nickel alloys, present few quality control problems. In contrast, raw materials such as ferrochromium and molybdenum oxide, which are used in making up a furnace charge, and those such as nickel co-

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lumbium and ferromolybdenum, which are used as late additions, may have variable processing histories and residual element contents.

The manufacturer must apply an effective system of quality control in purchasing and consuming these ferroalloys and alloying additives. As with all purchased items, adequate receiving inspection is fundamental to an effective system.

General Requirements of the Nuclear Industry

Production of nickel alloys for nuclear and other critical applications requires a quality assurance program that meets two specifications, one for military shipbuilding and one for commercial electricity generation. Materials supplied to the shipbuilding industry are covered by MIL-I-45208A, "Inspection System Requirements," administered by the Department of Defense. Materials supplied for commercial nuclear applications are covered by the ASME Boiler and Pressure Vessel Code, Section III, Subsection NCA-3800: "Metallic Material Manufacturers and Metallic Material Suppliers Quality System Program." The Nuclear Regulatory Commission has responsibility for commercial nuclear applications.

These, and other related specifications, have requirements for incoming raw materials, supplies, and services as listed in Table 1. Purchased raw materials as defined by the nuclear industry specifications extend only to ingots and ingot products. For the manufacturer of nickel alloys, however, purchased raw materials might well go beyond the ingot stage to the ferroalloys and alloy additives that are used in the melting operations. Self-imposed specifications for materials that are used in the melt shop will develop the

TABLE 1—*Applicable specifications for purchased raw materials, supplies, and services.*

	Specification
Raw Materials	
1. Ferroalloys and alloying additives	Internal
2. Ingots and ingot products	MIL-45208A ASME Section III NCA-3800
3. Flux materials (coated electrodes for welding products)	MIL-I-45208A
Supplies	
1. Marking inks	MIL-N-23229
2. Liquid-penetrant supplies	MIL-I-25135
3. Strapping	QQS-781
4. Lumber and boxing	MIL-C-3933
5. Containers, cans, etc. (packaging of welding products)	MIL-W-10430
Services	
1. Calibration of measuring and testing equipment	MIL-C-45662
2. Subcontracted material processing	ASME Section III NCA-3800

necessary controls to ensure that the end product meets both processing and specification requirements.

Development of a Quality-Control System

A quality control system for ferroalloys and alloying additives involves several factors, but an effective system must be built around (1) internal specifications that fully define the material being purchased and (2) receiving inspection to make certain that purchased materials meet specifications. Successful development and operation of the system require the cooperation of the purchasing, manufacturing, and quality-assurance departments.

Specifications

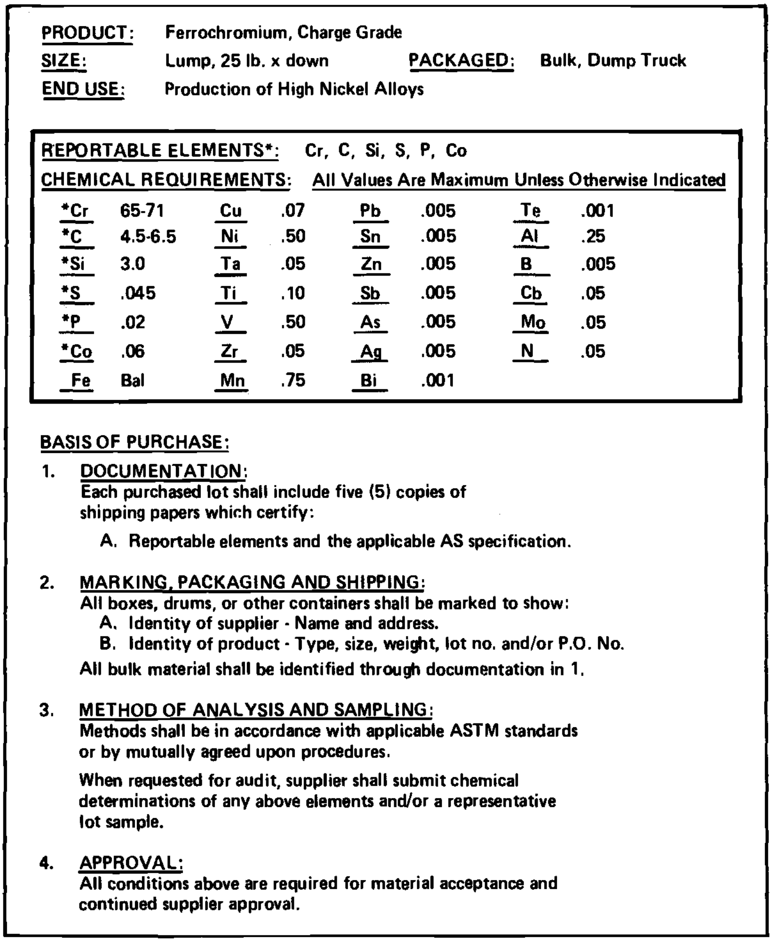
The first step in controlling purchased raw materials is writing a specification for each ferroalloy and alloying additive. Specifications for ferroalloys can be patterned after those prepared by ASTM Committee A-9. Quality Assurance should write the specifications in a standard format, and each specification should be approved by Purchasing and Manufacturing. All documents should be numbered, dated, and revision-controlled. Figure 1 is an example of a specification for ferrochromium. The two most important stipulations are chemical analysis and identification.

Chemical composition must be controlled within the limits needed to meet requirements for the final product and requirements for processing the alloy through the mill. Control of harmful residual (tramp) elements is especially important since nickel alloys, unlike steel are highly sensitive to their presence. Extremely small amounts of elements such as lead, bismuth, and zinc can be deleterious to hot malleability and high-temperature mechanical properties.

Methods for chemical analysis and sampling of raw materials should be specified. ASTM standards can be used, or other methods agreeable to both supplier and purchaser can be stipulated. Those elements most critical in melting should be reported by the supplier on a certificate of analysis or certificate of conformance for each lot of material. Ideally, the lot chemistry is established with an aggregate of samples from the shipment.

Proper identification of both product and supplier is necessary to avoid mix-up in use and to provide traceability. The identifying information must be posted on heat records when the material is melted, and the identification needed for accurate recordkeeping must be a part of the specification.

Packaging and sizes vary with the type of product but should be specified for ease in handling and to control fines. Materials such as ferrochromium used in quantity in making up a charge are generally of large size and delivered in bulk. Additives, particularly late additions such as nickel columbium, are normally best handled when crushed into small sizes and packaged in drums or boxes.



PRODUCT: Ferrochromium, Charge Grade

SIZE: Lump, 25 lb. x down **PACKAGED:** Bulk, Dump Truck

END USE: Production of High Nickel Alloys

REPORTABLE ELEMENTS*: Cr, C, Si, S, P, Co

CHEMICAL REQUIREMENTS: All Values Are Maximum Unless Otherwise Indicated

*Cr	65-71	Cu	.07	Pb	.005	Te	.001
*C	4.5-6.5	Ni	.50	Sn	.005	Al	.25
*Si	3.0	Ta	.05	Zn	.005	B	.005
*S	.045	Ti	.10	Sb	.005	Cb	.05
*P	.02	V	.50	As	.005	Mo	.05
*Co	.06	Zr	.05	Ag	.005	N	.05
Fe	Bal	Mn	.75	Bi	.001		

BASIS OF PURCHASE:

1. **DOCUMENTATION:**
   Each purchased lot shall include five (5) copies of shipping papers which certify:
   A. Reportable elements and the applicable AS specification.

2. **MARKING, PACKAGING AND SHIPPING:**
   All boxes, drums, or other containers shall be marked to show:
   A. Identity of supplier - Name and address.
   B. Identity of product - Type, size, weight, lot no. and/or P.O. No.
   All bulk material shall be identified through documentation in 1.

3. **METHOD OF ANALYSIS AND SAMPLING:**
   Methods shall be in accordance with applicable ASTM standards or by mutually agreed upon procedures.
   When requested for audit, supplier shall submit chemical determinations of any above elements and/or a representative lot sample.

4. **APPROVAL:**
   All conditions above are required for material acceptance and continued supplier approval.

FIG. 1—*Example of a specification for ferroalloys and alloying additives.*

An important aspect of the development of specifications is involvement of suppliers. A specification is of little use if its requirements cannot be met by suppliers or are interpreted in different ways by supplier and purchaser. Each specification should be reviewed with suppliers to make sure that all requirements are clearly understood and mutually agreeable. Good communication and relations with suppliers are needed for a quality control program to work smoothly.

Approved Suppliers List

A list of approved suppliers must be developed and maintained. A representative sample of the raw material should be obtained from each potential supplier. A complete chemical analysis should be performed on the sample with results checked against the specification. Analysis for trace elements is especially important since they usually are not reported for every lot of certified raw material. Any discrepancies must be resolved before the supplier is placed on the list of approved sources.

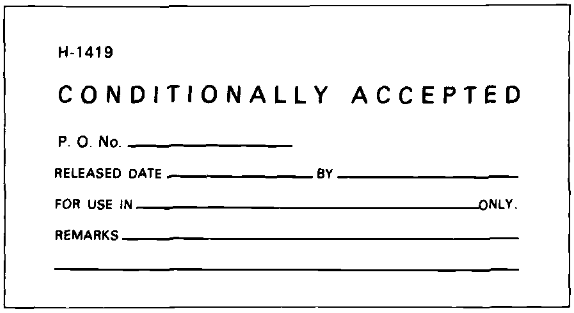
The suppliers list is used by Purchasing to place orders according to price and delivery. Suppliers remain on the list as long as their shipments comply with specifications. Removal of suppliers from the list is at the direction of Quality Assurance and depends on the results of receiving inspection.

Receiving Inspection

The cornerstone of a quality control system for raw materials is formal receiving inspection. Each incoming shipment must be checked for reported analysis and identification as required by the specification. Shipping papers must match the material marking.

When the reported chemical analysis shows that an element is outside specification limits, the raw material should be evaluated by the Melt Shop and Quality Assurance to determine whether it can be used. Depending on the out-of-definition element and specifications for the end product, the material may be conditionally accepted for certain alloys or product forms. Such material should be clearly marked with a label or tag similar to that in Fig. 2 specifying the restrictions for its use.

Material rejected for any reason should be conspicuously marked and set aside. The supplier and Purchasing must then reach a mutually agreeable resolution to the problem. Another chemical analysis of the material may be required, but analysis of a "grab sample" is not a valid means of rejection. The supplier should have a representative lot sample on which referee analysis can be performed as provided by the specification. Material determined to be unusable should be returned to the supplier and the supplier's status on the list of approved sources should be reevaluated.



H-1419

CONDITIONALLY ACCEPTED

P. O. No. ____________

RELEASED DATE ____________ BY ____________

FOR USE IN ________________________ ONLY.

REMARKS ________________________

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FIG. 2—*Identification of conditionally accepted material.*

Backup Surveillance

Periodic analysis of ladle samples is a useful supplementary control. For example, every tenth or twentieth heat could be analyzed for trace-element content. Analyses should also be performed on heats that show reduced hot malleability. Lot identities on melting records can be used to trace harmful elements to their sources and to help resolve *ex post facto* complaints.

Summary

Supplying alloy products to the nuclear industry requires a program of quality control and traceability for raw materials such as ferroalloys and alloying additives. In developing such a program, the alloy melter should

1. write definitive specifications,
2. work closely with suppliers,
3. maintain an approved-suppliers list,
4. inspect each shipment by formal procedures,
5. reject nonconforming materials, and
6. perform backup surveillance during processing.

W. H. Trethewey[1] *and J. R. Jackman*[1]

Trends in Rare-Earth Metal Consumption for Steel Applications in the 1980's

REFERENCE: Trethewey, W. H. and Jackman, J. R., "**Trends in Rare-Earth Metal Consumption for Steel Applications in the 1980's,**" *Ferroalloys and Other Additives to Liquid Iron and Steel, ASTM STP 739,* J. R. Lampman and A. T. Peters, Eds., American Society for Testing and Materials, 1981, pp. 99–109.

ABSTRACT: During the 1920's and 1930's, rare-earth metals (REM's), periodic chart Group IIIA—lanthanides, were virtually unknown to wrought, carbon, and steel alloy steel producers. Between 1940 and the late 1960's the proven hot and cold formability benefits of rare-earth usage in carbon, alloy, and stainless steels were over shadowed by inconsistent addition recoveries and poor microcleanliness. As a result, rare-earth metals had limited application until the late 1960's, when the development of 550 000-kPa (80 000 psi) high-strength low-alloy steel demonstrated that the formulation of stable globular rare-earth sulfide and oxysulfide inclusions led to substantial improvements in toughness and formability. As metallurgical technology advanced throughout the 1970's, REM consumption increased by a factor of five. The benefits of sulfide-shape control and hydrogen-induced cracking control aided diversification of REM's application while desulfurization technology and continuous casting to some extent had a negative impact upon consumption. It will be concluded that, as the demand for higher-performance steels increases, the steel producer will continue intensifying individualized plant searches toward sulfur control. Moreover, REM consumption during the 1980's will continue to increase as the diversification into additional steel applications continues.

KEY WORDS: desulfurization, hydrogen-induced cracking, sulfide-shape control, rare-earth metal, Charpy, consumption, oxysulfides, solidification, sulfur control, mold additions, recoveries, continuous casting, deoxidation, sulfide morphology

In the early 1920's and 1930's, the elements of Group IIIA, known as the lanthanides or more commonly referred to as the rare-earth metals, were virtually unknown to most carbon and alloy steel producers. Rare earths were being used at that time to improve hot and cold formability of carbon, alloy, and stainless steels [*1–3*].[2] Problems encountered with rare-earth additions, that is, inconsistent recovery and poor cleanliness, prevented a much broader application of these elements.

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

The rare-earth metals (REM) form extremely stable sulfides and oxysulfides [*4*]. Therefore, their use in aluminum-killed steels results in the improvement of toughness and formability by controlling the sulfide morphology. Maintaining a rare-earth/sulfur ratio of 3 to 1 in the final product results in globular rare-earth sulfides instead of the elongated Type II manganese sulfides. This was very dramatically demonstrated with the development of a 567-MPa (80 000 psi) high-strength low-alloy (HSLA) steel during the late 1960's [*5*].

During the early 1950's, there were significant contributions in rare-earth metal additions in stainless, tool steel, alloy, and electrical steel grades [*6*]. REM (mischmetal) was used to promote improved rollability of stainless and to improve Charpy impact at low temperature in armor plate and in wear- and abrasion-resistant steels. Again, use and acceptance of REM was limited because of the recovery and cleanliness problems. The development of the HSLA steels in the 1960's provided the necessary incentive for the rare-earth metal manufacturer and the steelmaker to solve some of these basic problems. This was done with development of new addition techniques and a more thorough understanding of the various mechanisms and side effects involved in the use of REM.

Since 1968 the Free World annual consumption of rare-earth metals for metallurgical applications has grown dramatically from 90 000 kg [200 000 lb (100 tons)] to 6 525 000 kg [14 500 000 lb (7243 tons)] in 1978, Fig. 1 [*7,8*]. As metallurgical technology advanced through the 1970's, several dramatic changes had taken place within the steel industry in rare-earth metal consumption. Not only will we review the history of this rare-earth metal consumption in the steel industry during the 1970's, but evaluate several trends that will affect consumption for the early 1980's.

Changes in Rare-Earth Metal Consumption During the 1970's

During the 1970's there were counteracting trends that affected rare-earth metal consumption in the steelmaking community. Several had a negative impact on actual REM consumption while others provided growth through a broader application of REM in the development of more critical grades of steel. The broader application of REM used in steelmaking during the past 10 years has more than offset the decrease in actual pounds of REM used per ton of steel treated.

As can be seen in Fig. 1, for 1968 and 1970, the initial rare-earth metal consumption growth came from the United States and Canada. This segment has continued to grow throughout the 1970's. During the 1972–1974 period, REM consumption in the rest of the Free World, primarily Europe and Japan, increased substantially. Over 90 percent of the foreign consumption for that period was in large-diameter line pipe production from ingot cast steel.

As the European and Japanese steelmaking communities moved toward

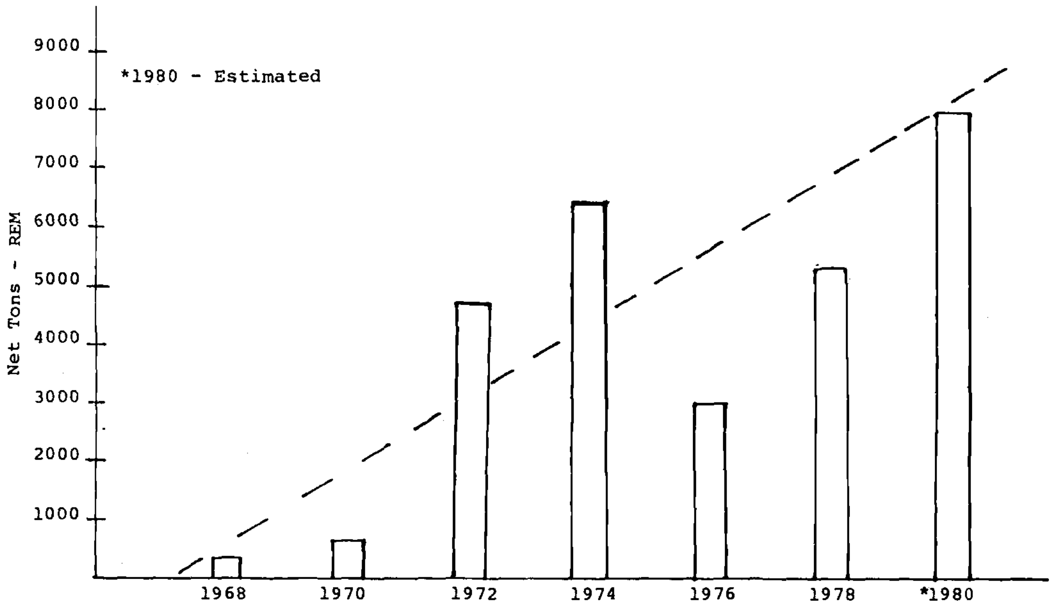

FIG. 1—*Free World consumption of rare-earth metals in iron and steel [1 U.S. (short) ton = 0.9 metric ton].*

continuous casting facilities, rare-earth metal consumption dropped due to technical difficulties encountered when attempting to produce rare-earth-treated continuous cast steels [*9*]. Simultaneously, the worldwide steel community was rapidly developing the technology to obtain lower-sulfur-level steels. For example, desulfurizing to 0.010 to 0.005 percent sulfur in some cases reduced or eliminated the need for sulfide shape control.

The move toward continuous slab casting and the development of desulfurization technology had a somewhat negative impact on total rare-earth metal consumption. The official or unofficial opinion among many metallurgists during the early 1970's was that REM in steel was trending toward limited usage. Beyond the previously mentioned trends, alleged welding problems with CO_2 gas metal-arc techniques, particularly in root passes of field girth welding of gas transmission lines, were creating additional doubt about REM value in steel. Based upon this performance feedback, some metallurgists became very skeptical about the use of REM in many steel products.

About 1973–1974, REM market development and steel process development efforts were accelerated by a U.S.A. producer of mischmetal and rare-earth silicide. The market development approach focused upon the mechanisms of rare-earth metal action on steel structures and rare-earth metal's subsequent positive impact and influence on steel product properties [*9*]. Moreover, the steel process development approach focused upon REM addition practices during steelmaking [*10*]. Primary emphasis was placed on proper deoxidation and desulfurization to levels of sulfur where the resultant sulfides and oxysulfides created would not cause secondary problems to the steelmaker. These secondary problems were sometimes more serious than what the initial REM treatment was designed to achieve.

Hence, the metallurgist was beginning to understand many other facets of rare-earth metal metallurgy in microalloying of REM in steelmaking. New areas of rare earth technology were being developed because of the better understanding of liquid steel alloying, liquid steel reactions, solidification, hot-rolling and cooling; and mechanical working and welding of steel containing REM [*9*].

REM Market Development

As illustrated in Table 1, and with the knowledge that rare-earth metal could have metallurgical benefits in the area of

1. sulfide shape control and
2. hydrogen-induced cracking control,

steel product groups were then isolated where both were known to be prevalent problems.

Sulfide Shape Control

As is now history, REM is added to high-carbon and HSLA steels for resistance improvement to spalling. Examples of steel product applications are sawblades, plow blades, and ordinance applications of armorplate.

TABLE 1—*Changes in REM consumption patterns.*

Negative Trends
- European and Japanese trend ingot cast to continuous cast
- Desulfurization technology development

Positive Trends
- Metallurgical realization of REM benefits
- —sulfide shape morphology control
- —hydrogen-induced cracking control
- Steel process technology leading to more cost-effective use of REM

REM is now being added to improve the weld quality of high-strength electric resistance welded tubes to the point where they successfully compete with seamless tubes in oil company goods applications.

The addition of REM to large structural beam steels, nonsemikilled, has minimized lamellar tearing around the welds as well as increasing low-temperature toughness for new rigid welded structure designs.

Small additions of REM after alloying and desulfurizing of pipe and plate steels to 0.003/0.005 percent sulfur were found to maximize impact properties. Japanese literature shows improvements are available by adding REM to 0.003 percent sulfur steels [*11*]. However, steel desulfurization by injecting with calcium compounds did not lead to 100 percent sulfide shape control. Manganese sulfide inclusions were observed at 0.005 percent sulfur levels after calcium treatment. These manganese sulfide inclusions were modified with additions of REM which resulted in improved properties.

Hydrogen-Induced Cracking Control

During the 1970's, it was found that well-calibrated additions of REM could have significant delaying effects on hydrogen-induced cracking, both in welds and the base metal, without affecting other properties [*12*].

Rare-earth metals are added routinely for hydrogen sulfide stress corrosion cracking resistance in high-strength deep oil and gas well casing as well as drilling stock for "sour gas" environments.

Considerable progress has been made in reversing the negative thoughts about REM use in gas transmission lines. Again, the benefit of a delaying effect on hydrogen-induced cracking, where critical pressures and hydrogen sulfide concentrations are known to exist, is being reevaluated.

This market development and acceptance has led to a much broader application of rare-earth metal in steel products. In the 1960's, there were essentially six broad steel product groupings using REM. Today there are approximately eleven product groups (see Table 2).

Process Development

During the 1960's and early 1970's, a rare-earth silicide (approximately 33 percent rare earth, 33 percent silicon, and 33 percent iron) alloy was the most

TABLE 2—*Steel Product Group Application.*

1960's	1980's
Superalloys	Superalloys
Stainless steels	Stainless steels
Special bar quality	Special bar quality
HSLA automotive	HSLA automotive
ERW line pipe	ERW line pipe
Armorplate	High-carbon steel
	ERW welded tubes
	Seamless tubes
	Rails
	Large structural
	Armorplate

commonly accepted form of rare-earth metal for REM additions in the ladle and ingot mold. Ladle addition levels generally ran between 4.5 and 10.8 kg (10 and 24 lb) of alloy per net ton[3] of steel treated with very low and sometimes erratic recoveries. This often resulted in inconsistent steel property results. The raw material treatment cost of this ladle addition practice was between $12.00 and $25.00 (in 1980 dollars) per net ton of steel produced.

Mold additions of rare-earth silicide were also used during this period. Although treatment cost was much lower per ton of steel treated because of higher recoveries, it often caused surface and subsurface problems. Some plants found mischmetal a more attractive mold addition and results usually were much better than a comparable mold practice with rare-earth silicide [*13,14*].

Based on the high-cost rare-earth silicide ladle practice, along with its very erratic recoveries and combined with the steelmakers desire to eliminate the mold addition technique, ladle plunging of mischmetal canisters won acceptance during the early 1970's [*15,16*]. Addition rates were in the area of 0.675 to 1.125 kg (1.5 to 2.5 lb) per ton of steel treated. The use of this practice brought the REM treatment down to $7.00 to $12.00 per net ton. The actual cost per ton depended on grade and particular application.

As the 1970's progressed, economic balances between reasonably low sulfurs and residual sulfide control reopened interest in the use of mischmetal in certain steelmaking applications. Some of these applications were HSLA automotive steels where cold formability, surfaces, and cost were criteria for steel product acceptance [*13*]. Steelmaking practices were developed to add mischmetal balls using standard mold addition and delayed mold addition techniques. The cost of these practices further reduced the addition of REM to steel to a level of 0.45 to 0.675 kg (1 to 1.5 lb) per net ton for a treatment cost of $5.00 to $7.00 per net ton of steel treated.

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[3] 1 U.S. (short) ton = 0.9 metric ton.

Table 3 summarizes this advancing metallurgical technology from the 1950's through the 1970's. The reduction in both the consumption of REM per net ton and the cost per net ton have been quite impressive.

For a moment, let us refer back to Fig. 1. After the initial examination of Fig. 1 and the review of the negative trends, namely, development of desulfurization technology and continuous casting, it would have been easy to conclude that rare-earth metal consumption was static or perhaps declining during the mid-1970's with little potential growth available for the balance of the 1970's. However, after the review of the market development and process development changes that impacted rare-earth metal consumption during the late 1970's, rare-earth metals are now positioned for a continued growth cycle during the early 1980's.

If we take all of the positive and negative impact trends and combine the data, some interesting conclusions can be drawn. Figure 2 shows that the net tons of steel treated with rare-earth metals has multiplied by a factor of five between 1972 and 1978. The key factor which is not apparent in Fig. 1, is the dramatic reduction in consumption of REM per net ton of steel treated during the 1970's. This increase in net tons of steel treated with rare-earth metals should continue through the early 1980's because of the broader acceptance and use of rare-earth metals in many applications requiring sulfide shape control and hydrogen-induced cracking control.

Trends During the 1980's

As we look forward into the 1980's, sulfur removal and control in steelmaking continues to be in the limelight.

Since steelmaking began, the need for lower and lower sulfur steel has been recognized. The need for improved surface and internal soundness varies considerably and is dependent upon product application. Moreover, not

TABLE 3—*Technological development of REM additions to steel.*

Period	Addition Method	REM Product	REM Addition Level, lb/ton	Cost/ton, 1980 dollars
1950's	1. mold	mischmetal 4-oz ingots	3/4 to 6	$ 4 to 30
1960's	1. mold	mischmetal 4-oz ingots	2 to 3	$10 to 15
	2. ladle	RE silicide 2 in. by down	3 to 8	$12 to 25
	3. mold	RE silicide 2 in. by down	2 to 3	$ 6 to 12
1970's	1. mold	mischmetal 4-oz ingots	1 to 2	$ 5 to 10
	2. ladle	RE silicide 2 in. by down	3 to 7	$12 to 23
	3. mold	RE silicide 2 in. by down	2 to 3	$ 5 to 10
	4. ladle plunging	mischmetal canisters	1 1/2 to 2 1/2	$ 7 to 12
	5. delayed mold	mischmetal 4-oz ingots	1/2 to 1 1/2	$ 3 to 7

NOTE: Mischmetal is 96 percent rare earth; rare-earth silicide is 33% rare earth. Conversion factors: 1 lb = 0.45 kg; 1 U.S. (short) ton = 0.9 metric ton; 1 oz = 28 g.

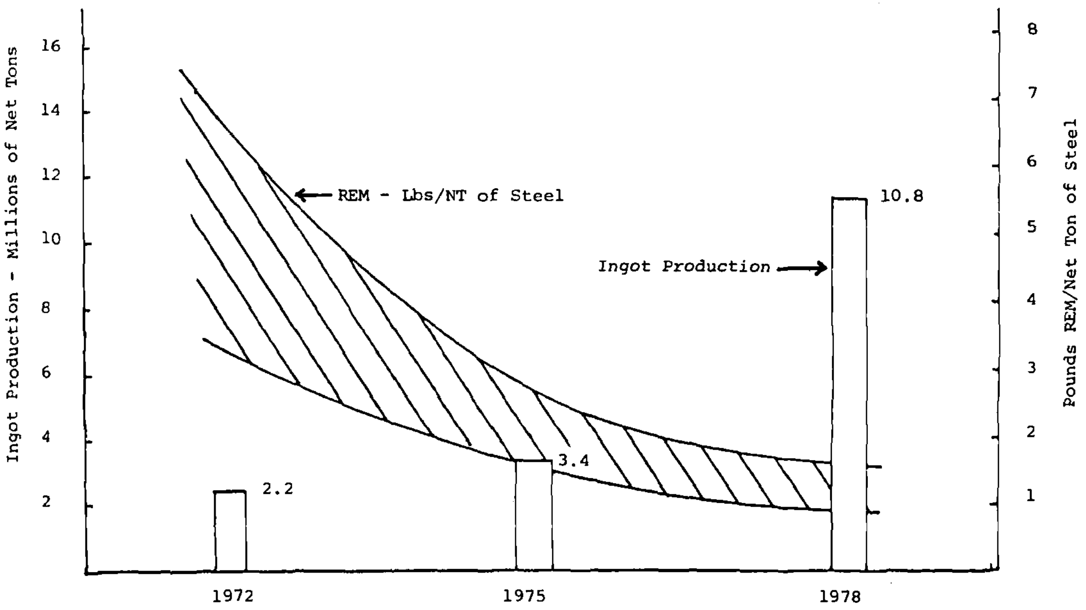

FIG. 2—*North America ingot tons steel treated with REM versus lb REM/NT [1 U.S. (short) ton = 0.9 metric ton; 1 lb = 0.45 kg].*

only does the incentive for producing low-sulfur steels vary, but the approaches to sulfur control vary as well [*17*].

Today and as we look into the 1980's the need for lower sulfur steels to meet the improved property requirements at reduced costs have forced the steel producer toward intensifying individualized plant searches for the "best" approach to sulfur control. These trends which became apparent during the mid-1970's are being magnified as we go forward into the 1980's. At one end of the spectrum, steel producers are faced with a trend toward a supplying higher-performance steels with minimal sulfur contents and sulfide inclusion shape treatment. However, at the other end of the spectrum, only higher-sulfur raw materials are available, such as higher-sulfur coke, iron ore, and scrap.

Due to the capital intensity of the steel industry, investments in fixed assets such as blast furnaces, electric furnaces and Basic Oxygen Furnace (BOF) shops are made with the intent to maximize production. These fixed assets generally have to operate at higher sulfur levels to maximize production.

As an example, blast furnaces operating to hot metal specifications of 0.045 percent sulfur will use less coke, work at higher wind rates, and generally increase the net tons of hot metal per square foot of hearth area versus similar operations casting hot metal at 0.025 percent sulfur levels. In open hearth, electric, and basic oxygen steelmaking furnaces, lower tap sulfur requirements generally tend to increase the furnace refining time.

Considering the foregoing factors and in an attempt to reverse the lower-quality/higher-sulfur raw material trend which enables the finished steel product to meet the higher performance specifications, the steel producer has proceeded toward external desulfurization and sulfide shape control. Currently, the most widely accepted techniques are shown in Table 4.

The steelmaker will use the most economical approach to external desulfurization and sulfide shape control to obtain the desired performance properties in the steels of the future.

If historical fact can be used to predict the future, once the integrated steel producer has obtained the desired performance properties, the most economical approach to external desulfurization or sulfide shape control or both will be chosen.

As was suggested earlier, during the 1970's economic balances between reasonably low sulfurs and residual sulfide shape control opened interest for

TABLE 4—*Techniques for desulfurization and sulfide shape control.*

Hot metal desulfurization—injection
Steel ladle desulfurization—ladle additives
Steel ladle desulfurization—injection
Sulfide shape control—rare-earth metals

mischmetal applications in HSLA automotive steels. In these applications, cold formability, surface, and cost must be balanced. It is visualized that this concept will be extended to other applications such as low-sulfur line pipe, plate steels, and structural steels.

We have already seen the rare-earth metal consumption per ton of steel treated drop from 1.35 to 3.15 kg (3 to 7 lb) to 0.45 to 0.675 kg (1 to 1.5 lb) per net ton for the same level of improvements in properties. We are forecasting that rare-earth metal consumption could be hovering around the 0.45-kg (1 lb) per net ton level by 1985 when added to lower deoxidized and desulfurized steels. We are entering an era where the steelmaker will be deoxidizing and desulfurizing to much lower levels than ever before in order to produce the high-performance steels required. This of course reduces the amount of REM required per net ton of steel produced and also the cost of REM per net ton. However, it is anticipated that increasing diversification of steel applications for rare-earth metals will continue in the early 1980's.

To summarize, it is conceivable that REM consumption in the United States steel industry will reach 10 000 to 12 500 net tons by 1985 [*18*]. That tonnage converts to the treatment of approximately 20 to 25 million net tons of steel in the United States.

Major new uses for REM in the 1980's are expected to be in continuously cast steels, ferritic stainless steels, free-machining steels, electroslag melted steels, vermicular and nodular graphite cast irons, high-energy magnets, and energy-storing devices [*19*]. The future growth of the rare-earth industry looks very promising as we enter a new decade.

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Rare-Earth Additions to Blast Furnace Iron for the Production of Large Castings

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ABSTRACT: Additions have been made to foundry iron for castings to modify the graphite shape from flake to compacted form. This has been done to improve the mechanical properties of the iron to a level desirable for more diverse applications. The graphite modification has been accomplished by treatment with controlled levels of magnesium, magnesium-titanium combinations, and also rare-earth alloys.

Reportedly, compacted graphite iron has also been produced in blast furnace iron modified to near foundry iron composition.

The work reported here was instituted on the premise that compacted graphite iron could be made from blast furnace iron with only modest modification as would be possible and practical in a foundry producing large castings, such as ingot molds.

Preliminary work involved the confirmation of the ability of rare earths to produce compacted graphite in blast furnace irons. Three-hundred-pound laboratory heats were evaluated for a range of major element levels (carbon, sulfur, silicon, manganese, and silicon-manganese ratios), the effect of pouring temperatures, and cooling rates.

The castings were examined for graphite type and amount, as well as possible presence of carbides. The matrix structures were examined for ferrite and pearlite amounts and distributions. Mechanical properties were also determined.

With production of a desirable structure of compacted graphite surrounded by ferrite and containing a minimum of pearlite, it should be possible to produce castings from blast furnace iron with high strength, good thermal conductivity, and acceptable erosion resistance for an application such as ingot molds, with a resultant major improvement in the life of the mold.

KEY WORDS: ingot molds, blast furnace iron, rare-earth treatment, compacted graphite cast iron, microstructure, mechanical properties

Flake graphite cast iron (gray iron) was the mainstay of industry for many years. Ductile iron, since its development in the late forties, has replaced gray iron in some areas and also has found areas of new applications for cast

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irons. In more recent years a new category of cast iron has come on the scene. Designated as compacted/vermicular graphite (CG) cast iron, it has properties intermediate between gray and ductile iron.

Compacted graphite is short and stubby with a length-to-width ratio of 2:1 to 10:1. It has a segmented nature suggesting orientation differences in the basal plane of the graphite in adjacent segments. In contrast, flake graphite is long and straight, having a length-to-width ratio of up to 50:1. Flake graphite does not show any segments, and has the graphite crystal basal planes parallel and regular along the length of the graphite flake with no sharp change in direction [*1*].[3] See Fig. 1.

A number of techniques have been advocated for the production of CG cast iron in iron foundries. These processes are based upon the addition of several types of alloys, including magnesium, magnesium plus titanium, and rare earths of varied compositions (high cerium, yttrium-containing, 50Ce-30La, etc.) [*2–7*], using ferrosilicon as a base. It has also been reported that CG cast iron has been produced from blast furnace iron modified to approach conventional iron foundry compositions [*8–9*].

The work reported here was instituted on the premise that CG could be produced in blast furnace iron with only modest modifications as would be practical and possible in a plant producing large castings, such as ingot molds. There have been instances where ingot molds have been produced from CG cast iron, as opposed to gray cast iron, but in all reported cases the basic iron composition has been modified for the purposes of controlling CG formation [*8–9*]. On the other hand, this study has attempted to use blast furnace iron which is produced on a daily basis, not to the in-house mold shop specifications, but to the specifications of the steelmaking division.

Ingot molds, with the graphite modified from Type A flake (gray cast iron) to compacted graphite, have demonstrated improvement in mold life, reportedly from 20 to 70 percent [*9–10*]. With an annual production of over three million tons,[4] this would result in substantial savings and increased productivity to the steel industry in those shops producing their own ingot molds, and make more hot metal available for steelmaking.

Potential for Compacted/Vermicular Graphite Cast Irons in Ingot Molds

At present, most ingot molds are produced with a flake graphite structure; the matrix structure is governed by the composition requested or received. Reported compositions are quite varied [*11–16*]:

C	3.9 to 4.6%	Mn	0.3 to 1.8%	Si:S	1 to 4:1
Si	0.75 to 2.50%	S	0.02 to 0.08%	Mn:S	20 to 40:1
CE[5]	4.4 to 5.2%	P	0.03 to 0.20%	CE = C + 1/3 Si	

[3] The italic numbers in brackets refer to the list of references appended to this paper.

[4] 1 U.S. (short) ton = 0.9 metric ton.

[5] CE = carbon equivalent.

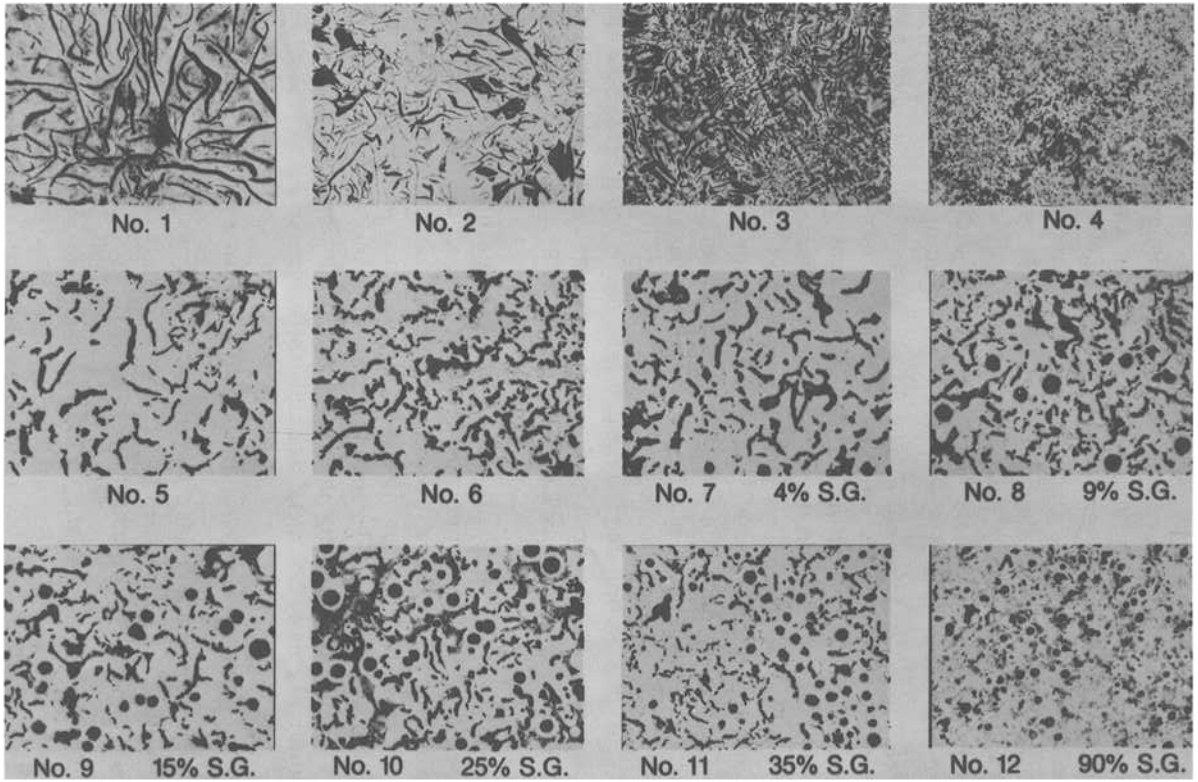

FIG. 1—*Graphite shape classification and amount of spheroidal graphite [(1/2 original size)×100 reduced to 62.5 percent to fit].*

Reportedly, the normal structure of flake graphite cast iron ingot molds is a coarse flake graphite surrounded by ferrite, with pearlite outlining the eutectic cells [*17*]. This structure depends mainly upon the silicon and manganese content of the iron, and on the cooling rate through the critical temperature. Naturally, the wide range in the silicon-manganese ratio cited in the foregoing would result in an expected matrix structure variation of 10 to 100 percent pearlite.

Mold life appears to vary from shop to shop, as well as with mold size configuration. Mold life often varies from an average of 35 to 100 pours [*11,15*]. The reasons a mold is scrapped are numerous, but the major causes [*17*] are: (1) major vertical cracking, (2) excess erosion, (3) crazed surface, (4) broken lugs, (5) torn seats, and (6) stickers. Most of these causes are related to the mechanical and physical properties of the ingot mold.

Major vertical cracking starts on the external surface as a result of uneven thermal expansion. Crazing is related to oxidation and growth (oxidation along the graphite, thermal expansion, and contraction). For maximum resistance to crazing, good oxidation resistance and oxide penetration resistance are required, along with a low modulus of elasticity. Oxide penetration resistance is enhanced by fine graphite or by graphite which presents a smaller surface area to volume ratio, that is, stubbier graphite, as well as by stable pearlite (preventing subsequent graphitization). On the other hand, coarse graphite and ferrite results in a low modulus and good resistance to thermal shock or thermal fatigue. The resistance to thermal fatigue can be correlated to mechanical and physical parameters by the factor P [*11*]

$$P = \frac{K \times S}{E \times A}$$

where

K = thermal conductivity,
S = ultimate tensile strength,
E = modulus of elasticity, and
A = coefficient of thermal expansion.

As factor P increases, so does the resistance to thermal fatigue.

Erosion resistance is related to strength, among other things. For good strength and hardness, fine graphite (or stubby graphite) with a pearlite matrix is necessary. High strength is also required to reduce broken lugs and torn seats. However, a pearlite matrix is likely to undergo transformation to ferrite and secondary graphite as high-temperature thermal cycling occurs [*18,19*]. Stickers result for numerous reasons.

The mechanical and physical properties of cast irons depend upon the graphite and matrix structures of the iron. Flake graphite properties are the lowest. Considering the graphite as voids or inclusions, this is easier to understand. The flakes are such as to provide planes of weakness within the structure. This is less so with the compacted graphite because it is more rounded and random. The highest properties of course are obtained with spheroids, which are much like the globular inclusions desirable in steel.

The other major effect on mechanical properties is the matrix structure. Yield and tensile strength both increase with increased pearlite, and also with increased silicon (hardens ferrite). The inverse is true of the elongation. Hardness appears to be more directly related to pearlite.

Typical mechanical and physical properties [*20*] are given in Table 1. It is apparent that to achieve optimum mold life, a tradeoff in selected mechanical and physical properties must be reached. However, analysis of the structure and properties of flake and compacted graphite containing cast irons indicates that mold life should be improved substantially using compacted graphite cast iron ingot molds. Accordingly, this study was directed at evaluating the effect of certain processing variables in controlling the microstructures and mechanical and physical properties of rare-earth-treated compacted graphite cast iron produced from blast furnace iron with minimum modification of composition.

Rare-Earth Treatment

Previously reported studies [*7*] demonstrated the microstructure-processing variable relationships of rare-earth-treated compacted/vermicular graphite cast irons produced at 3.7C-2.1Si-4.4CE-0.01S. After the melts were stabilized at 1465°C (2670°F), they were treated with various amounts of rare earths (RE's) and cast into chill pins, wedges, and bars 12.5 to 63.5 mm (0.5 to 5.0 in.) in diameter. It was determined that approximately 0.10 percent RE

TABLE 1—*Properties of cast irons.*

	Graphite Type		
	Flake	Compacted	Spheroidal
Tensile strength, MPa	170 to 300	300 to 600	400 to 700
Elongation, %	nil	3 to 6	3 to 25
Modulus of elasticity, GPA	95 to 110	140 to 160	170 to 185
Thermal conductivity, W/m-K	0.46 to 0.59	0.42 to 0.50	0.34 to 0.38
Damping capacity	13.2×10^{-4}	$4 \text{ to } 6 \times 10^{-4}$	$2 \text{ to } 5 \times 10^{-4}$
Unnotched fatigue, MPa	95 to 110	205 to 275	165 to 250
Coefficient of thermal expansion (0 to 500°C), K^{-1}	13	13.2 (est)	13.5
Charpy impact, J	nil	4 to 10	23

1 MPa = 145 psi.
1 GPa = 145 ksi.
1 W/m-k = 0.58 Btu·ft/h·ft^2.
1 J = 0.74 ft-lb.

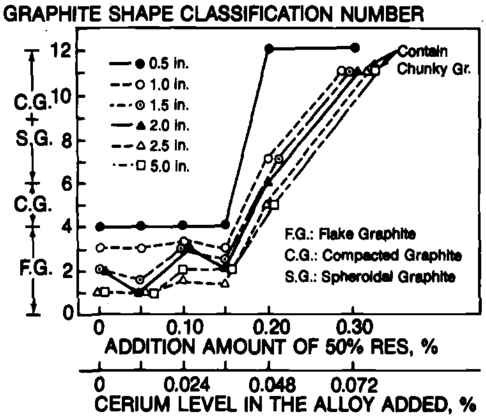

FIG. 2—*Effect of 50 percent rare earth additions on graphite shape.*

(0.05 percent cerium) was required to produce a CG structure in bars over 12.5 mm (0.5 in.) in diameter, Fig. 2. In was also observed that there was little if any, variation in the graphite structure in bars over 63.5 mm (2.5 in.) in diameter. This is illustrated in Fig. 3. In other words, there was no apparent section size sensitivity in these sections, and one could be confident that the results could be extrapolated to larger castings, such as ingot molds.

In addition, the holding time before pouring (fading) was determined for a group of heats. By examining the depth of chill in castings poured at various intervals, it was possible to ascertain that fading did not start until approximately 15 min after RE treatment and the effect of the RE treatment diminished significantly after about 20 min [5] as shown in Fig. 4.

The influence of post-inoculation, with various levels of calcium silicon, or 75 percent ferrosilicon, has also been reported [21] for melts of the same chemistry and cast in the same manner as those just discussed. It was shown that with adequate RE treatment, post-inoculation does not appear to be necessary in large castings such as ingot molds. But if the holding time before

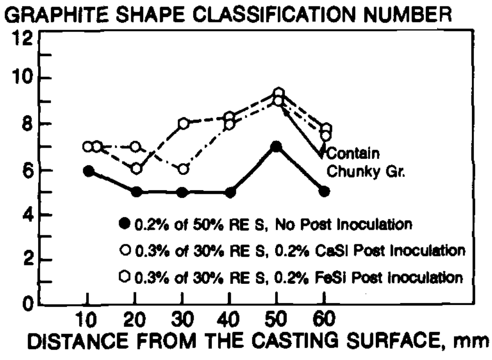

FIG. 3—*Graphite shape variation with distance from surface in 5-in. (12.7 cm) bar casting..*

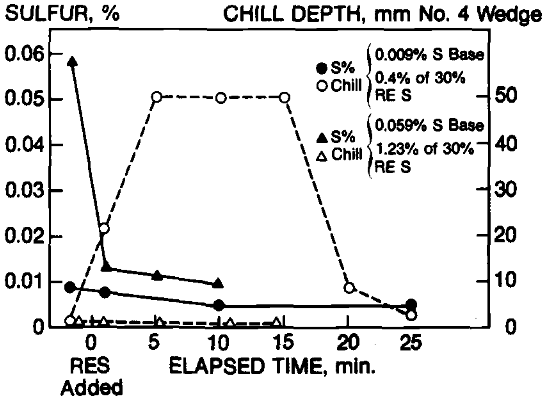

FIG. 4—*Effect of holding time on sulfur level and chill depth.*

pouring is excessive or the treatment is borderline, calcium silicon is the most desirable post-inoculant. On the other hand, 75 percent ferrosilicon requires much closer control to assure adequate RE treatment and avoidance of overinoculation.

Conversion of Blast Furnace Iron to Compacted Graphite Cast Iron

A quantity of low-sulfur (0.01 percent) blast furnace iron was employed to study the effect of base iron composition variations. The initial composition of this iron was 4.1C-0.9Si-0.26Mn. Maintaining a constant carbon equivalent of 4.4 percent, the silicon content was varied from 0.9 to 2.0 percent and manganese was adjusted from 0.26 to 0.75 percent. At the 0.9Si level, these heats were treated with 0.10 percent RE, post-inoculated with 0.30CaSi, and cast into 127 by 229 by 229 mm (5 by 9 by 9 in.) blocks. It was observed that a late addition of silicon to adjust the composition would result in a flake graphite structure when treated with 0.10 percent RE. Further tests indicated the necessity to increase the RE by 0.025 times the increase in silicon content to maintain a compacted graphite structure. This was determined from the graph in Fig. 5. Variations in the manganese content had no apparent effect on the graphite structure.

Tests were also conducted on high-sulfur-content heats (0.042 percent) with various additions of RE. At 3.75C and 2.55Si an addition of 0.192 percent RE yielded a fine Type A graphite structure. With an addition of 0.384 percent RE to a 3.48C-2.74Si iron the structure was 70 percent spheroidal graphite and the balance was chunky, compacted, and deteriorated graphite. A third series was run at 3.55C-2.60Si with a 0.288 percent RE addition and resulted in over 80 percent compacted graphite with the balance appearing to be spheroidal.

It had originally been determined [7] that 0.10 percent RE would produce CG in a 0.01 percent sulfur iron, resulting in residuals of 0.04 to 0.06

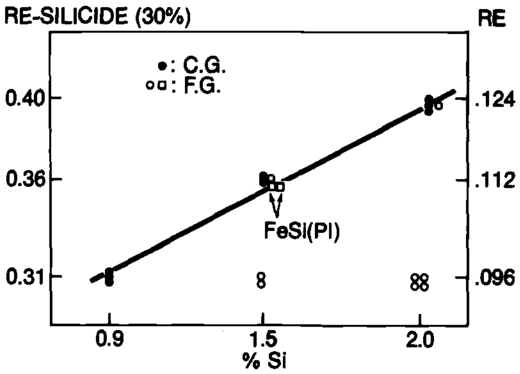

FIG. 5—*Rare-earth silicide requirements for various base iron silicon contents for compacted graphite structures.*

percent RE and 0.005 to 0.007S. Compared with the results of the 0.042S series, this indicates a need for a treatment level of 0.04 percent RE plus six times the initial sulfur content. This ratio is somewhat lower than that previously reported [*22*] from which a factor of 8 was calculated.

This study was also concerned with the potential for carbon flotation in higher carbon equivalent CG iron. The carbon content of the 0.9Si blast furnace iron was raised to 4.4 percent (4.7CE) and cast into a 127 by 229 by 229 mm (5 by 9 by 9 in.) block to determine the effect of this high carbon equivalent. Figure 6 shows that the structure is compacted graphite; however, the flotation which occurs is spheroidal and exploded near the surface. This condition is primarily an effect observed at the extreme top surface of the casting.

It is well known that other elements can also affect the graphite structure. For example, small amounts of aluminum or titanium or both reduce the tendency for spheroidal graphite formation.

It appears that the principal chemical constituents in normal blast furnace irons which affect the matrix structures are silicon and manganese. This is not unexpected since silicon is a strong ferrite promoter, while manganese is a strong pearlite stabilizer. The effect of these elements on the percentage of pearlite in the matrix is shown in Fig. 7 for various Si:Mn ratios. It is noted that the silicon-manganese ratio is more significant in determining the matrix structures than either the silicon or manganese content alone. It must be remembered that the matrix structure can also be affected by the presence of additional elements, chiefly those which act as pearlite stabilizers. As a result, the effect of the Si:Mn ratio on the pearlite content and mechanical properties may differ from that given in Table 2, depending upon other composition effects.

The other major factor affecting the matrix structures is the rate of cooling through the critical temperature range. Slower cooling rates favor ferrite formation while more rapid cooling rates promote additional pearlite. This

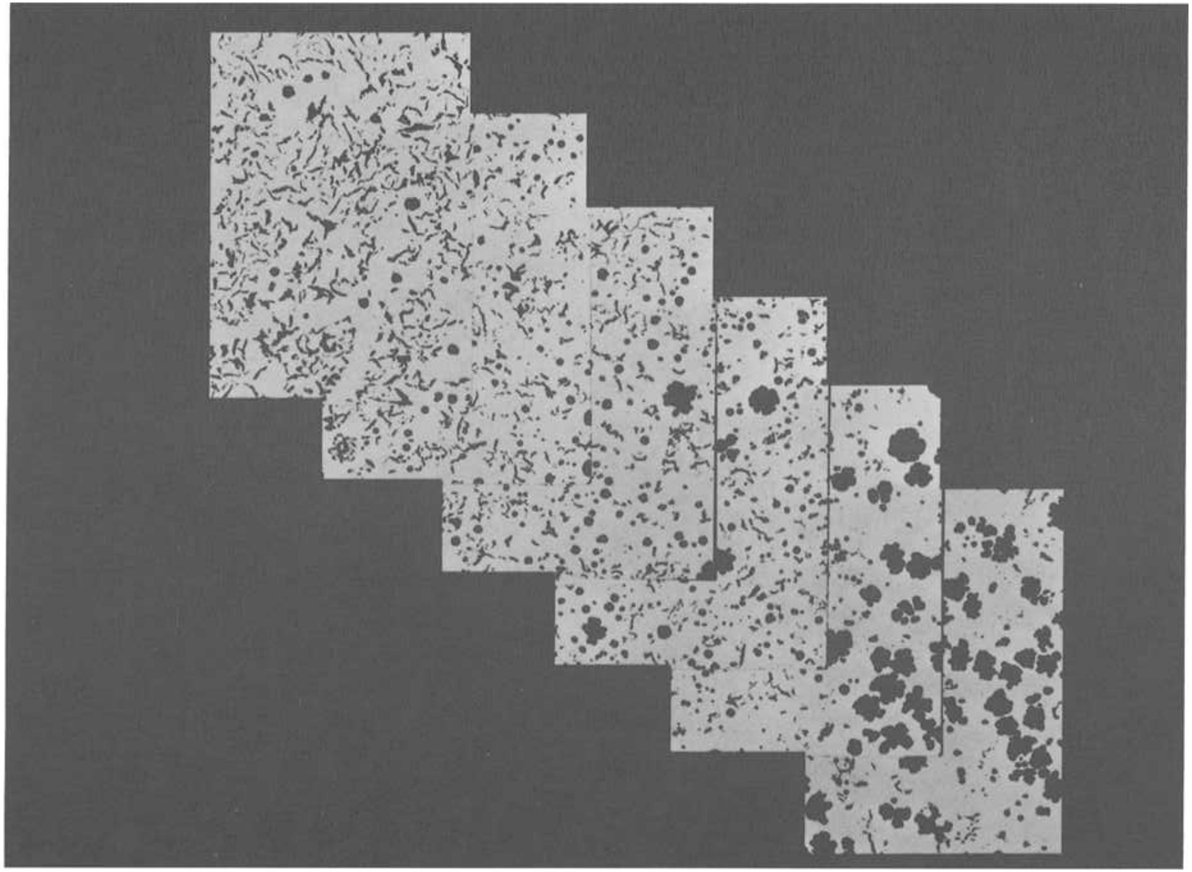

FIG. 6—*Carbon flotation in a large casting (high carbon equivalent compacted graphite; ×60 reduced ¼ size).*

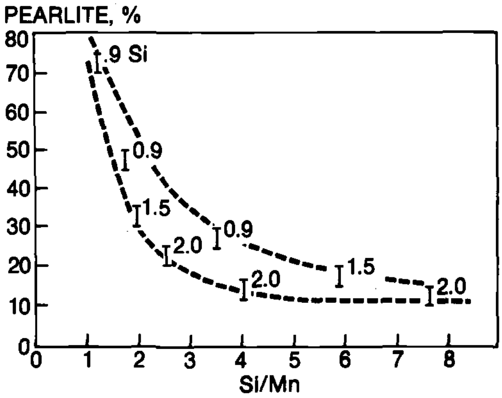

FIG. 7—*Effect of silicon-manganese ratio on the matrix pearlite content.*

is shown in Table 3, which gives the effect of pouring temperature (with resulting change in cooling rates). At the lower temperature the amount of pearlite is increased by approximately 50 percent and the percentage of carbides doubled. The graphite structure is virtually unchanged.

The matrix structure and properties of the cast irons can also be affected by the handling of the castings after pouring. If they are not left to cool at a moderate rate, but instead are shaken out early without providing facilities to control cooling, results such as those given in Table 4 may occur.

Summary

A number of the significant operating variables involved in the production of rare-earth-treated compacted graphite cast irons cast into ingot molds have been reviewed and discussed. Compacted graphite can be produced from blast furnace irons over a broad range of silicon contents, although the amount of rare-earth treatment necessary to obtain these structures was found to increase slightly as the silicon content was raised. The matrix structure was found to be related to the rate of cooling through the critical temperature range, and to the Si:Mn ratio of the iron. For a given casting process, and for a given blast furnace iron, the pearlite content of the matrix can be altered by adjusting the silicon-manganese ratio.

The base iron sulfur content also affected the amount of rare earths necessary to obtain compacted graphite. It was determined that a treatment level of 0.04 percent rare earths plus six times the initial sulfur content was required for production of compacted/vermicular graphite cast irons.

When excessive carbon contents are present in the blast furnace iron, carbon flotation can be expected to occur, just as it would in flake graphite cast irons. In rare earth treated, compacted graphite irons, however, graphite flotation occurs as spheroidal graphite, or as exploded graphite near the extreme top surface of the casting.

TABLE 2—*Effect of silicon-manganese ratio on mechanical properties.*

Heat No.	C, %	Si, %	Mn, %	Si/Mn	CE	Yield Strength, ksi	Tensile Strength, ksi	Elongation, %	Hardness, HB
2-1	4.10	0.90	0.26	3.5	4.40	22.0	34.5	3.2	137
2-2	4.10	0.90	0.50	1.8	4.40	25.0	35.0	3.1	159
2-3	4.10	0.90	0.75	1.2	4.40	26.3	37.1	2.8	159
2-6	3.90	1.50	0.26	5.8	4.40	27.0	38.0	3.1	145
2-7	3.90	1.50	0.50	3.0	4.40	...	...	...	...
2-8	3.90	1.50	0.75	2.0	4.40	27.2	39.2	3.1	159
2-15	3.75	2.00	0.26	7.7	4.40	27.0	38.0	3.6	145
2-17	3.75	2.00	0.50	4.0	4.40	26.7	39.0	4.0	152
2-18	3.75	2.00	0.75	2.7	4.40	30.2	43.0	2.8	159

Note: Tension specimens are from test block of 127 by 229 by 229 mm (5 by 9 by 9 in.).
1 ksi = 6.8948 MPa.

TABLE 3—*Effect of treatment temperature on structure and properties.*

Heat No.	Casting Temperature, °F	C, %	Si, %	Mn, %	S[a], %	S[b], %	Ce[b], %	Graphite Structure	Pearlite, %	Carbide, %	Hardness, HB	Yield Strength, MPa (ksi)	Tensile Strength, MPa (ksi)	Elongation %
2-1	Treatment temperature 2680 to 2700 Pouring temperature 2500	4.10	0.90	0.26	0.009	0.006	0.017	compacted graphite (>90%)	25 to 30	4 to 6	139	151.9 (22.03)	248.0 (35.96)	3.2
2-19	Treatment temperature 2500 Pouring temperature 2400	4.10	0.90	0.26	0.009	0.006	0.019	Compacted graphite (>85%)	40 to 45	10 to 12	187	193.2 (28.02)	255.3 (37.02)	2.8

[a] Initial.
[b] After treatment.
°C = (5/9) (°F −32).

TABLE 4—*Effect of cooling rate on structure and properties.*

Heat No.	Cooling Condition	C, %	Si, %	Mn, %	Graphite Structure	Pearlite, %	Carbide, %	Hardness HB	Yield Strength, MPa (ksi)	Tensile Strength, MPa (ksi)	Elongation %
2-8	Cool in the mold	3.90	1.50	0.75	compacted graphite (>90%)	30 to 35	2 to 4	159	187.7 (27.22)	270.5 (39.23)	3.1
2-20	Cool in the furnace	3.90	1.50	0.75	compacted graphite (>85%)	25 to 30	2 to 4	149	180.1 (26.12)	257.4 (37.33)	3.1
2-21	Early shake-out	3.90	1.50	0.75	compacted graphite (>90%)	90	~10	255	...	...	...

Attention must also be directed to the level of residual elements present in the blast furnace iron, a condition which will vary from shop to shop. These residual elements may require an adjustment of the rare-earth treatment additions to insure compacted graphite formation, and the silicon level to control the matrix structure.

The advantages of compacted/vermicular graphite cast irons used to produce ingot molds are based upon the improvement of mechanical and physical properties resulting from the modification of the graphite form. Conversion of the graphite from flake, with a length-to-width ratio of up to 50:1, to compacted, with a length-to-width ratio of 2:1 to 10:1, is principally responsible for these property improvements. The improvement in properties resulting from graphite modification obtainable with only slight adjustment of blast furnace iron composition has been reported to result in a 20 to 70 percent increase in mold life. Treatment of the iron using rare earths can be a simple, efficient, and economical method of obtaining these graphite modifications.

Acknowledgments

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Properties and Uses of Alloy Additives for the Modification of Cast Iron

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ABSTRACT: Foundrymen have long recognized the value of adding special additives to gray and ductile cast irons to modify structure and control properties. While graphite growth mechanisms are better understood today than just a few years ago, comprehensive theories have yet to be established and accepted. Nevertheless, efforts to comprehend and control the inoculation and nodularizing processes have resulted in a variety of products and treatment techniques. This paper endeavors to summarize the present status of the alloys used to modify cast iron.

A very diverse product line of inoculants exists in today's market. While most inoculants are based on ferrosilicon and contain some aluminum and calcium, they may also contain barium, titanium, strontium, rare earths, or other elements.

The method of addition, as well as the location and time of addition of special alloys to cast iron, plays a prominent role in determining the addition levels and the effectiveness of a particular treatment. For example, inoculants may be added to the ladle, or later in the process as the metal stream enters the mold, or in the mold itself. Inoculants used in the ladle are normally added in the stream entering the ladle and are usually granular in nature. In late inoculation, on the other hand, the inoculant may be added as a powder, an encapsulated powder, or a bonded or cast insert. Today, the bulk of inoculants are added in the ladle. However, due to metallurgical and economical considerations plus production restrictions, the practice of late inoculation has grown in recent years.

The nodularizing treatment for ductile iron is commonly accomplished by ladle treatment with magnesium-ferrosilicon alloys. A variety of other additives, including pure magnesium, is finding use. Recently, particularly in the automotive industry, many foundries have begun to convert to the Inmold Process.

Efforts are currently being made within the foundry industry to produce an intermediate iron to gray and ductile iron, known as compacted graphite iron. At least one additive is available commercially for this purpose.

KEY WORDS: additives, cooling rate, eutectics, ferrites, ferroalloys, graphite, granular material, hypereutectic, hypoeutectic, inoculation, iron carbide, magnesium containing alloy, microstructure, pearlite, precipitation, rare-earth metal, solidification

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The family of cast irons is a large one, comprising five major types: gray cast iron, ductile cast iron, compacted graphite cast iron, malleable cast iron, and white cast iron. This paper is primarily concerned with the modification of properties in gray and ductile cast irons. In addition, some attention is given to the relatively new compacted graphite cast irons, which are of current interest to foundrymen. In particular, the paper offers a review of the alloys and techniques used for the inoculation of gray and ductile irons, the nodularization of ductile iron, and the production of compacted graphite iron.

The structure and distribution of the uncombined carbon or graphite in cast iron have a major influence on the mechanical and physical properties of the iron. Special additives, introduced late in the processing of cast iron, may alter the graphite by providing nuclei for graphite precipitation or by modifying growth conditions in the melt. This process is referred to as inoculation. Other additives may completely alter the final form of the graphite. In ductile iron production, this process is referred to as nodularizing. The inoculating and nodularizing processes must be differentiated from true alloying, in which elemental additions are made to alter the properties of the metal matrix by mechanisms such as solid solution strengthening or precipitation strengthening.

Foundrymen inoculate gray cast iron primarily to improve strength, reduce hardness, and improve machinability. Inoculation assures that the graphite present in cast iron is of the desired type and size by improving nucleation in the molten phase, thus preventing undercooling and formation of iron carbides (chill) during solidification. Consequently, cell size, cell count, dendrite length, and shrinkage are also affected by inoculation. As a secondary effect, the type of graphite formed during eutectic solidification will affect the structure of the matrix formed on cooling, which markedly affects the mechanical properties.

The nodularizing treatment modifies the chemistry and condition of the melt in the production of ductile irons such that the graphite precipitates as spheroids or nodules. Consequently, the iron matrix is continuous, giving ductile irons their characteristic high strength and ductility compared with gray cast iron.

Structural Comparison of Gray, Ductile, and Compacted Graphite Cast Irons

Cast iron represents a family of irons containing carbon levels greater than 2 percent, with most ranging between 2.0 and 3.6 percent, and with silicon levels ranging between 1 and 3 percent. The presence of silicon promotes the formation of the stable graphite phase rather than metastable iron carbide. The formation of free graphite, as opposed to iron carbide, during solidification distinguishes gray, ductile, and compacted graphite irons from malleable irons and white irons.

Thus, the type of iron, whether gray, ductile, or compacted graphite, is largely established during solidification. Several reviews of the different nucleation and growth theories have been published [*1–5*].[2] Under normal conditions the graphite tends to precipitate in the form of flakes that are associated with gray irons [*6*]. Flake graphite, which may be seen in Fig. 1 as plate-like and interconnected, exerts a major influence on properties of gray cast iron. For graphite to precipitate in the form of nodules, characteristic of ductile iron, or as compacted graphite—an iron intermediate to gray and ductile iron—certain elements such as magnesium, cerium, or other rare earths are introduced into the melt. The scanning electron microscope images in Figs. 2 and 3 provide a three-dimensional look at the graphite morphology found in ductile and compacted graphite irons, respectively. In ductile iron, the graphite is present as discrete particles and the matrix is

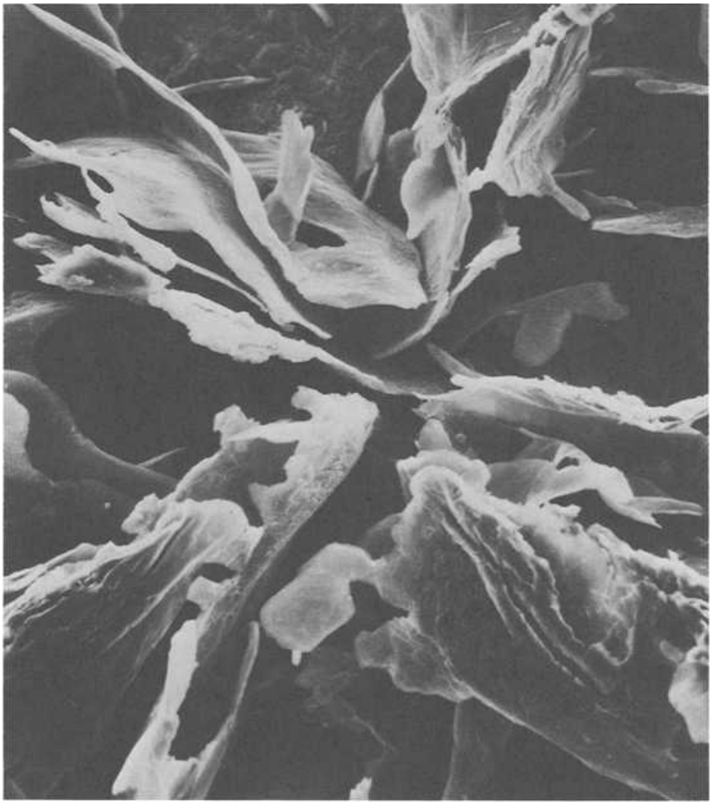

FIG. 1—*Scanning electron microscope image showing interconnected plate-like flake graphite structure of gray cast iron. Deep etched,* ×400.

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

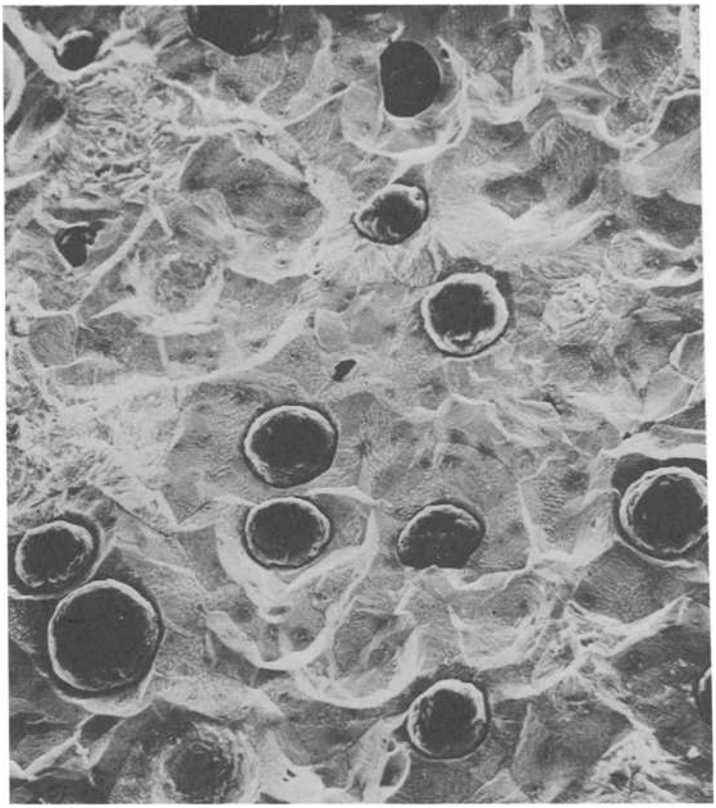

FIG. 2—*Scanning electron microscope image showing discrete nodular graphite structure of ductile cast iron. Deep etched,* ×400.

continuous. Thus, mechanical properties such as tensile strength, ductility, and toughness are significantly better than those of gray iron.

Compacted graphite cast iron combines some of the better properties of both gray and ductile cast iron. These irons have mechanical properties such as strength and toughness which are significantly better than those of gray cast iron and approach those obtained in ductile cast iron. At the same time some properties such as castability, machinability, and thermal conductivity are substantially better than those found in ductile iron and are more nearly like those found in gray cast iron.

Characterization of Graphite in Gray Cast Iron and General Effects of Inoculation

Graphite in cast iron is categorized into seven general types in accordance with the ASTM Standard Method for Evaluating the Microstructure of Graphite in Iron Castings (A 247-67). Graphite type is designated by Roman nu-

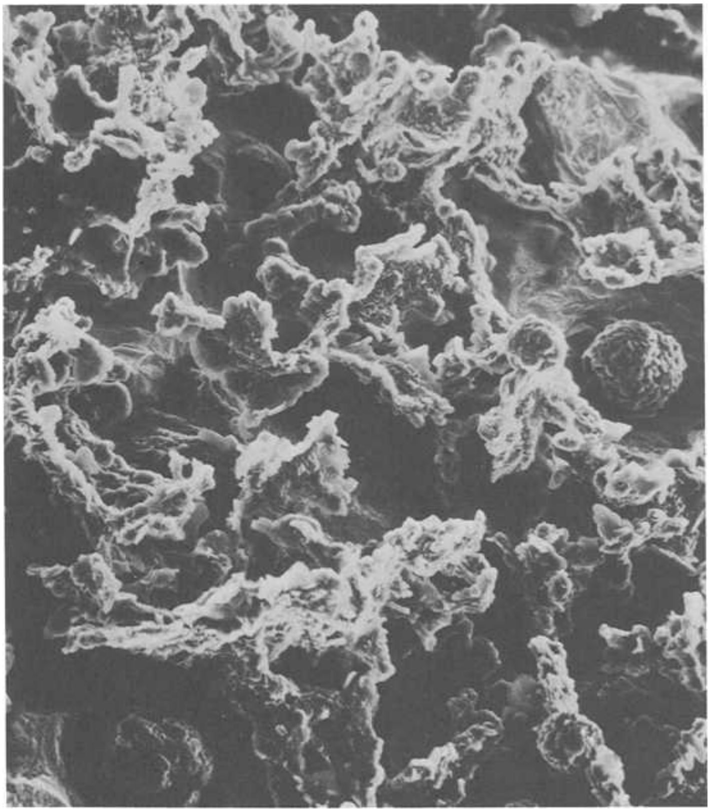

FIG. 3—*Scanning electron microscope image showing graphite structure of compacted graphite cast iron. Deep etched,* ×400.

merals I through VII, as may be seen in Fig. 4. Type VII is the flake graphite form usually seen in gray iron. The distribution of flake graphite, Type VII, may be seen in Fig. 5 and is designated by capital letters A through E. The classification of Type VII graphite according to size is listed in Table 1 and is designated by Arabic numerals 1 through 8.

When equilibrium conditions exist during solidification and good nucleation occurs, the eutectic graphite will precipitate and grow as Type VII A flakes. The size of the flake is affected by both cooling rate and the number of nucleation centers. Gray irons containing a random distribution of medium-sized Type VII A graphite flakes are typically more desirable than gray irons with other flake sizes and distributions. Inoculants are used to provide nucleation during solidification, thus preventing undercooling and insuring Type VII A graphite.

If equilibrium conditions do not exist and there is an insufficient number of nuclei present, a small amount of undercooling will occur and Type VII B

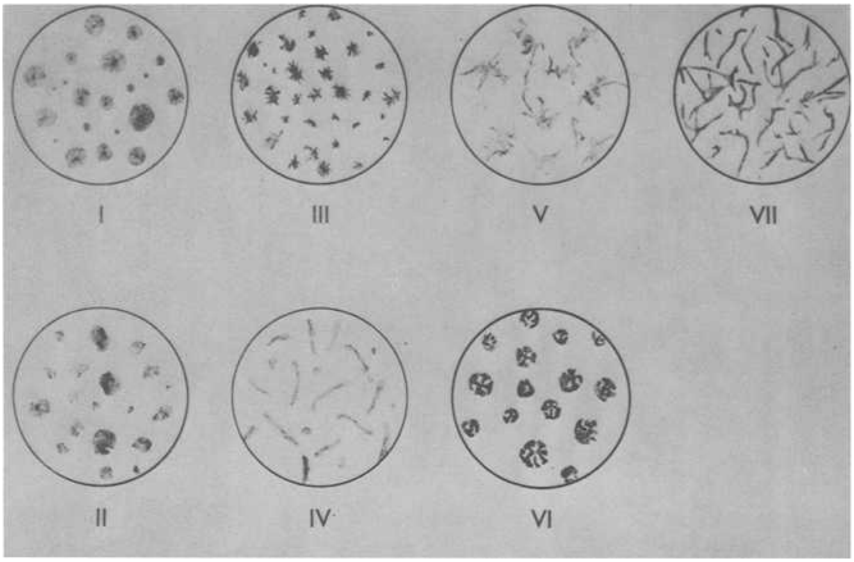

FIG. 4—*Photograph illustrating the seven types of graphite found in cast iron.* ×100.

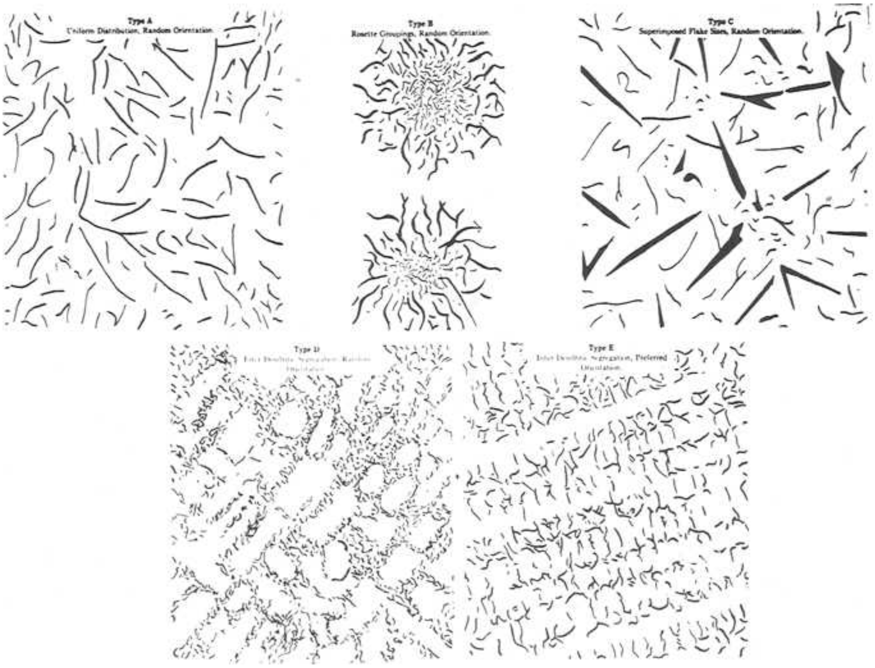

FIG. 5—*Photograph illustrating the distribution of flake graphite, Type VII, found in gray cast iron.* ×100.

TABLE 1—*Classification of Type VII graphite according to size (measured at ×100).*

Size 1 (4 in. +)	Size 5 (1/4 to 1/2 in.)
Size 2 (2 to 4 in.)	Size 6 (1/8 to 1/4 in.)
Size 3 (1 to 2 in.)	Size 7 (1/16 to 1/8 in.)
Size 4 (1/2 to 1 in.)	Size 8 (−1/6 in.)

1 in. = 25.4 mm.

or rosette-type graphite will result. This results in slightly lowering the final strength of the iron. If further undercooling occurs, however, Type VII D graphite, which is dendritically segregated, may form. Type VII D graphite is frequently associated with an increase in the amount of ferrite in the matrix. Thus, strength is lowered further. Even greater undercooling will lead to the formation of iron carbides (chill), resulting in poor machinability (hard iron).

Type VII E flakes, also dendritically segregated but with preferred orientation, are usually associated with strongly hypoeutectic (less than 4.3 percent carbon equivalent) cast irons, in which the graphite flakes precipitate in the interstices after the initial precipitation of primary austenite dendrites [*7*]. Irons that solidify with Type VII E graphite generally have higher tensile strength than is associated with Type VII D due to the strong interaction of dendrites. Because of the low carbon equivalent (relatively low concentrations of carbon and silicon) in these hypoeutectic irons, there is a strong tendency for severe supercooling and chill formation. Therefore, inoculation is particularly useful in these irons to minimize the chill-forming tendency. Inoculation of a strongly hypoeutectic gray iron has also been reported to produce smaller, more randomly oriented, primary austenite dendrites [*8*].

Type VII C graphite flakes are generally found in hypereutectic irons (greater than 4.3 percent carbon equivalent), where the first material to precipitate during solidification is primary graphite rather than the austenite dendrites which precipitate first in hypoeutectic irons. Irons that solidify with Type VII C graphite have the lowest strength of any of the gray irons, but possess excellent castability [*6*]. Due to the low modulus of elasticity of these irons, they are often used for ingot molds and other applications subject to severe thermal stress.

Inoculants for Gray Iron

As has been indicated, inoculants are thought to be able to modify nucleation and growth conditions for flake graphite in gray cast irons, largely by reducing supercooling through providing an adequate number of suitable nuclei for graphite growth. Thus, inoculation promotes the formation of Type VII A graphite, which minimizes the tendency to form carbides and, consequently, improves mechanical and physical properties of gray cast irons.

In practice, inoculants are classified either as standard or proprietary. Standard inoculants are available from a wide variety of ferroalloy producers and are basically ferrosilicon alloys containing small amounts of calcium and aluminum as inoculating ingredients. As the name implies, individual compositions of proprietary inoculants are particular to a given producer. These inoculants usually contain varying amounts of barium, titanium, zirconium, strontium, rare earths, or other elements in addition to calcium, aluminum, and the ferrosilicon base. Generally, the proprietary inoculants are more potent than the standard inoculants, and although more costly on a pound-for-pound basis, can be used in smaller quantities (that is, two to six pounds per ton[3] for proprietaries compared with four to ten pounds per ton for the standard ferrosilicon inoculants). Tables 2 and 3 list many of the available standard and proprietary inoculants, respectively.

It has been theorized that ferrosilicon enhances nucleation by providing regions of high silicon concentration [*9*]. In actual practice this has not proven entirely to be the case. Thus, as Table 2 illustrates, commercial alloys normally contain from 0.2 to 0.8 percent calcium and 1 to 1.5 percent aluminum.

Specifically, 75 and 85 percent ferrosilicons are available in two calcium grades, 0.50 percent minimum and 1.50 percent minimum. The higher calcium content is believed to reduce the fading tendency of the inoculant, especially at higher temperatures [*10*]. Due to cost and other considerations, however, the lower-calcium 75 percent ferrosilicon alloys are by far the most popular standard inoculant in the United States.

The 50 percent ferrosilicon (Table 2) has been found to be less potent than the 75 and 85 percent ferrosilicons, but is considerably cheaper on a pound-for-pound basis and is finding some use in the foundry industry. The 50 percent ferrosilicon alloy is customarily used in foundries that are mainly interested in controlling chill and not enhancing mechanical properties. On the

TABLE 2—*Typical composition of standard cast iron inoculants.*

		Composition, %			
Inoculant	Inoculant No.	Si	Ca	Al	Fe
75% FeSi	1	76.5	0.75	1.0	balance
75% FeSi	2	76.5	1.50	1.0	balance
85% FeSi	3	85.0	0.75	1.0	balance
85% FeSi	4	85.0	1.50	1.0	balance
50% FeSi	5	47.5	0.20	1.0	balance
CaSi	6	62.5	30.00	1.0	balance

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[3] 1 U.S. (short) ton = 0.9 metric ton; 1 lb = 0.45 kg.

TABLE 3—*Typical composition of some proprietary cast iron inoculants.*

Inoculants	Inoculant No.	Composition, %											
		Si	Ca	Al	Ti	Mn	Ba	Zr	Ce	Sr	Mg	$NaNO_3$	Fe
Si-Ti-Ca	1	52.5	6.00	1.15	10.0	. . .	. . .	. . .	. . .	. . .	. . .	. . .	balance
Si-Mn-Ca-Ba	2	62.5	2.25	1.25	. . .	10.0	5.00	. . .	. . .	. . .	. . .	. . .	balance
Si-Mn-Ca-Ba-Zr	3	62.5	0.80	1.00	. . .	6.0	0.75	6.0	. . .	. . .	. . .	. . .	balance
Si-Ce	4	38.0	0.5 max	0.5 max	. . .	. . .	. . .	. . .	10.0	. . .	. . .	. . .	balance
Si-Sr	5	75.5	0.1 max	0.5 max	. . .	. . .	. . .	. . .	. . .	0.8	. . .	. . .	balance
Si-Sr	6	48.0	0.1 max	0.5 max	. . .	. . .	. . .	. . .	. . .	0.8	. . .	. . .	balance
Si-Zr	7	80.0	2.40	2.00	. . .	. . .	. . .	1.5	. . .	. . .	. . .	. . .	balance
$Si-Mg-NaNO_3$	8	61.0	0.50	1.10	. . .	. . .	. . .	. . .	. . .	. . .	2.5	10	balance

other hand, little difference in inoculating effects has been found between 75 percent ferrosilicon and 85 percent ferrosilicon. Thus, since 75 percent ferrosilicon is less costly to manufacture than 85 percent ferrosilicon, it is normally used.

Although popular in past years, calcium silicide is used only in limited quantities today. The very high level of calcium in calcium silicide increases slag-forming tendencies in iron and, as a result, the incidence of slag defects in castings. Calcium silicide also emits a considerable amount of smoke and flash during use.

The first proprietary inoculant given in Table 3 is a silicon-titanium-calcium ferroalloy that is an effective graphitizer as well as deoxidizer. The titanium in this alloy also ties up nitrogen and helps prevent nitrogen porosity in casting. The inoculant is an effective chill reducer and, when substituted for 75 percent ferrosilicon, permits a 50 to 60 percent reduction in the amount of inoculant needed. This alloy is often used in irons made from charges which are high in rusty scrap.

The second inoculant is a manganese-calcium-barium-ferrosilicon and is also an effective chill reducer. The primary nucleating elements are barium and calcium and their combination is known to resist fade. One theory claims that barium protects the calcium during inoculation, thereby enhancing the nucleating effect of the calcium. Compared with 75 percent ferrosilicon, only one-third to one-half the amount of inoculant is normally required.

The third inoculant is similar to the second except it contains zirconium, which reacts with nitrogen as well as functioning as a deoxidizer. The manganese in the two alloys lowers their melting point, thereby increasing their rate of solubility in irons.

The fourth inoculant, which is finding increased use, contains cerium and is a potent deoxidizer and desulfurizer. It is effective in combating the carbide-forming tendencies of certain residual elements such as chromium, and neutralizes the tramp elements such as lead that are detrimental to Type VII A graphite. This inoculant is normally used in small quantities of one to four pounds per ton, and has been shown to significantly increase the strength of gray cast iron. The cerium-silicon alloy provides superior resistance to fading and goes into solution in the iron cleanly.

Inoculant 5 is a popular graphitizer designed to minimize shrinkage by reducing chill without decreasing eutectic cell size. Since it contains little if any calcium, it minimizes slag formation. Inoculant 6 is similar to Inoculant 5 except that it is based on 50 percent ferrosilicon.

Inoculant 7 also contains some zirconium, but is unique in that it is produced at two separate aluminum levels for control of pinholes in castings. Like the other proprietary inoculants, it is more potent than 75 percent ferrosilicon.

The last inoculant shown is an exothermic ferrosilicon designed to dissolve readily in iron, even at low temperatures. The magnesium in the inoculant enhances the nucleating efficiency. The alloy can be added to small ladles to overcome fading of inoculants added previously in the transfer ladles [*10*].

There are numerous factors that determine the effectiveness of a particular inoculant. For example, the prior history of the base iron, the melting technique, residual elements, sulfur content, and inoculation technique are all known to effect the performance of an inoculant. For this reason it is impossible to say one inoculant is superior to another; hence, each foundry must evaluate individual inoculants for gray iron under its own conditions.

Inoculation Techniques

Inoculation processes can be divided into two separate categories: ladle inoculation and late inoculation. The method most universally used is the ladle method. In the ladle inoculation process, the inoculant is usually added in the stream of the metal as it is poured from the furnace into the ladle. Best results are obtained when a well of three to four inches[4] of metal is in the ladle bottom and the inoculant is added quickly to the iron at the point where the stream hits the metal in the ladle [*11*]. If this is done properly, good mixing will occur between the inoculant and the molten iron.

The ladle process has the advantage of simplicity. However, ladle inoculation has a major disadvantage: the inoculating effect fades with time. Thus, to varying degrees the effectiveness of an inoculant is lost during the pouring operation. To minimize the problem of fading, molds must be poured as quickly as possible after inoculation, proper selection of the base charge must be made, correct mesh size of inoculant must be used, and treatment temperature must be as low as feasible for casting.

Because of the limitations of ladle inoculation, interest in late inoculation has grown rapidly in the last few years. With this method, which involves adding the inoculant in the mold or to the metal stream just prior to its entering the mold, fading is essentially eliminated. In addition, the inoculation effect is more potent; thus the amount of inoculant used can be reduced to about 0.1 percent. Better inoculating effects can also be achieved in castings that have been traditionally difficult to inoculate (that is, castings with very thin sections).

The most frequently employed late inoculation technique involves adding the inoculant in the mold. This inoculation technique is a relatively new one. The use of a granular inoculant in a specially designed mold chamber was proposed by Dell and Christ in 1964 [*12*]. In in-mold inoculation, inoculants may be added to the bottom of the sprue, in the pouring basin, or in a specially designed chamber as granular material or a bonded or cast insert. Two requirements must be met for proper inoculation: first, the material must dissolve readily and uniformly, and secondly, the undissolved particles must

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[4] 1 in. = 2.54 cm.

be prevented from entering the casting cavity [*13*]. Thus, inserts must be of proper composition and a specialized gating system frequently must be designed to prevent inclusions.

A recently patented process for inoculation involves feeding an inoculated core wire into the downsprue of a mold during casting [*14*]. The key elements of this process, illustrated in Fig. 6, are an encapsulated powder containing the inoculant and the wire feeding device with appropriate instruments for controlling the feed rate [*14*]. Ferrosilicon is normally used as the inoculant in the low-carbon steel tube. It is the dissolution rate of the steel tube that limits the velocity of the wire, and typically 0.02 to 0.03 percent by weight of the wire is used to inoculate gray iron. Metallurgical properties have been reported to be excellent in iron inoculated by this process.

Another process centers around automatically dispersing inoculant into the metal stream as it enters the mold [*15*]. Automatic controls feed granular inoculants in a stream of air onto the metal stream as it enters the mold. A diagrammatic sketch of this process may be seen in Fig. 7. This method is well suited for automatic pouring, is adaptable to castings of various size, utilizes available inoculants, and is economical. A similar device employs a screw feeder which advances the inoculant to the injection chamber, then transporting by low-pressure air to the nozzle directly into the molten metal stream [*16*]. Both systems have found limited use in the inoculation of cast irons.

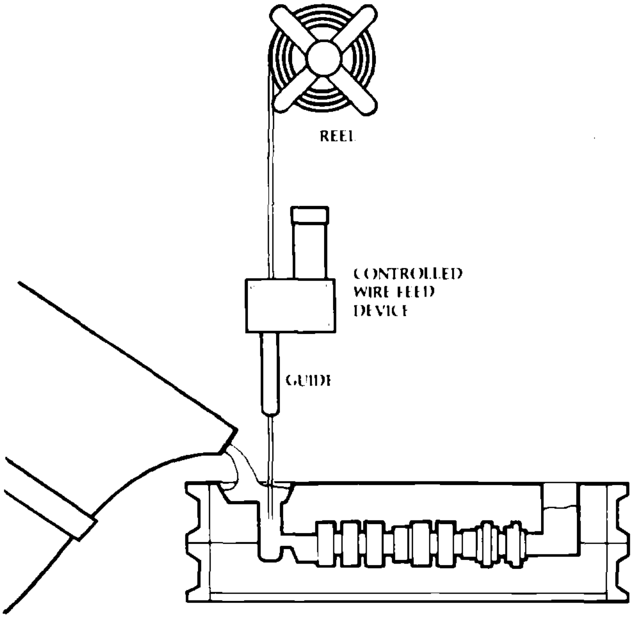


FIG. 6—*Diagrammatic sketch illustrating the inoculation of gray iron by feeding an inoculated core wire into a downsprue of a mold during pouring.*

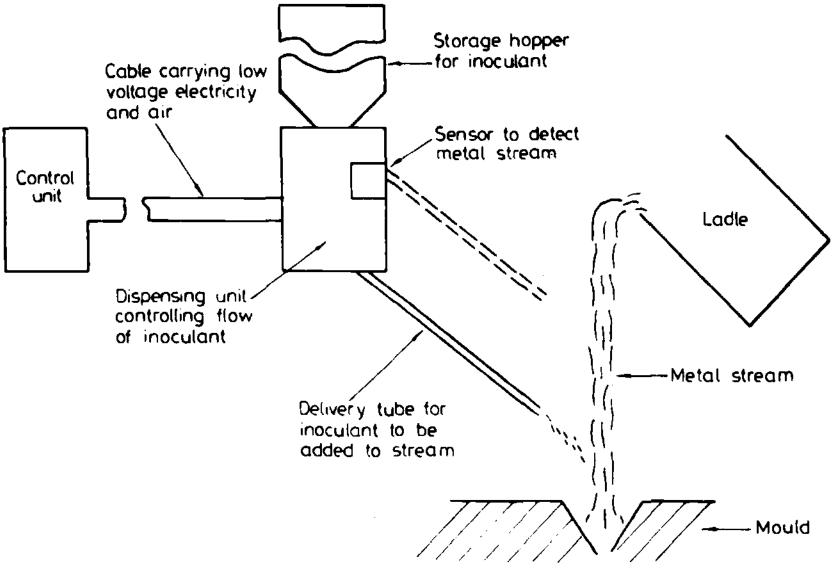


FIG. 7—*Diagrammatic sketch illustrating equipment used in metal stream inoculation of gray iron.* (*Courtesy of Cast Metals Institute.*)

Characterization of Graphite in Ductile Iron and General Effects of Nodularizing and Inoculation

Ductile iron is a relatively new material in the cast iron family. The discovery of ductile iron was made simultaneously by the International Nickel Co. and the British Cast Iron Research Association in the late 1940's. The British process consisted of adding cerium in molten iron while the International Nickel process utilized magnesium. The addition of either of these elements, or certain other rare earths, in the proper amounts to molten iron causes the graphite to solidify as spheroids rather than flakes.

The exact mechanism by which magnesium produces graphite spheroids in ductile iron is not known. Graphite spheroids are heterogeneously nucleated in the liquid, similar to gray iron, but growth occurs in a different direction along the graphite crystal [*2*]. The contrasting growth responses of gray and ductile cast irons are believed to be associated with the sulfur and oxygen level in the melt. It has been shown that both sulfur and oxygen affect the surface tension and that the resulting change in interfacial energies plays a major role in determining growth direction [*17*].

As indicated, ductile cast iron is composed of discrete graphite spheres present in an iron matrix. A number of other types of graphite are found to be associated with ductile cast irons as illustrated in Fig. 4. Type I nodules are preferred and are associated with the best mechanical properties in ductile iron. Type II are more irregular in shape, although their presence normally has little effect on properties. However, the presence of graphite Types

III, IV, V, and VI is undesirable in ductile iron and significantly reduces strength and ductility. Type IV, known as vermicular graphite, has the most adverse effect on strength in ductile iron, while Type VI is most often found in castings with thick sections. These degenerate nodules may be associated with insufficient magnesium content or improper post-inoculation. If sufficient magnesium is present, post-inoculation increases the number of nuclei for graphite precipitation, thereby increasing the final nodule count, and by so doing minimizes carbide-forming tendencies.

Nodularizing Ductile Irons

Magnesium is the most widely used element for nodularizing. However, due to its low boiling point, low solubility in cast iron, and the violent reaction associated with it, the use of metallic magnesium has been limited. Consequently, the bulk of the ductile irons produced are nodularized with magnesium ferrosilicon alloys, which contain from 3 to 9 percent magnesium. Normally, the higher the magnesium content, the more reactive the addition and the lower the magnesium recovery. Other elements, such as rare earths, can assist in the nodularizing process and may reduce the alloy requirements by 10 percent or more. Typical compositions of these magnesium ferrosilicon alloys and other nodularizing alloys are given in Table 4, which indicates that the magnesium contents of the ferrosilicon alloys range from 3 to 9 percent. The 3 percent magnesium alloy provides the best recovery, while the 9 percent alloy minimizes the amount of silicon added during treatment.

TABLE 4—*Typical composition of some nodularizing alloys used in ductile iron production.*

	Composition, %								
Alloy No.	Mg	Si	Ca	Al	Ce	Total Rare Earths	C	Ni	Fe
1	3.0	46	1.0	1.2 max	. . .	. . .	. . .	. . .	balance
2	5.5	46	1.0	1.2 max	. . .	. . .	. . .	. . .	balance
3	9.0	46	1.2	1.2 max	. . .	. . .	. . .	. . .	balance
4	5.5	46	1.0	1.2 max	0.3/1.2	[0.35/1.35]	. . .	. . .	balance
5	9.0	46	1.3	1.2 max	0.3/0.75	[0.35/0.85]	. . .	. . .	balance
6	3.5	46	1.0	1.2 max	[1.25]	1.75	. . .	. . .	balance
7	5.5	46	1.0	1.2 max	0.3/1.0	[0.45/2.0]	. . .	. . .	balance
8	9.0	46	1.0	1.2 max	0.40	[0.75]	. . .	. . .	balance
9	3.3	45	0.5	1.0	1.6	1.9	. . .	. . .	balance
10	6.0	45	0.5	1.15 max	0.45	[0.5]	. . .	. . .	balance
11	15.0	. . .	. . .	. . .	. . .	. . .	2.0	balance	. . .
12	15.0	30	. . .	. . .	. . .	. . .	. . .	balance	5 max
13	4.5	. . .	. . .	. . .	. . .	. . .	2.0 max	balance	. . .
14	4.3	. . .	. . .	. . .	. . .	. . .	2.5 max	balance	34

[ ] = nominal analysis range.

These alloys are often used in heavy section castings where relatively pure charge materials are utilized and it is desirable to maintain rare earths at low levels. In conventional castings, rare earths can be added in conjunction with magnesium ferrosilicon alloys as misch metal, rare-earth silicide, or as the 10 percent cerium-containing proprietary alloy, No. 4, listed in Table 3.

Magnesium ferrosilicon alloys containing rare earths may be divided into two groups: those containing high-cerium rare earths (ratio of cerium to other rare earths—greater than 90 percent) and those containing low-cerium rare earths (ratio of cerium to other rare earths—approximately 50 to 70 percent). It has been shown that the greatest efficiency, that is, highest nodule counts and lowest carbide forming tendency, is obtained in irons treated with the low-cerium rare-earth alloys [*18*]. As indicated in Table 4, these alloys are also available with varying magnesium contents. They are designed to provide from 0.005 to 0.011 percent cerium and an appreciable amount of other rare-earth elements, principally lanthanum, in the cast iron for optimum nodule count and iron carbide control.

Alloy No. 10 is a magnesium ferrosilicon alloy designed specifically for use in in-mold nodularization of ductile iron. As shown in the chemical analysis, the calcium content is sufficiently low to improve the reactivity of the alloy and minimize the chances for inclusion from undissolved particles.

Other alloys containing magnesium are based on nickel. Alloy Nos. 11 through 14, listed in Table 4, have the advantage of being more dense than iron, which means the alloy will sink to the bottom of the ladle during treatment, thus providing excellent magnesium recovery. While these alloys are effective their use is limited generally to those applications where the cost of the nickel carrier can be credited. Another product available is a magnesium-impregnated coke. The coke contains 42 percent magnesium by weight and, although magnesium recoveries are low, at less than 30 percent, some commercial irons are produced with this nodularizing material.

The sandwich method of pouring molten iron over a magnesium-containing alloy in the bottom of a ladle remains the most commonly used process for treating ductile iron [*19*]. In this process, the magnesium alloy (usually magnesium ferrosilicon) is placed in the bottom of a ladle with steel punchings or clippings used as a cover material. The molten iron is poured onto the alloy and magnesium recoveries of 50 percent or slightly higher are usually obtained. Occasionally, the open ladle process in which no cover material is used is employed.

The plunging process is the next most popular means of nodularizing ductile iron. The plunging method gives relatively high recoveries and allows usage of relatively reactive alloys containing higher levels of magnesium. In this process the alloy is placed in a refractory or graphite bell and plunged beneath the surface of the molten iron. Another technique, the porous plug process, is gaining in popularity. In this process, magnesium is stirred into iron in a porous plug ladle by bubbling nitrogen gas.

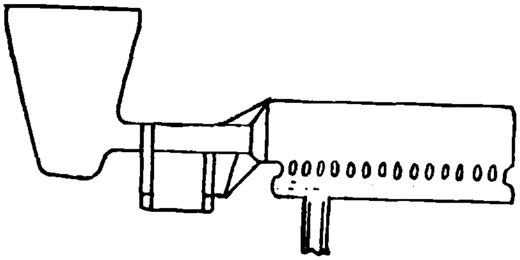
The use of pure magnesium has grown in recent years, mostly due to development of better mechanical means of controlling the magnesium-iron reaction. For example, pure magnesium may be submerged in the molten iron in a pressure-tight vessel or in a converter. Alternatively, magnesium may be coated with a refractory in order to control the reaction and then plunged into a ladle. This process, known as MAP process (U.S. Patent No. 3598575, 10 Aug. 1971), uses a conventional plunging bell to introduce the coated magnesium, thus providing relatively high recoveries and manageable pyrotechnics, particularly in lower-temperature irons used for pipe production. Alternatively, magnesium-impregnated coke may be used instead of the coated magnesium.

The converter process encompasses a specially designed converter vessel with a reaction chamber for controlling the magnesium reaction [*20*]. In the horizontal position, pure magnesium is added at one end of the vessel and a nodular base iron is introduced in the spout at the opposite end. The vessel is then tilted into a vertical position for treatment. After treatment, the vessel returns to the horizontal position for pouring into the ladle. The converter is capable of simultaneous desulfurization and nodularization.

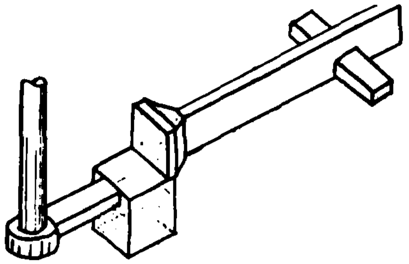
The ability to nodularize ductile iron in the mold is one of the most important recent developments in the foundry industry. The Inmold Process proposed and patented by Dunk and McCauly (U.S. Patent No. 83632, 10 Nov. 1970) offers the advantages of low pyrotechniques and adaptability to automated pouring. By treating within the mold, utilizing a specialized gating system, alloy recoveries as high as 80 percent or greater are achieved. Normally, better metallurgical properties in the iron are obtained and the problems associated with magnesium fading are completely overcome. Further, no post-inoculation is normally necessary in irons treated in the mold. However, there are certain disadvantages in the Inmold Process—notably, a specialized gating system must be designed for each casting, casting yield may be lower due to the gating system, inclusions may form from untrapped dross or undissolved alloy, and quality control of each casting may be necessary due to the individual treatment [*13*].

In the Inmold Process, the alloy may be added as granular material or as a cast or bonded insert. At present, granular 5 percent magnesium-ferrosilicon, sized 5 by 8 mesh, is standard. This magnesium-ferrosilicon alloy contains a lower than normal calcium content and is used at an addition level ranging from 0.6 to 1.0 percent, depending on the sulfur level. Experimental and commercial work has also been performed with a blended mixture of elemental magnesium and ferrosilicon [*21*].

There are some characteristic process limitations associated with using granular in-mold alloy. For example, the process is not easily adapted to molds characterized by a vertical parting plane, and inclusion traps may be needed in the gating system [*22*]. Because of these limitations the use of cast or bonded inserts has been studied in recent years. An isometric sketch of



Vertical Parting, Cast Insert



Horizontal Parting, Granular Insert

FIG. 8—*An isometric sketch illustrating the nodularizing devices used in the Inmold Process.*

both the horizontal parting and the vertical parting nodularizing devices is shown in Fig. 8.

Inoculation of Ductile Cast Irons

In the case of ductile iron, inoculation, or post-inoculation as it is usually called, differs from gray cast iron inoculation in that it follows the magnesium treatment process. Higher levels of inoculation are required to neutralize the carbide-forming tendencies of magnesium, and because nucleation is also more difficult in irons with low oxygen and sulfur levels, which are characteristic of ductile iron. Usually, a ladle addition of between 0.4 and 1.0 percent of a 75 percent ferrosilicon, listed in Table 2, is required for good nucleation. Some foundries find some of the proprietary inoculants given in Table 3 to be useful for ductile iron as well. The manganese-calcium-barium-ferrosilicon listed as No. 2 in Table 3 has been found to be particularly useful.

If no post-inoculation is used, or less than the required amount, nodules may be irregular in shape, giving the appearance of irons treated with insufficient nodularizing alloy, or iron carbides (chill) may be present. Even with larger inoculation additions and careful control of magnesium, rare earth, and sulfur levels, ductile irons are in general more difficult to inoculate than gray irons.

Compacted Graphite Iron Treatment

Compacted graphite iron was first referenced in 1948 by Morrogh [*23*]. However, only in recent years have serious attempts been made to utilize the special properties of this iron which have been briefly referred to earlier in this paper.

The lack of reliable production techniques is one of the primary reasons why compacted graphite irons have not been developed more extensively. Like ductile iron, compacted graphite iron may be produced by carefully controlling the residual magnesium and rare-earth levels in cast iron. However, as little as 0.005 percent change in residual magnesium may alter the shape of the graphite from gray iron flakes to compacted graphite to nodules. Thus, the control of magnesium, cerium, and sulfur is critical in the production of compacted graphite iron. To consistently produce compacted graphite iron, the range of magnesium contents over which compacted graphite irons can be produced may be extended by adding modifying elements such as titanium. At least one alloy takes advantage of this fact and is available commercially for the production of compacted graphite iron by a single alloy addition [*24*]. The alloy has the following composition: 4.0/5.0 Mg-8.5/10.5Ti-0.20/0.35Ce-4.0/5.5Ca-1.0/1.5Al-48.0/52.0Si, with the balance being iron. The alloy is designed so that the key alloying elements—magnesium, titanium, cerium and calcium—are added in suitable proportions over a range of addition levels. Typically, depending on sulfur level, an addition of 0.7 to 1.3 percent is required to produce compacted graphite iron.

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A. C. Demos[1] *and D. W. Kremin*[1]

Titanium and Its Alloys for Use in Iron and Steelmaking

REFERENCE: Demos, A. C. and Kremin, D. W., "**Titanium and Its Alloys for Use in Iron and Steelmaking,**" *Ferroalloys and Other Additives to Liquid Iron and Steel, ASTM STP 739,* J. R. Lampman and A. T. Peters, Eds., American Society for Testing and Materials, 1981, pp. 144–150.

ABSTRACT: This paper covers the various titanium alloys that are available to the foundry and steelmaking industry. It describes ferrotitanium products and titanium alloy scrap materials, comparing the analysis of the ferroalloy with the scrap products. A brief description of the method of preparation is included for both the ferro and the scrap metal additives.

KEY WORDS: ferroalloys, titanium alloys, steelmaking, irons, steels, briquettes

The discussion of the titanium alloys described in this paper covers the more commonly used raw materials available to steelmakers. These include the simple alloy combinations used for deoxidation or alloying.

Some of the titanium alloys used today relate back to the feed stocks used for eutectic ferrotitanium production started about two decades ago. These are listed in Table 1 and cover most of the commonly produced titanium alloys used in aircraft or other industrial applications. The first three columns are those titanium alloys produced in largest volume and they represent the 6-4 alloy, the 99 or "CP" alloy—commonly called "commercially pure"—and the 5-2 1/2 alloy. The 6-4 alloy is a nominal 90 percent titanium, 6 percent aluminum and 4 percent vanadium product. The CP alloy is of 99.5+ percent titanium anlaysis and contains only small percentages of iron and, in some alloys, palladium. The palladium content is approximately 0.20 percent and the iron levels about 0.35 percent. The 5-2 1/2 alloy simply contains 5 percent aluminum and 2 1/2 percent tin. The remaining alloys contain varying amounts of aluminum, vanadium, tin, molybdenum, columbium, or manganese. The last alloy listed is the 92-8 alloy and is now produced in minor quantities.

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TABLE 1—*Commercial titanium alloys.*

	6-4	99	5-2 1/2	6-2-4-2	6-6-2	8-1-1	92-8
Titanium	90%	99.5%	92.5%	86%	86%	90%	92%
Aluminum	6%	. . .	5%	6%	6%	8%	. . .
Vanadium	4%	. . .	. . .	. . .	6%	1%	. . .
Manganese	. . .	. . .	. . .	. . .	. . .	. . .	8%
Tin	. . .	. . .	2.5%	2%	2%	. . .	. . .
Carbon	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Columbium	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Molybdenum	. . .	. . .	. . .	2%	. . .	1%	. . .
Zirconium	. . .	. . .	. . .	4%	. . .	. . .	. . .

Procedure

From each of the alloys listed in Table 1, scrap material is generated in the form of machine turnings or cut solid scrap. The turnings can range from the very-low-density bushy type to short heavy chips. The oil and moisture content for the turnings can vary from as low as 2 percent to as high as 35 or 40 percent. The term "solids" we will apply to any form of scrap other than turnings, and this would include bar ends, rod ends, pipe, tubing, flashings from forging operations, plate or sheet cutoffs, and so on.

Figure 1 illustrates typical titanium bulky turnings. Figure 2 shows solids which have been cleaned and shot-blasted in preparation for alloy additions. Note that all "solids" are not cleaned and shot-blasted for steel mill melting and that this expensive procedure is generally applied to the critical additives used for vacuum melting. Those alloys used in steel mill applications do not always require the same extensive preparation.

The largest volume of titanium additives used in steelmaking is derived from titanium briquettes. Figure 3 illustrates a typical "hockey puck"-type briquette. This is about 12.7 cm (5 in.) in diameter and approximately 5.0 to 7.6 cm (2 to 3 in.) thick. It contains no binder and is pressed at around 618 to 772 MPa (40 to 50 ton/in.^{2}).

Prior to briquetting, the oily and wet titanium turnings are crushed and sent through a series of conveying systems equipped with magnets to remove contaminating magnetic material. The crushed chips are then processed through a chemical washing system to completely remove oil, moisture, or any other extraneous material clinging to the chip. After crushing and cleaning, the chips are briquetted as shown in Fig. 3.

Regarding the quality of titanium briquettes, Table 2 lists four nominal compositions. The first three we will identify as Ti90, Ti92, and Ti99 because they correspond in titanium content to three of the commercial alloys produced by the primary titanium manufacturers. To make briquettes of these alloy compositions, the chip feed stock must be well segregated and thor-

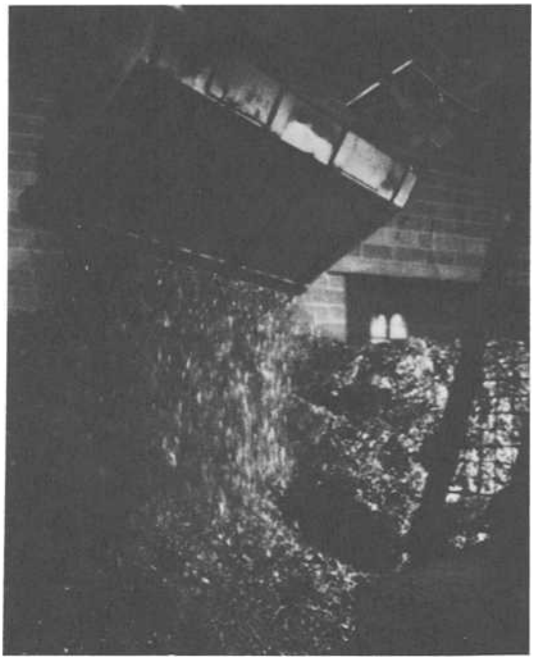

FIG. 1—*Bulk titanium turnings.*

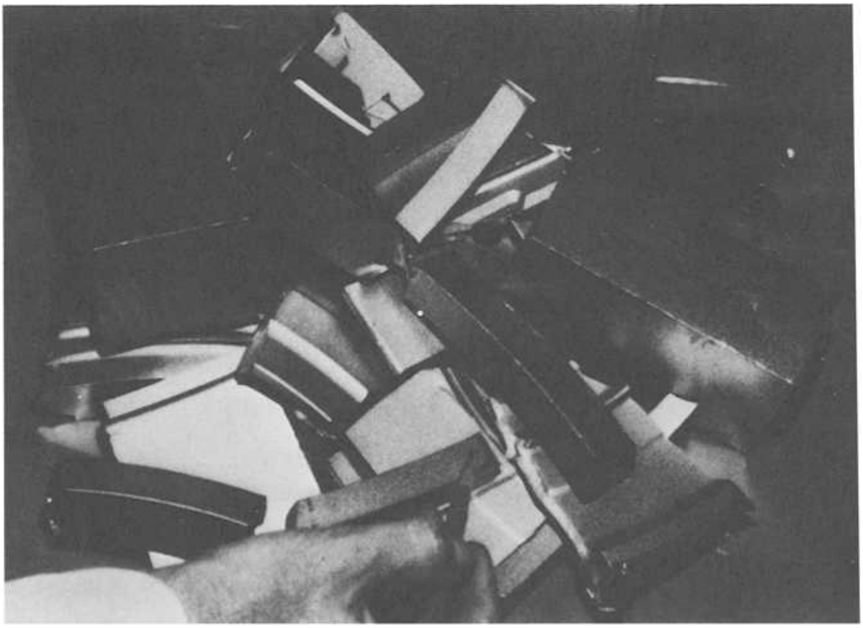

FIG. 2—*Titanium solids.*

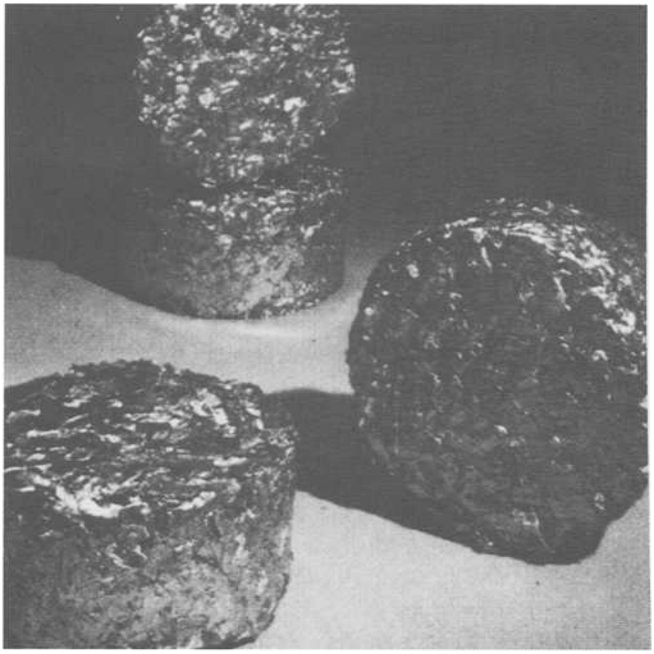

FIG. 3—*Titanium briquettes.*

oughly analyzed. However, it is not always possible to obtain well-segregated scrap machine turnings, and for this reason we have listed a typical analysis for a product identified as Ti85 in the right-hand column. This would contain mixed or contaminated chip raw material which could include any or all of the alloys given in Table 1. In addition to this product being a mixture of several titanium grades, it also contains small quantities of nickel, chrome, and iron which come from high-nickel alloys or stainless steel alloys

TABLE 2—*Typical analyses of titanium briquettes.*

Element	Ti90	Ti92	Ti99	Ti85
Titanium	90%	92 1/2%	99%	85 to 87%
Aluminum	6%	5%	. . .	3 to 5%
Vanadium	4%	. . .	. . .	0 to 2%
Tin	. . .	2 1/2%	. . .	0 to 2%
Zirconium	. . .	. . .	. . .	0 to 3%
Nickel	. . .	. . .	. . .	0 to 3%
Chrome	. . .	. . .	. . .	0 to 3%
Iron	. . .	. . .	. . .	1 to 5%
Molybdenum	. . .	. . .	. . .	0 to 1%
Columbium	. . .	. . .	. . .	0 to 1%
Oil + H_2O	1.0% max	1.0% max	1.0% max	1.0% max

used in aircraft manufacture and which are accumulated in the same areas as the titanium chip product is collected. For many steel applications these contaminants are not a serious problem, and product of this type affords the steelmaker a low-cost titanium addition source.

Cost

Comparing cost, we find that Ti99 is the most expensive alloy addition because it is of highest quality. The Ti90, which is in strong demand for other recycle areas, is the second highest-priced material, and the Ti92 or Ti85 products are the lower-priced alloys. For steelmaking, the Ti85 and Ti92 products are most commonly used because of cost. If, however, low-tin residual is required (that is, stainless production), then the Ti90 or Ti99 products would be preferred.

It should be kept in mind that in addition to the demands for titanium additives for steelmaking, the primary titanium producers are continually researching means for recycling these by-product titanium chips and solids. For this reason, a pure or segregated scrap commands a much higher price when recycled to the titanium mill producer than when converted to a titanium additive for steel plants. For instance, slightly contaminated or mixed turnings can be used by steel mills at a typical briquette price of $2.00 to $2.50 per pound of contained titanium. A nonmixed chip—comparable to a similar briquette product,—could be recycled to a titanium producer for the same price range but without requiring removal of 2 to 40 percent oil and moisture, crushing, magnetic treatment, washing, briquetting, packaging, and delivery costs. Thus, the titanium producer could afford to pay 1 1/2 or 2 times as much as the steel producer, and in the case of solids this differential often goes up to 3 to 5 times as much.

Ferrotitanium

The same raw materials used to prepare titanium briquettes or solids can also be used to produce ferrotitanium alloys. The ferrotitanium products are also a significant part of titanium additives available to the steelmaker today. Twenty or 30 years ago the commonly used ferrotitanium products were high-carbon ferrotitanium and 40 percent grade ferrotitanium. In 1954, and because of the increasing availability of titanium scrap, 70 percent ferrotitanium alloys were initiated. Note from Table 3 that high-carbon ferrotitanium contained only 15 to 18 percent titanium and had the disadvantage of carrying 6 to 8 percent carbon. The 40 percent ferrotitanium alloy was suitable from an analysis standpoint, had the advantage of low carbon content, and provided some aluminum or silicon where this was desirable. But this product is generally made by an aluminothermic reduction of ilmenite or rutile or some mixture thereof, and, in producing the alloy, huge quantities of fume are liberated, bringing about associated pollution control problems. In

TABLE 3—*Common ferrotitanium alloys used for steel making.*

Element	High-Carbon Ferrotitanium	40% Grade Ferrotitanium	70% Grade Ferrotitanium		
			Commercial Quality "CQ"	High Purity "HP"	Utility Quality "UT"
Titanium	15 to 18%	38 to 43%	68 to 72%	68 to 72%	67 to 72%
Aluminum	. . .	3 to 10%	3 to 5%	0.50%	2 to 6%
Carbon	6 to 8%	0.10%	0.25%	0.15%	0.25%
Silicon	1 to 4%	1 to 5%	. . .	. . .	. . .
Vanadium	. . .	. . .	2.5%	. . .	1 to 3%
Tin	. . .	. . .	. . .	. . .	0.5 to 1.5%
Zirconium	. . .	. . .	. . .	. . .	0 to 2%
Nickel	. . .	. . .	. . .	. . .	0 to 2%
Chrome	. . .	. . .	. . .	. . .	0 to 2%
Iron	balance	balance	balance	balance	balance
Approximate melting point, °C (°F)	1454 (2650)	1343 (2450)	1066 (1950)	1066 (1950)	1066 (1950)

addition, the finished product must be separated from the by-product slag generated in the reduction.

The 70 percent ferrotitanium product is a eutectic composition, melting about 260 or 315 deg C (500 or 600 deg F) lower than the high-carbon or the 40 percent ferrotitanium products. This allowed the alloy producers to use induction furnaces and the now readily available titanium scrap to produce a relatively low-melting 70 percent product free of excessive fume and pollution and without slag separation problems.

For a number of years, the first 70 percent ferrotitanium products were made from the same raw materials used to produce briquettes. That is, commercial quality (CQ) alloy was generally made from a 6-4 alloy scrap and, as a result, carried proportionate amounts of aluminum and vanadium. The high-purity (HP) ferrotitanium or higher-purity material was made from the CP titanium scrap and was essentially free of contaminating elements. The grade identified as "utility quality" (UQ) was made from mixed or contaminated alloy scrap similar to that used to produce the Ti85 briquette covered earlier. It has the same residuals of chrome, iron, vanadium, tin, and, of course, it is controlled by regulating the type of mixed scrap going into the induction heat.

Conclusion

In this discussion we have presented the leading titanium alloy sources for lowest-cost titanium additions to iron and steel. However, there are numerous other product possibilities which are commercially used, but more often in special applications. These are proprietary compositions which often contain 25 to 45 percent titanium, 10 to 30 percent or more aluminum, 1 to 3 percent boron, and with other alloying elements such as zirconium, silicon, and manganese. The important point to bear in mind is that either the briquetting technique or the induction-furnace procedure allows the steelmaker to prescribe his own alloy—within limits—so that he arrives at the most desirable composition commensurate with optimum costs.

G. G. Larsen[1]

The Role and Use of Aluminum in Steel Production

REFERENCE: Larsen, G. G., "**The Role and Use of Aluminum in Steel Production,**" *Ferroalloys and Other Additives to Liquid Iron and Steel, ASTM STP 739,* J. R. Lampman and A. T. Peters, Eds., American Society for Testing and Materials, 1981, pp. 151-156.

ABSTRACT: Aluminum is very important in controlling steel oxidation level. As a result it also controls the ingot structure and hence the steel properties. This paper discusses the various types of aluminum used in steel production. The recovery of aluminum as a function of steel type and carbon level as well as the importance of consistent recovery are also discussed.

KEY WORDS: steelmaking, steel deoxidation, ferroalloys, aluminum

Aluminum is of tremendous importance in steel production because it is a powerful controller of steel oxidation level. As a result, it also controls the ingot structure and influences the steel properties.

Steelmaking

As the steel is tapped from the furnace, it contains some dissolved oxygen. Oxygen is used in the steelmaking process to remove carbon, phosphorus, silicon, and manganese that are present in the steel scrap and iron from the blast furnaces. However, by the time the desired levels of these elements are obtained, there is a certain amount of oxygen dissolved in the steel bath. The amount of oxygen is dependent upon the carbon level of the bath; the lower the carbon, the higher the oxygen. The final ingot structure is determined by controlling the amount of dissolved oxygen left in the steel during tapping and teeming.

Only in the case of rimmed and mechanically capped steel is it desired to retain all or most of the dissolved oxygen present at the time the heat is tapped. The actual process of removing the unwanted oxygen is called deoxidation and is accomplished by adding an element which forms a stable oxide at steelmaking temperatures. Although aluminum is not the only element which can be used to deoxidize the steel, it is, because of its high affinity for

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oxygen and relatively low cost, the most common. The choice of deoxidizers used, or even whether to deoxidize at all, may be made internally based upon the intended end use of the steel. Other times, the chemical composition as specified by the customer may not leave that choice up to the steelmaker.

Rimmed and Mechanically Capped Steels

As previously mentioned, the rimmed and mechanically capped steels are produced by either not deoxidizing or partially deoxidizing the steel during the tap. Small amounts of up to 1/4 kg/tonne (t) (1/2 lb/ton) of aluminum are sometimes added to the ladle to control the behavior of these steels during teeming. The rimmed steels are generally at the low end of this addition rate, and in the case of medium-carbon (0.1 to 0.2 percent) rimmed steel no additions are needed. The mechanically capped steels are at the high end of this addition rate because the required ingot structure requires very light deoxidation.

In addition to the possibility of having aluminum added to the ladle on rimmed and mechanically capped steels, small amounts of aluminum shot of up to about 60 g/t (2 oz/ton) may be made to each ingot as it is being poured. This is used as a final adjustment, determined by visual observation of the steel in the mold, to obtain the desired ingot structure and may be changed throughout the pour as needed. Although the amount of these aluminum additions seems small compared with the weight of steel involved, they play an extremely important part in the production of these steel types.

Killed and Semikilled Steels

For the production of semikilled steels a somewhat greater amount of aluminum or other deoxidizer is added to the ladle. This addition normally is in the range of 1/2 to 1 kg/t (1 to 2 lb/ton). This amount will tie up most of the dissolved oxygen. However, some oxygen is left so that some carbon dioxide gas will form and disperse the shrinkage cavity ("pipe"). The actual amount added to any given heat is based upon the amount of dissolved oxygen in the steel at tap. Since that value is related to carbon, the schedule can be based on the tap carbon. Once again, not all the required aluminum is added to the ladle. A small amount, on the order of 30 to 90 g/t (1 to 3 oz/ton), is added to each ingot in order to obtain the proper level of deoxidation.

The Al_2O_3 formed as a result of the deoxidation tends to float out of the steel into the slag. As a result, if the proper weight is added, there will be no measurable amount of aluminum left in the steel.

To produce fully aluminum-killed steel an addition of 1.3 to 2.3 kg/t (2.5 to 4.5 lb/ton) is needed. This amount will tie up almost all of the dissolved oxygen. As a result, these ingots do not give off any carbon dioxide gas and lie very quiet or dead in the mold; hence the name killed steel. To insure that the oxygen is removed, an excess amount of aluminum is added, the excess going into solution. As in the case of the semikilled steel, most of the Al_2O_3 floats out of the steel into the slag, although a small portion may be retained in the steel. These steels will have aluminum analyses between 0.02 and 0.08 percent aluminum.

Larger amounts of aluminum are sometimes used to produce alloy steels where the higher contents are needed to develop specific properties such as magnetic permeability in silicon electrical steels. Aim analyses here may be on the order of 0.20 to 0.25 percent aluminum or even higher with addition rates of 3 to 4 kg/t (6 to 8 lb/ton).

Aluminum Recovery

The recovery of aluminum is highly variable, depending upon the weight being added, as shown in Fig. 1. The small amounts added to control the behavior of unkilled and semikilled steels do not yield a measurable recovery because the aluminum is oxidized, by intention, and most of the resulting alumina floats out of the steel. Production of killed steels aiming for 0.03 to

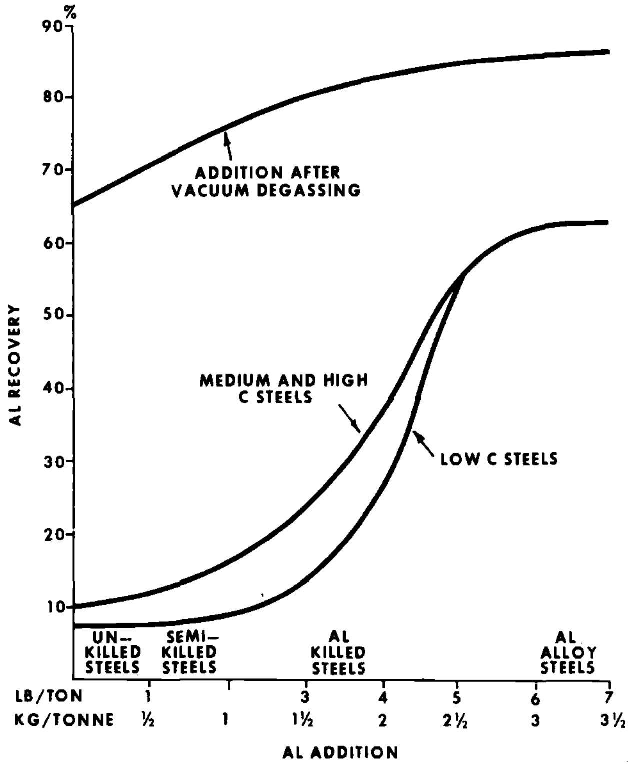

FIG. 1—*Effect of weight of aluminum addition to steel on its recovery.*

0.08 percent aluminum gives recoveries of about 25 percent in low-carbon and slightly higher in medium- and high-carbon steels. The more weight added, the higher the percent recovery because once the residual dissolved oxygen is reduced (after about 0.02 percent aluminum is exceeded) the subsequent aluminum additions show significant recoveries. Aiming for aluminum contents of 0.3 percent or higher gives recoveries exceeding 50 percent. Recoveries of over 80 percent may be obtained when adding the aluminum to already killed vacuum-degassed steels.

Common Aluminum Additions

Even more important than percent recovery, especially from an application standpoint, is the consistency of recovery for a given grade of steel. If the recovery is erratic and off-specification heats are made, it is possible that alternative applications are not readily available and the steel becomes very-slow-moving inventory.

Aluminum used for steel deoxidation is covered by ASTM Standard B-37 which specifically refers to this application. Although unstated, in practice most of this aluminum is secondary remelted aluminum scrap. The 95 percent purity grade, referred to in the trade as "Grade I," is usually preferred to the 85 percent purity or Grade IV. Intermediate grades are not in common usage.

One of the most common forms of aluminum used is shot, 6 to 13 mm (1/4 to 1/2 in.) in diameter. If used as a ladle addition it should be bagged, both because of improved storage and handling and better recovery. When used in the pouring pit it is fed by hand. For this purpose it is important that the shot be uniform in size both within and between shipments so that the standard volumetric measuring cups always yield the same weight.

Another common ladle aluminum addition is small pigs weighing about 1800 to 4550 g (4 to 10 lb). These piglets are often wired together into larger bundles and because of their size are used only as ladle additions.

There are two relative newcomers; the first is chopped wire from scrapped electrical installations. All insulation must be removed. Copper, copper clad, or steel reinforced wire are undesirable to have mixed in with the aluminum wire, the copper because of its detrimental effect on some steel types and the iron (and copper) because of its effects on the true weight of aluminum addition. If bagged, it is usable in the ladle, giving results the same as Grade I shot; however, briquetting or pressing the wire before bagging tends to give more consistent recoveries. Chopped wire is not useful for pit additions; the loose material is blown away from the steel stream by air currents and the agglomerated shapes are of course too large.

At present the supply of this material is plentiful, but due to the trend back to copper for electrical applications the supply may become limited.

The second relative newcomer is chopped aluminum cans. Because of the steel tops and the possibility of steel cans mixed with the aluminum, the chopped material must be magnetically separated. If not, inconsistencies in weight would produce intolerable fluctuations in the product quality or aluminum analysis. The utility of this material is the same as for chopped wire.

Sometimes, especially if added to the ladle improperly, the aluminum tends to float, often giving low or erratic recoveries. This tendency may be reduced by weighing down the aluminum with another element, the most common being manganese. The usual form is either a briquette or some form of pressed shape of ferromanganese fines and aluminum. Unfortunately, true alloys of manganese and aluminum are difficult to produce because, when mixed as liquids, the two tend to separate quickly. One problem with the use of this material is that the melter must remember that he recovers this manganese in the steel and he must reduce his ferromanganese addition or he will overshoot his aim manganese range. In the case of a high residual manganese coupled with a low aim range, this material may not be usable because by itself it may cause the heat to be above the manganese specification.

Another way to counteract the floating tendency is to cast the aluminum into rings which attach to either the stopper rod in the ladle or an auxiliary rod. The heat is then tapped into the ladle and as the metal rises around the rings it melts the aluminum. This method of course prevents the use of that ladle for any other steel type unless the aluminum is removed. If a last-minute change in aim specification is necessary, production delays may be caused by either changing ladles (if available) or removing the aluminum. If the rings are on the stopper rod, the tendency to float may pull the rod out of the well and cause a leaker under the furnace. If used on an auxiliary rod, then there is additional work involved in preparation and maintenance of the rods.

An aluminum alloy necessary for specific applications but used in very small amounts for control of rimmed steel ingots is an alloy of aluminum and 6 percent magnesium. The role of the magnesium is to disperse the aluminum by generation of a vapor. This material is usually produced as small slugs weighing about 60 g (2 oz).

Another product that from a tonnage standpoint is also very small, but critical in some continuous casting operations, is aluminum wire fed to the molds or the tundish for porosity control or to produce fine-grained steel without resorting to submerged casting or the use of expensive grain refiners like columbium or vanadium. The wire is usually pure aluminum, although some silicon may be specified for hardness. However, it is more commonly cold drawn to some desired temper.

A last type of aluminum that is used is ferroaluminum, an alloy containing about 35 to 40 percent aluminum, the balance being iron. Its main use is as a controller of oxidation level in the furnace. (There is another paper in this volume dealing with the use of ferroaluminum so I will not discuss the topic any further.)

Summary

In summary, aluminum is extensively used in steel production because of its high efficiency as a deoxidizer and its relatively low cost. Recovery is highly dependent upon the amount added and steel oxygen content, which is somewhat reflected by the tap carbon level. From an application standpoint, consistency of recovery is even more important than actual recovery. Aluminum is commercially available in many different forms. Which one to use is a decision that must be made based upon the operating and metallurgical parameters of each steelmaking shop.

P. D. Deeley[1]

Ferroaluminum—Properties and Uses

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ABSTRACT: The use of ferroaluminum is increasing in steel mills and foundries in the United States and overseas. The paper reviews aluminum deoxidation briefly, with emphasis on efficiency and oxide inclusion removal, then discusses the properties of ferroaluminum which give it superiority over metallic aluminum as a deoxidizer. Current steel mill and foundry experience and operating practice are reviewed, with special attention to the use of ferroaluminum as a furnace blocking addition, a primary and final deoxidizer, and as a means for increasing the accuracy and precision of oxygen probe measurements.

KEY WORDS: ferroaluminum, aluminum, ferroalloy, deoxidation, grain refining, steel cleanliness, inclusions, oxygen probe, steelmaking, steel plant, steel foundry

The past two decades have seen a much greater awareness on the part of steel producers and fabricators of the role played by cleanliness on the useful properties of steel. This has been especially true for suppliers of heavy plate for welded construction and plate and skelp for arctic linepipe, as well as for users of forging-quality products. Response by the steel industry to this increased quality consciousness has been in the form of a vast new array of steelmaking and refining processes, coupled with advanced chemical analysis and quality-control instrumentation. It is significant that the new processes and techniques not only meet the cleanliness demands, but that they do so with higher reliability, greater speed, and lower cost.

A major element in many of these developments has been the variety of approaches made toward more thorough and reliable deoxidation. The benefits are well known: Cleaner steels exhibit higher mechanical properties, improved machinability and formability, and better surface quality, to name just a few. To the steelmaker, low—or at least, consistent—oxygen contents facilitate process control. They lead to higher alloy recoveries and, as an added feature, improve the efficiency of ladle desulfurization processes.

It has been shown that ferroaluminum can be an effective and reliable means by which thorough deoxidation and improved steel cleanliness can be achieved. Ferroaluminum also offers advantages when used in conjunction

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with modern process control instrumentation, yet it avoids problems associated with the more traditional deoxidizers. The present paper explores some of these attributes and describes the operating experiences gained by a number of steel mills and foundries over the past few years. It concludes with some thoughts on how ferroaluminum may be used in the future.

Why Aluminum Deoxidation?

Before describing ferroaluminum itself, it may be helpful to review briefly the reasons for using aluminum in any form as a steel deoxidizer. With this as a basis, it will be easier to understand how the specific advantages offered by ferroaluminum are now being applied.

Obviously, aluminum deoxidation is neither necessary nor technically applicable to all steelmaking processes and products. Where it is or can be used, however, it offers several advantages. First, it is highly effective. Both from considerations of free energy of formation [*1*][2] (Fig. 1) and related solubility product data [*2*] (Fig. 2), it can be seen that aluminum is one of the more powerful deoxidizers, exceeded only by zirconium, calcium, and the rare-earth metals at steelmaking temperatures. Aluminum is therefore theoretically able to reduce soluble oxygen contents to quite low levels and, in so doing, protect and raise the recoveries for other oxidizable alloying elements added to the steel. Free aluminum remaining in the liquid steel after "equilibrium" has been achieved can protect against reoxidation before solidification.

Second, aluminum is a very rapid and efficient deoxidizer [*3*]. Measurements taken of *total* oxygen content (Fig. 2) taken after various deoxidizers were added to the ladle show that aluminum is, in fact, faster than silicon, zirconium, and titanium. The fact that total oxygen contents were considered in constructing Fig. 3 is significant since this gives some indication of the rate at which solid deoxidation products are removed from the melt. The figure unfortunately does not show the partition of oxygen between dissolved and precipitated states. From thermodynamic considerations, silicon would be expected to leave more oxygen in solution, while zirconium would tie up more of the gas as a solid oxide. The actual removal of solid inclusions from the melt depends on fluid dynamic factors, including the density, morphology, size distribution, and surface properties of the particles. Studies have shown, for example, that oxides with densities nearest to that of liquid steel [7.0 to 7.2 g/cm^3 (0.2529 to 0.2601 lb/in.^{3})] are removed most rapidly from the melt [*4*]. Other work has indicated that under conditions of even gentle turbulence—such as might be expected in the natural convection within a standing ladle—alumina inclusions are removed at interfaces such as the slag layer and refractory linings almost as quickly as the rare-earth oxides (whose density is nearest to that of steel) and decidedly faster than silica

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

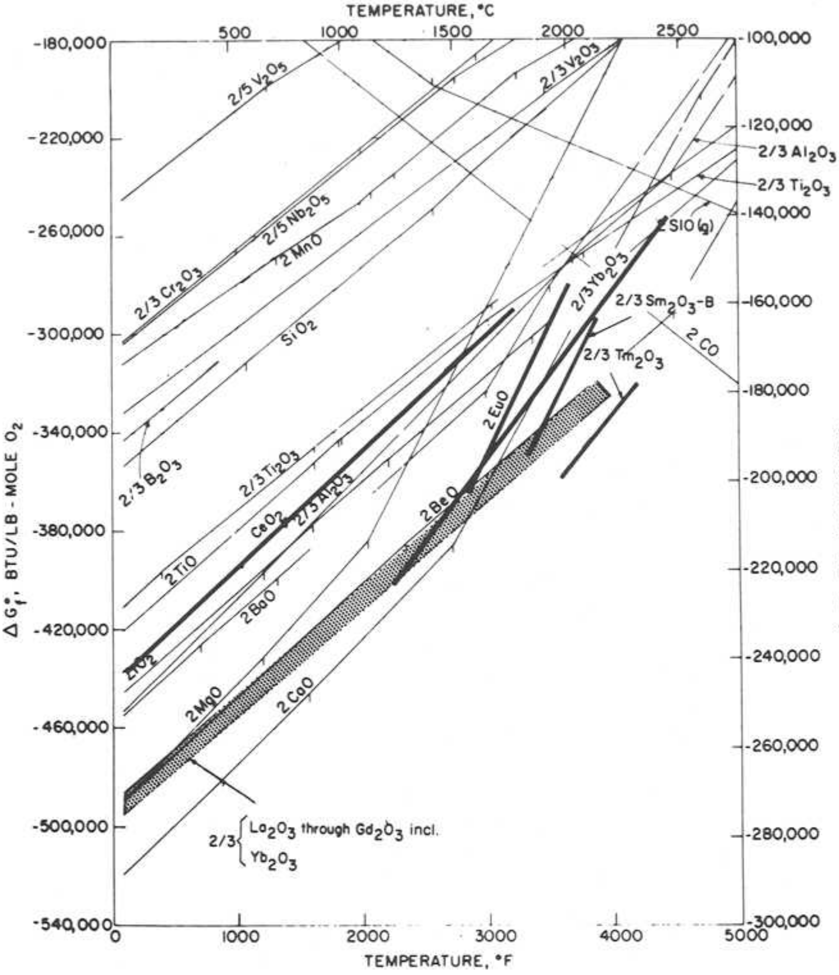

FIG. 1—*Standard free energies of formation of the oxides per pound-mole (or gram-mole)* of O_2 *(gas)* [*1*].

[*5*]. While it is clear that more research is needed in this area, it appears that aluminum deoxidation, when properly controlled, can result in a cleaner steel, faster than can a silicon-killed practice.

Aluminum is a good nitrogen scavenger and is widely used for the production of nonaging steels. For related reasons, it is an effective grain refiner. Aluminum has also generally been widely available and, until recently, reasonably inexpensive.

There are, of course, a few problems associated with aluminum deoxidation. Excess aluminum contents results in poor surface quality, which increases reject rates and conditioning costs. Tundish nozzle blockage prob-

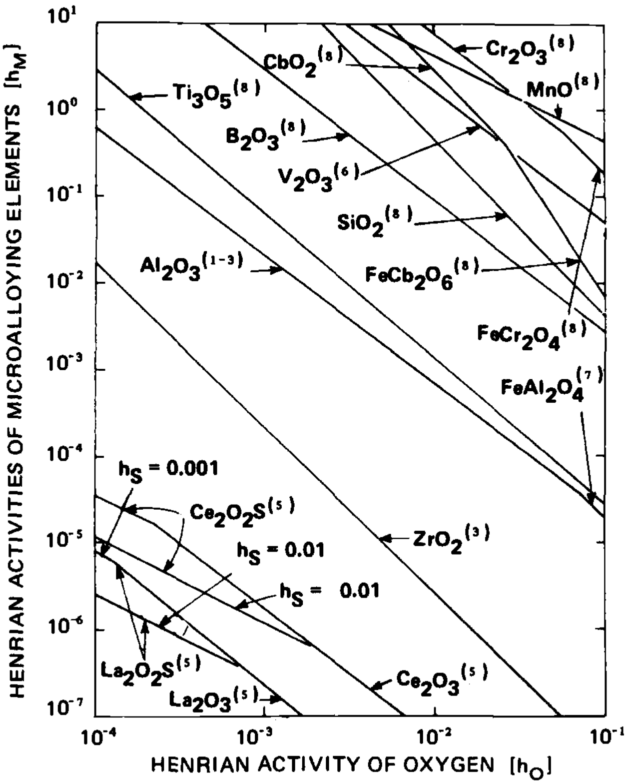

FIG. 2—*Henrian activities of microalloying elements versus the Henrian activities of oxygen in equilibrium with selected oxides in steel at 1600°C (2912°F)* [2].

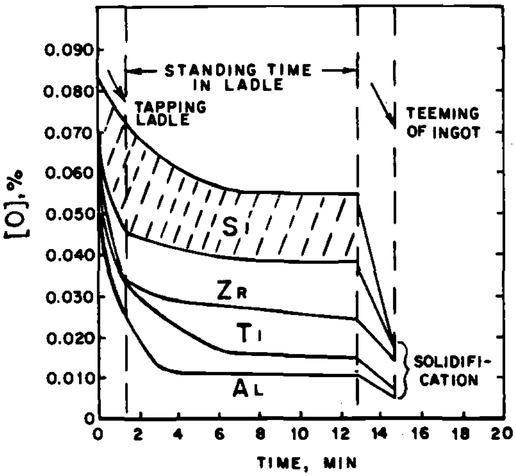

FIG. 3—*Variation in total oxygen content after addition of 0.3 percent of the various deoxidants in the ladle* [4].

lems occur when aluminum exceeds about 0.005 to 0.007 percent [*6,7*]. These problems are controllable since the only aluminum present in the steel when it solidifies is that which has been intentionally added. The solution to the problem, therefore, involves three factors:

1. an accurate and precise knowledge of the oxygen activity of the steel before aluminum is added,
2. reliable and reproducible performance on the part of the aluminum deoxidizer used, and
3. adequate protection against reoxidation.

It will be shown that ferroaluminum has demonstrated the required reliability and reproducibility while maintaining all the benefits of aluminum deoxidation described in the preceding.

Properties of Ferroaluminum

Most ferroaluminum sold in the United States and Europe today contains between 35 and 40 percent aluminum, which corresponds to a two-phase field in the iron-aluminum equilibrium phase diagram [*8*] (Fig. 4). Commercial alloys of this composition have a melting range between 1230 and 1270°C (2246 and 2318°F), density around 5.1 g/cm^3 (0.1842 lb/in.^{3}), and are readily soluble in liquid steel. Melting range, density, and solubility have been cited as being important in raising an addition's recovery factor, especially when the addition is highly reactive [*9*].

Why should the aluminum content be limited to only 40 percent when, after all, most ferroalloys are much richer than this? Increasing the aluminum concentration would, among other things, reduce the bulk of the addition, saving transportation costs and making material handling a little easier. It would also reduce the chill factor of the addition since not so much cold iron would be added to the ladle.

There are two principal reasons for restricting aluminum content to the level stated: one deals with the production of the ferroalloy, the other with its use. Alloys of iron and aluminum containing much more than 40 percent aluminum can be produced, but they cannot be stored for any appreciable length of time. Left to themselves, the richer—say, 50/50—alloys will decrepitate, that is, crumble into powder. These fines, as with other ferroalloys, are usually undesirable from the users' point of view. They are hard to handle; they tend to float on the slag and therefore cut down on recovery, etc. The decrepitation problem is not fully understood, but it may be related to residuals present and the formation of intermetallic compounds. At any rate, a 35/40 percent aluminum alloy represents the practical limit for a ferroaluminum stable enough to be stored for extended periods and be tough enough to withstand normal handling. The 35/40 percent aluminum range for ferroaluminum also provides a reasonable production spread. As the aluminum content approaches 35 percent the alloy becomes tougher and if

Al-Fe

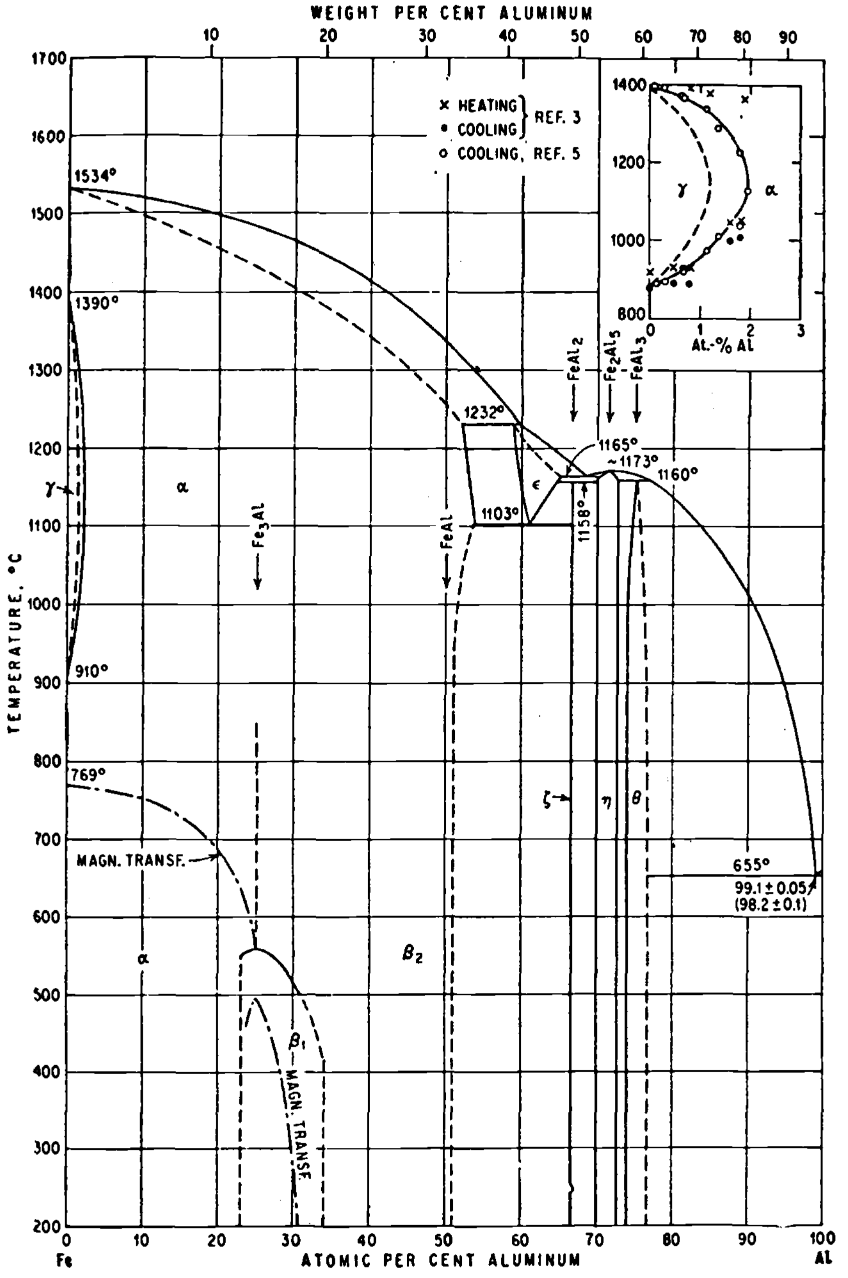

FIG. 4—*Iron-aluminum phase diagram. A 40 percent aluminum alloy is the most concentrated composition that can be produced without danger of decrepitation during storage* [8].

reduced further it becomes so tough that normal ferroalloy crushing equipment cannot be used for producing lump or crushed forms.

Quite fortunately, 35/40 percent ferroaluminum is also the composition known to give the best results in steelmaking. Compositions ranging from 17 to 57 percent aluminum have been tried in Russia, but under normal addition conditions the 35/40 percent aluminum grade gave the highest aluminum recovery, the lowest number of rejects during rolling, and a general improvement in the steel's mechanical properties [*10*]. These effects, we believe, are intimately related to the fact that 35/40 percent ferroaluminum represents the best balance between alloy richness and density.

Importance of Density

Ferroalloy density (here we refer to actual density rather than bulk density, which has more to do with shipping and storage considerations) has been recognized as being an important contributor to alloy recovery. Ideally, a ferroalloy should have a density near to that of liquid steel so that it will neither float at the slag-metal interface nor sink to the bottom of the furnace or ladle. Rather, it should be retained below the surface and be carried along with the natural turbulence of the liquid. This assures thorough mixing, subsurface melting and dissolution, and a reduction of oxidation losses at the bath surface. Unless the aluminum is used for grain size control, oxidation is exactly what is desired, but it must take place within the bath, not on top of it.

The importance of density to the melting and dissolution of alloy additions has been rather extensively studied over the past few years [*11–15*]. From heat-transfer and hydrodynamic analyses made in Canada and Japan, the following picture has now become fairly well understood.

When an alloy addition is made to the steel bath, a shell of solid steel immediately freezes around the addition particle. The addition may or may not melt inside this shell, depending on its melting range, heat capacity, thermal conductivity, and the degree of superheat in the bath. A low-melting, high-conductivity addition like aluminum metal will likely melt completely within the shell before the shell has itself melted back. A high-melting, relatively low conductivity addition such as ferromanganese may not melt completely before the shell melts, especially if the addition particle is large. Ferroaluminum has a melting range of 1230 to 1270 C (2246 to 2318°F); thus, it will probably experience some melting before shell breakthrough. Internal melting for all but very large particles takes only a few seconds while total melting times (shell plus core) can easily be an order of magnitude longer [*9*].

Density is of utmost importance because it largely determines where the addition particle will be when final shell melting occurs. As Fig. 5 shows, buoyant additions like metallic aluminum [density = 2.0 to 2.7 g/cm^3

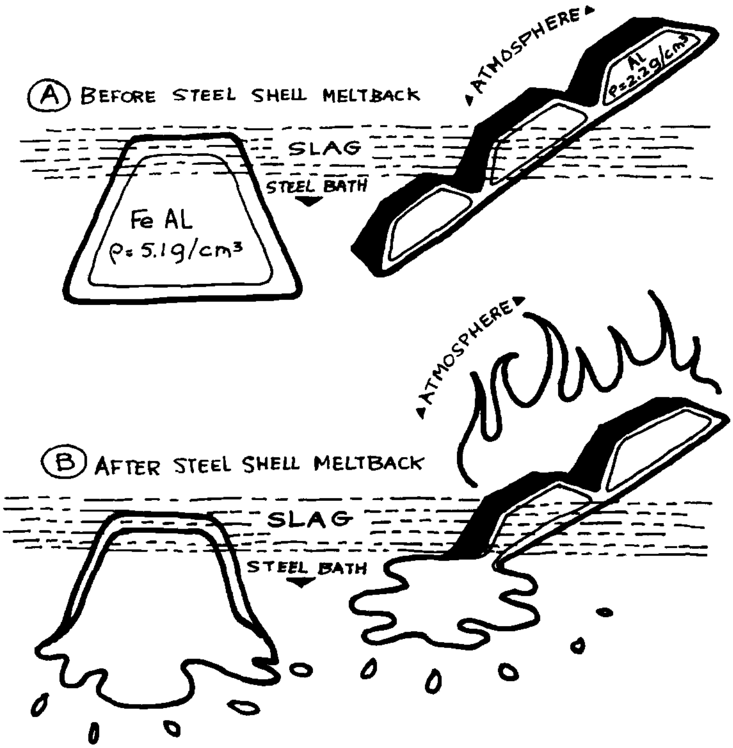

FIG. 5—*Relative buoyancy of ferroaluminum and metallic deoxidized aluminum. Ferroaluminum floats with 72 percent of its volume immersed in the liquid steel; metallic aluminum has over two thirds of its volume above the steel meniscus, where wasteful oxidation can occur.*

(0.0726 to 0.0980 lb/in.^{3})] density ratio to liquid steel $\gamma = 0.28$ to 0.38) will resurface in less than one second when dropped into the bath from normal heights [*10*]. Even denser materials such as ferroaluminum [average density = 5.1 g/cm^3 (0.1842 lb/in.^{3}), $\gamma = 0.72$] will resurface before total melting has taken place, although depth of penetration into the bath and total immersion time exceed those for metallic aluminum by about a factor of 10.

If we consider, however, what takes place at the time steel shell meltback occurs, the beneficial effects of ferroaluminum's higher density become apparent, as shown in Fig. 5. A particle of ferroaluminum will, from simple buoyancy considerations, be immersed to a depth such that about 72 percent of its volume is beneath the slag-steel interface. Shell meltback takes place from the bottom due to combined temperature gradient and dissolution effects. The now-liquid contents of the steel shell are thereupon released downward, where convection currents carry them farther into the bath. Only a small portion of the ferroaluminum is released upward, where wasteful oxidation or entrapment in the slag can occur. In the case of metallic aluminum, over two thirds of the addition particle remains *above* the steel meniscus, and there is a much greater chance that once shell meltback occurs the liquid aluminum will be released into, and quickly oxidized in, the slag or atmosphere. Anyone who has ever added aluminum metal to the surface of an open ladle or charged it to a heat still in the furnace has seen the results: bright flares of aluminum burning outside the bath.

A few observations are in order at this point. First is the caveat that all conclusions drawn from the thermo- and hydrodynamic analyses cited in the foregoing are based on spherical particles impinging on quiescent nonturbulent baths. Since real ferroalloys are in the form of irregular shapes, and since these are frequently added to the pouring stream (for ladle additions), actual melting conditions may differ from the results predicted in the foregoing. Second, mention should be made of the so-called "bullet shooting technique" that attempts to propel cylindrical aluminum projectiles deep enough into the bath to permit at least some subsurface melting [*15*]. While the technique has some drawbacks, it has been shown to increase aluminum recovery. It is interesting to speculate on how much more recovery could be improved if the bullets were made of ferroaluminum. Finally, we should consider the possibility of injecting ferroaluminum powder through an argon lance. At least one injection equipment supplier makes provisions for the sequential addition of different materials [*16*], and a thorough deoxidation with aluminum should precede the injection of desulfurizers.

User Experience and Practice

Several steel producers have reported their experience in using ferroaluminum as a deoxidizer. Equipment, practice, and product varied somewhat, but the universal conclusion was that ferroaluminum gave much better results than the notch-bar or stick aluminum previously used [*17–22*].

Chaparral Steel [*18*] represents an interesting case because it points out the benefit of using ferroaluminum in conjunction with an oxygen probe. This instrument makes use of a solid-state electrolyte to measure the oxygen activity, or concentration, directly in the bath, and virtually instantaneously. Because of the way the probe works, however, it is important that the bath not be on an active boil at the time the reading is taken. Otherwise, carbon dioxide bubbles impinging on the probe's sensing head will disrupt the instrument's output, causing enough oscillation in the strip-chart traces to make accurate readings impossible. Chaparral therefore begins the measurement procedure by knocking the heat off the boil with a "mini-block" furnace addition of 50 lb (22.5 kg) of ferroaluminum. (Heat size is approximately 130 tons.[3]) It was found that this practice is immediately effective in flattening the bath across the full 18-ft (~5.5 m) hearth diameter, resulting in a stable and reliable probe reading. Chaparral then uses this oxygen measurement as the basis for further ferroaluminum additions. They use 3 lb (1.35 kg) of fer-

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[3] 1 U.S. (short) ton = 0.9 metric ton.

roaluminum per 10 ppm active oxygen for their nominal heat size. Actually, 7 lb (1.45 kg) are required from stoichiometric considerations, but operators were concerned over potential nozzle blockage problems. Initial trials were at 4 lb (1.8 kg)/10 ppm, but this gave occasional problems; 3 lb (1.35 kg) proved satisfactory from both caster performance and product quality standpoints. The latter was reflected in an analysis of billet surfaces, based on observed seam depths. After evaluating a large number of heats, Chaparral cited three results of its ferroaluminum practice: there was consistency of performance over all heats for all product sizes; there was very good control in meeting the required quality levels; and individual seam depth distributions for each grade were virtually identical to that for the total of all grades tested. At the time their data were published, Chaparral had shipped 80 000 tons of Special Bar Quality product without a rejection for seams.

Atlantic Steel [*19*] also uses ferroaluminum as a furnace blocking addition, having begun the practice on the recommendation of their continuous casting equipment supplier. For soft wire grades (0.06C-0.10/0.20Si-0.30/0.50Mn) the practice is as follows: When the furnace temperature reaches 1620°C (2950°F), an addition of 100 lb (45 kg) of ferroaluminum is made, followed by 600 lb (270 kg) of 50 percent ferrosilicon and 2800 lb (1260 kg) of silicon-manganese. Heat size is 100 tons. Although it was not stated whether an oxygen probe is used for each heat, one was used for a series of heats to establish the amount of ferroaluminum needed. The result is that Atlantic Steel significantly reduced the incidences of underdeoxidation and thereby minimized pinholing. There have been no problems with nozzle flow or clogging; manganese and silicon levels have been more easily met and steel quality has improved, all as a result of the ferroaluminum blocking practice.

CF&I Steel [*20*] had been having problems with deoxidation control prior to using ferroaluminum for the production of SBQ billets. Pinholing was reported to be a particularly serious problem. Raising the amount of deoxidized aluminum used was not acceptable since this led to the expected nozzle blockage difficulties. CF&I tried feeding aluminum wire to the caster mold stream, but this gave inconsistent results throughout a heat and was therefore considered unsatisfactory. Experience had taught that a maximum oxygen level of 100 ppm could be tolerated in the furnace, prior to tap, in order to prevent pinholing and still cast the steel successfully. The problem was to stay below this oxygen content consistently. CF&I's solution was to use ferroaluminum in conjunction with an oxygen probe. After the chemistry is adjusted for phosphorus, sulfur, and carbon, a miniblock of 0.2 to 0.3 lb (0.09 to 0.14 kg)/ton ferroaluminum is added to the 120-net ton furnace and an oxygen probe reading taken. Ferroaluminum is then added at the rate of *1 lb* (0.45 kg) per ppm oxygen and a second and final probe measurement made. If the bath oxygen is still above 100 ppm, more ferroaluminum is added until the oxygen level is acceptable. The results of using ferroaluminum and an oxygen probe are significant: (1) Steel could be sent to the caster with oxygen consistently below 100 ppm but without excessive aluminum levels; (2) alloy recoveries (silicon and manganese) have been more consistent; and (3) billet yields after inspection improved from 24 percent before the ferroaluminum oxygen probe practice was initiated to 90 percent thereafter.

Experiences at steel foundries bear out the steel mill data and shows how ferroaluminum can be used under quite different conditions. It should be understood that foundry practice yields metallurgical conditions that are considerably more severe than those found in a wrought steel mill electric furnace shop. Tap temperatures are higher, frequently over 1760°C (3200°F), to compensate for extended pouring times and fading. Oxygen activities at these temperatures can become quite elevated. The steel may be transferred between several ladles before it is cast, and this increases the opportunities for reoxidation. Aluminum deoxidation must be carefully controlled since excessive or large alumina inclusions can be very detrimental to casting quality. They impair machinability and cause surface defects. Insufficient deoxidation leads to pinholing and porosity. Careful control over deoxidation practice is especially important in foundries because defects frequently are not discovered until most of the costs of production (steelmaking, moulding, casting, cleaning, machining, inspection) have gone into the product.

It was reported almost 10 years ago by a large European foundry that deoxidation with 35/40 percent ferroaluminum gave the highest degree of repeatability in aluminum yield. The deoxidation practices used varied with product specifications, but in the case of a 13 percent chromium steel, primary deoxidation with at least 0.10 percent aluminum (as ferroaluminum) at the beginning of the refining period proved advantageous. This was followed by an addition of 0.1 percent calcium-silicon-manganese and 0.05 percent aluminum (again as ferroaluminum) to give a high-purity steel with oxygen below 50 ppm. Other chromium-molybdenum-vanadium steels required a furnace addition of 0.10 percent aluminum (as ferroaluminum) as a final deoxidation, followed by 0.05 percent titanium and 0.04 percent Calcium-Silicon-Manganese Alloy in the ladle. It was found that a maximum final aluminum content of 0.04 percent could definitely be maintained, as aluminum recovery from the ferroaluminum was a consistent 30 percent [*21*].

Several U.S. foundries producing pressure-vessel-quality castings have been using ferroaluminum for a number of years. One such installation [*22*] uses ferroaluminum in the amount of 6 to 12 lb (2.7 to 5.4 kg)/ton (based on alloy grade), adding it to the furnace no sooner than 3 min. before tapping. This is followed by an addition of 3 lb (1.35 kg)/ton Calcium-Silicon-Barium Alloy to the ladle. Depending on compositions, tap temperature, pouring time, and the number and type of ladles used, aluminum recoveries can be up to 50 percent, but is consistent for each practice and grade.

Summary

A survey of ferroaluminum deoxidation leads to the following observations:

1. Aluminum is one of the most rapid and efficient of deoxidizers, and the products of aluminum deoxidation are removed from the melt faster than those of silicon.
2. Thirty-five to 40 percent grade ferroaluminum represents an optimum concentration from the standpoint of alloy recovery and product quality.
3. The reduced buoyancy of 35/40 percent ferroaluminum (high density) promotes subsurface melting of semisubmerged ferroaluminum additions. This reduces wasteful oxidation in air or slag.
4. Users' experiences with ferroaluminum have, according to the published literature, resulted in greater alloy efficiency, reliability, and reproducibility, and an improvement in steel product uniformity. Use of ferroaluminum in conjunction with an oxygen probe appears to be particularly effective, and is strongly recommended.
5. Ferroaluminum used as a primary deoxidizer maximizes the opportunity for inclusion removal.
6. Ferroaluminum is very effective as a furnace blocking addition, particularly when used in conjunction with an oxygen probe. Use of a miniblock to stabilize initial probe readings has become an accepted practice.
7. Proper use of a ferroaluminum blocking practice leads to a reduction in continuous caster problems, while at the same time improving product quality.
8. Ferroaluminum has been described as the most efficient aluminum deoxidizer for steel foundry practice. Recoveries of 30 to 50 percent have been reported.

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Jerry Silver[1]

Alloys and Metals for the Production of High-Strength Low-Alloy Steels

REFERENCE: Silver, Jerry, "**Alloys and Metals for the Production of High-Strength Low-Alloy Steels,**" *Ferroalloys and Other Additives to Liquid Iron and Steel, ASTM STP 739,* J. R. Lampman and A. T. Peters, Eds., American Society for Testing and Materials, 1981, pp. 170–179.

ABSTRACT: The production of high-strength low-alloy (HSLA) steels represents the fastest-growing segment of the flat rolled steel market. Weight reduction programs by automotive producers and other steel consumers have provided the impetus for developing efficient production practices for these grades. Yield strength levels of 276 000 to 966 000 kPa (40 000 to 140 000 psi) are currently available.

The majority of HSLA grades are microalloyed with either columbium, vanadium, titanium, or combinations of these elements. The columbium and vanadium steels are produced either as semikilled or fully killed grades, with and without inclusion shape control. Titanium-alloyed grades are produced fully killed. These three alloy grade series are routinely produced using ferroalloys added to the steel ladle in conjunction with ferrosilicon and aluminum to control deoxidation. Selection of the alloying element depends upon end use, mill processing parameters, and customer specifications and requirements.

Other grades, produced on a less-frequent basis, require the additions of copper, nickel, chromium, and molybdenum. The form of these alloy additions varies, and all but chromium can be added to the furnace during charging.

This paper emphasizes the relative cost of the alloys and the methods used to achieve the desired analysis of each element. Particular attention is devoted to melt shop practices used to maximize alloy recovery, and thereby minimize costs. Included are considerations of ferroalloy sizing, packaging, and sequence of addition to the steel ladle. The importance of consistent quality from the alloy supplier has become rather apparent; the methods employed by Jones and Laughlin's Cleveland Works to monitor the quality of alloying materials is also reviewed.

KEY WORDS: ferroalloys, steelmaking, hot rolling, cold rolling, alloy recovery

The rapid increase and expansion in high-strength low-alloy (HSLA) steel applications, particularly in the automotive field, have placed greater demands on the suppliers and users of ferroalloys. This market growth can be attributed to the development of yield strengths up to 550 MPa (80 ksi) in hot-rolled sheet and plate, superior cold formability through inclusion shape control, improved weldability because of reduced carbon levels, and hot strip mill facilities with controlled-cooling capability.

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Much of the increase has occurred in cold-roll applications as automakers strive to reduce car weights. This application to automobile skins has been a very real challenge in HSLA usage and has required changes in chemistry and processing to achieve the needed properties and suitable surface quality. Yield strengths up to 965 MPa (140 ksi) are available.

Hot- and cold-rolled sheet steel makes up 50 to 60 percent of the weight of each vehicle. Although several types of materials are available, HSLA steels currently possess the greatest weight-savings potential in line with maintaining product integrity. To optimize the use of microalloying elements, one must know how a steel containing these elements reacts to different ways of processing. The most important of these elements are columbium, vanadium, and titanium; they have varying affinities for carbon, nitrogen, and sulfur.

Figure 1 exhibits the growth of hot-roll HSLA steel since 1970 at Jones & Laughlin's (J&L's) Cleveland Works, particularly during 1978 and 1979. More importantly, HSLA as the percentage of total hot-roll shipments increased dramatically during this two-year period.

Figure 2 displays an interesting pattern, with the increasing trend in the 485 to 550 MPa (70 to 80 ksi) yield-strength grades displacing the 310 to 415 MPa (45 to 60 ksi) grades, as consumers moved toward lighter gage, higher-strength materials.

Selection of HSLA Steels For Various Applications

The choice of HSLA grade depends upon several factors: customer specifications, processing capabilities, end use, and cost of production. Table 1 illustrates the various types of chemistries that can be provided for a given ordered yield-strength level, the choice being one of customer preference or

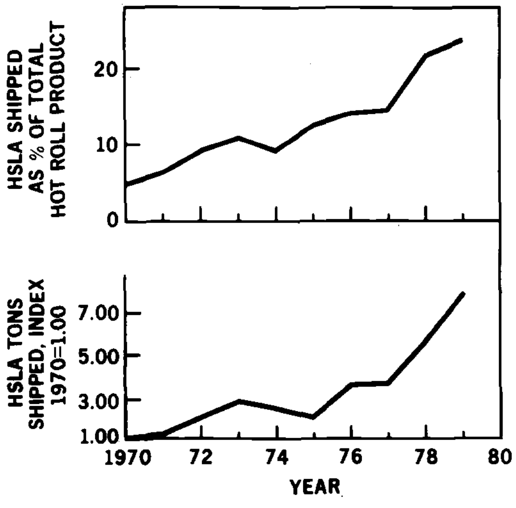

FIG. 1—*Growth of hot-roll HSLA steels, Cleveland Works.*

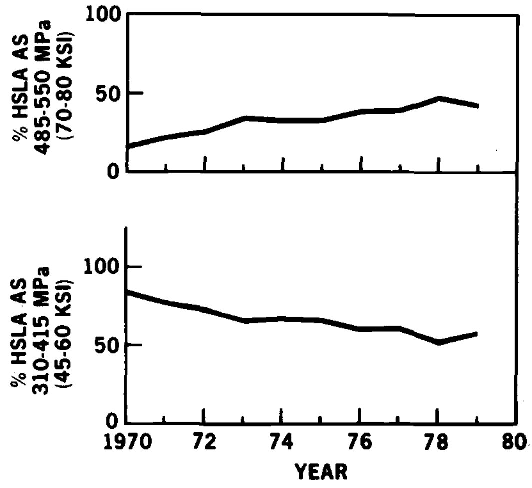

FIG. 2—*Hot-roll HSLA steels by yield-strength level.*

supplier experience. For example, columbium and high-titanium grades require more power on the hot strip mill than the vanadium-bearing grades. There are more gage, shape, and cobble problems, particularly at the lighter hot-band gages.

The wide variation in alloy cost is best illustrated in the hot-roll 345 and 550-MPa (50 and 80 ksi) yield-strength levels, particularly in the latter group. Costs in Table 1 are based on November 1979 ferroalloy prices and differences in grades are calculated in comparison with low-carbon hot-rolled aluminum killed fine grain steel. Note one apparent advantage of titanium-bearing grades, where sulfide shape control additions are unnecessary. Lower carbon and manganese levels are also a feature of the titanium-bearing grades. The columbium-bearing grade in the 345-MPa (50 ksi) range is produced normally as semikilled; therefore, the alloy cost is lower and sulfide shape control is not required.

The corrosion-resistance grades have been in existence for many years and were among the original HSLA grades. However, formability of these steels is decidedly poorer than the grades currently offered.

In the cold-roll area, processing plays a major role, and, therefore, similar chemistries can be used for a wider range of strength levels in comparison with hot-rolled product.

Ladle Additions: Effects of Sequencing and Material Size

Melt shop practices differ depending on alloy addition systems, but generally deoxidation materials are added first, followed by the rest. Additions of strengthening alloys are normally interspersed between the main ferroalloys during the tap to get the best efficiency and end-to-end distribution of analysis.

TABLE 1—*Chemistry ranges for various finished-product strength levels.*

A. Cold Roll	Ordered Analysis, %							Alloy Cost/Ton-Ratio[a]
Yield Strength	C	Mn	Si	V	Cb	Ti	N	
345 MPa (50 ksi)	0.09	0.30/0.60	...	...	...	0.15/0.19	...	3.16[b]
415 to 550 MPa (60 to 80 ksi)	0.09	0.30/0.60	...	...	...	0.23/0.27	...	4.35[b]
B. Hot Roll								
345 MPa (50 ksi)	0.08/0.09	0.80/0.95	0.10	0.06/0.08	...	...	...	4.72
345 MPa (50 ksi)	0.05/0.08	0.40/0.55	0.03	...	...	0.08/0.12	...	2.47[b]
345 MPa (50 ksi)	0.08/0.10	0.50/0.65	0.10	...	0.02/0.03	...	...	1.56
415 MPa (60 ksi)	0.10/0.12	1.10/1.30	0.10	0.06/0.08	...	...	...	...
485 MPa (70 ksi)	0.09	1.20/1.40	0.20/0.35	0.11/0.13	...	...	0.018/0.022	...
550 MPa (80 ksi)	0.11/0.13	1.25/1.45	0.30/0.45	0.12/0.14	...	...	0.018/0.022	7.28
550 MPa (80 ksi)	0.09	1.00/1.10	0.05/0.15	0.11/0.12	0.04/0.07	...	0.018/0.022	9.11
550 MPa (80 ksi)	0.07/0.11	0.75/1.00	...	...	...	0.20/0.28	...	4.11[b]
C. Corrosion Resistance Applications								
345 MPa (50 ksi)	0.08/0.11	0.65, 85	0.35/0.45	...	...	0.015/0.050	...	...
(Ni-Cu-Ti)	...	Cu-0.25/0.40	...	Ni-0.60/0.70	...	...	...	...
345 MPa (50 ksi)	0.06/0.11	0.25/0.50	0.30/0.50	...	...	...	...	...
(Corten)	...	Cu-0.25/0.40	...	Ni-0.25/0.50	...	Cr-0.30/1.10	...	P-0.075/0.100

[a] Compared with hot-roll low-carbon aluminum killed fine grain steel—November 1979 alloy prices.
[b] No sulfide shape control addition.

In shops with older alloy addition systems such as the Cleveland Basic Oxygen Furnace Shop, built in 1961, ferrosilicon, ferrochrome-silicon, and any exothermic alloys are placed on the bottom of the ladle before tap on heats requiring large additions. Usually some of the aluminum addition is also placed on the bottom in these cases to protect the other alloys and to increase efficiency. The balance of the aluminum plus the balance of the alloys are added after the initial reaction takes place. On normal aluminum killed grades, the aluminum is added after approximately 0.3 m (1 ft) of steel is in the ladle; the rest of the alloys are added starting at one-third ladle, aiming to have all in by one-half ladle.

Table 2 exhibits the efficiencies of various alloying elements used by the Pittsburgh Works Electric Furnace Shop to calculate the required additions. These numbers are continually reviewed, revised, and updated as needed. The second column in both groups is standard deviations. These efficiencies, while in the normal expected range, are unique to this melt shop with its more sophisticated addition system (automatic weigh hoppers and feeders) and should not be considered as transferable to other melt shops with different systems or melting practices or both. It does allow for computerization, thereby giving the melter more precise addition information rather than by using his past experience as a guide.

Chilling Effects of Ferroalloy Additions to Liquid Steel

The decision as to which combinations of ferroalloys should be used in the various grades of steel also requires knowing what temperature changes occur during the addition of various ferroalloys. The amount of heat absorbed by ladle additions depends on the composition of the ferroalloys

TABLE 2—*Efficiencies used to calculate additions of ferroalloys and other alloying materials—Pittsburgh Works Electric Furnace Shop.*

Alloying Element	All Heats		HSLA Heats		Method of Addition[a]
	% Efficiency	σ	% Efficiency	σ	
Silicon	77	14	75	20	F, L
Manganese	75	14	84	20	F, L
Titanium	...	...	65	13	L
Chromium	55	20	76	12	L
Columbium	75	11	76	13	L
Vanadium	81	11	86	15	L
Boron	...	...	67	4	L
Zirconium	67	13	80	...	M
Nitrogen	35	6	35	6	L
Copper	84	16	90	...	F
Nickel	90	4	90	...	F
Molybdenum	86	10	86	10	F

[a] F = furnace; L = ladle; M = mold.

chosen. These are important in setting tap temperatures to meet prescribed ladle temperatures, as too low a ladle temperature often results in skulls and pouring problems, while too high a temperature can result in higher refractory consumption and possible sticker ingots. Some charts have been published on the chilling effects of various materials; these are noted in the references [*1*–*7*].[2]

Effect of Material Size

During 1973, sizing trials of standard ferromanganese (FeMn) were conducted at the Aliquippa Works BOF Shop. A truckload of 5.08 by 10.16-cm (2 by 4 in.) standard FeMn with no fines was charged through the alloy system into an empty storage bin. The FeMn was then reexamined on the BOF charging floor; this showed that 4.3 percent fines [that is, under 6.35 mm (1/4 in.)] were generated just through the BOF alloy handling system. A check of routine FeMn indicated 8 to 12 percent fines were normally present at the charging floor. Open heats produced with the trial "fine-free" material averaged approximately 2 percent higher manganese recovery than comparison heats with normal FeMn.

Steelmaking practices generally advocate approximately 5.08 by 5.08-cm (2 by 2 in.) size lump FeMn additions to promote rapid melting and even distribution in the teeming ladle. Even smaller-size additions of approximately 2.54-cm (1 in.) diameter will become coated with a steel shell and rise up to the steel surface before the core contents are released. Since these additions are not particularly buoyant, the turbulence during ladle filling should result in the additions generally following the liquid steel flow patterns during the course of their melting time.

Studies have indicated that melting time for a 2-cm-diameter (0.8 in.) addition is approximately 40 s, while a 12-cm-diameter (4.75 in.) addition is about 300 s, and, in actual practice, melting times are likely to be shorter. Since typical furnace tapping times are 5 to 8 min, it would appear that larger-size additions, for example, 10.16 by 5.08 cm (4 by 2 in.) or larger, could be handled with decreased crushing costs and reduced fines.

Recent problems at the Cleveland Works' Electric Furnace Shop with columbium recoveries on columbium-bearing semikilled heats for 345 MPa (50 ksi) yield-strength grades prompted a trial of bulk ferrocolumbium (FeCb) on these heats. This melt shop consists of two 6.7-m-diameter (22 ft) furnaces tapping 195-ton[3] heats. It has a rather unsophisticated alloy addition system—a metal box suspended by the auxiliary hoist of the teeming crane, with a capacity of approximately 1364 kg (3000 lb) of alloys.

For many years, cans of 11.36 kg (25 lb) contained columbium, usually FeCb of 42 percent columbium, were added manually during the tapping

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

[3] 1 U.S. (short) ton = 0.9 metric ton.

operation, immediately following the FeMn. While the success rate in meeting the columbium analysis was generally satisfactory at this shop, far too many heats were diverted for off-analysis. Since mid-1979, recoveries of columbium added this way were extremely variable; in addition, 6.2 percent of the heats were diverted for low-columbium levels. The canned FeCb is ordered as 1.27 cm (1/2 in.) by down, with samples of the material showing upward of 30 percent less than 0.64 cm (1/4 in.). Occasional problems with cans floating caused melters to open the cans and empty the contents into the alloy box along with the ferrosilicon and ferromanganese. Although care was taken to sandwich the FeCb between the other alloys, the high percentage of fines resulted in a high loss of FeCb.

The recent trials of larger-sized 5.08 by 1.27-cm (2 by 1/2 in.) FeCb, which is more similar in size to other bulk alloys, indicated much more consistent practice and recoveries. For the canned material, recoveries ranged from 41 to 70 percent; a much tighter range of 62 to 67 percent recoveries has been experienced during the trials with the bulk FeCb material.

Effect of Material Form on Suitability as Ladle Addition

For many years, J&L has produced the 345-MPa (50 ksi) yield-strength nickel-copper-titanium HSLA grade noted earlier, utilizing scrap materials to economically meet these three specifications. Monel scrap (67Ni-30Cu) or combinations of scrap nickel pig and copper bundle were charged to the furnace, while 22.7-kg (50 lb) bags of the standard 90Ti-6Al-4V alloy, in the form of scrap material, were manually thrown into the ladle during tapping. In more recent years, briquettes composed of the machinings of this latter material were used with equal success, but at a more economical cost.

With the increased production of the higher titanium-bearing HSLA grades, it was virtually impossible to manually add the required quantities to the ladle, and the physical size and form of the briquettes would not feed properly through the existing alloy chute and feeder at the Cleveland Works.

A switch was made to the 70 percent ferrotitanium alloy (2 in. by down) with successful feeding characteristics through the alloy chute and satisfactory titanium recoveries. In fact, the actual cost per ton of steel decreased somewhat with this ferroalloy because of the increased recoveries at the higher titanium levels.

Sulfide Shape Control in HSLA Heats

The anistropy of ductility, toughness, and formability—attributed mostly to elongated sulfide inclusions—has been largely overcome by the application of inclusion shape-control additives during steelmaking. Sulfide shape control is as effective as the reduction of sulfur to extremely low levels and contributes to the improved transverse properties typical of these grades.

While not alloying agents for HSLA steels in the true sense, these additions are necessary in most applications and, therefore, deserve some discussion. The two major elements used for sulfide shape control are zirconium and rare earths, the latter as either rare-earth silicide or misch metal, depending on the silicon tolerance of the HSLA grade being produced. The mechanisms for these elements combining with sulfur to change from the deleterious stringer sulfide-type inclusions to the globular form have been well documented and will not be reviewed here.

Zirconium is added to the mold during ingot teeming at rates of 0.45 to 1.36 kg (1.0 to 3.0 lb) per ton, depending on ordered sulfur level, carbon level, and criticalness of the end use. Zirconium is added as either scrap plates, tubes, etc., or as pressed briquettes. Experiments of various sizes have indicated that a rather wide range of sizes can be tolerated without solution problems. Occasional problems with contamination have occurred with zirconium-columbium alloy being mixed with regular zirconium scrap at the supplier. The effect on steel properties is obvious; the columbium analysis is run as a check on all heats using zirconium. Another problem with zirconium is its affinity for nitrogen, which limits its use in some HSLA grades.

The misch metal or rare-earth silicide is also added during ingot teeming, the former at a rate of 0.91 kg (2.0 lb) per ton and the latter at 2.73 kg (6.0 lb) per ton. The detrimental rare-earth oxysulfide inclusions which sometime occur at the edges of flat rolled products led to trials of ladle additions. Adding double the normal mold quantity during tapping resulted in erratic recoveries and equally erratic sulfide control, without significantly reducing the inclusion problem. Therefore, the mold addition remains as the most economic, versatile approach.

Sampling Incoming Materials for Control

Most steel plants and melt shops today do varying amounts of sampling of incoming materials, including ferroalloys, to insure quality and reliability of the product. At J&L's Aliquippa Works, all ferroalloys are interchangeable due to the purchasing specifications, that is, low silicon and low aluminum in ferromanganese, etc., which make them suitable for both ingot cast or strand cast steels. All ferroalloys are purchased to vendor or ASTM specifications.

An adequate sample is taken from the lot sizes (90.7 to 136.1 kg = 200 to 300 lb) at the various inspection areas and processed according to ASTM procedures. Samples are checked for key elements on each ferroalloy and for sizing (major commodities) as listed in Table 3. The sampling program has been responsible for the rejection and rescreening of ferroalloys containing excessive fines; this has been worth as much as $672 000 in one year to the No. 2 BOF Shop on ferromanganese.

Routine tests are obtained at the Pittsburgh Works Electric Furnace Shop as materials are trucked to bins in the shop; sampling is performed at the exit end of the bin from a chute. Table 4 provides the materials sampled routinely.

TABLE 3—*Sampling program, ferroalloys— Aliquippa Works.*[a]

Material	Elements Analyzed	Lot Sampling Location[b]
Ferrosilicon	Si, Al, C, sizing	1
Ferromanganese (standard)	Si, Al, C, Mn, sizing	1
Ferromanganese (medium C)	Si, Al, C, Mn, sizing	1
Ferrophosphorus	Si, Al, P, sizing	1
Ferrocolumbium	Si, Al, C, Cb	2
Ferromolybdenum	Si, Al, C, Mo	2
Mo trioxide	Mo O_3, C, Cu	2
Ferrovanadium	Si, Al, C, Cr, V	2
Ferrochromium	Si, Al, C, Cr	2
Calcium silicon	Si, Al, C, Ca	2
Boron additive	Si, Al, Mn, S, Ti, Zn, Zr	2

[a] Other materials sampled in lot size as required.

[b] Sample size = 90.7/136.1 kg (200/300 lbs).

Location 1 = warehousing areas.

Location 2 = BOF shop and warehousing areas.

It also displays sampling of nonroutine materials. These latter alloys are trucked to bins in the shop, but access to the chutes is difficult; grab samples are taken from the truck.

For nonroutine canned or bagged materials, two containers are sampled per truckload. These are weighed where applicable; size and moisture are checked if applicable. Chemistry is checked on recarburizers, molybdenum, titanium, boron, vanadium, etc. On nonroutine bulk materials, samples are visually inspected and checked for the required chemistry. Many more materials not listed in Table 4 are also monitored as part of the quality-control program.

TABLE 4—*Sampling program, ferroalloys—Pittsburgh Works.*

Material	Elements Analyzed	Frequency
A. Routine Bin Tests—Sample Size 36.3 to 45.4 kg (80 to 100 lb)		
Ferromanganese (standard)	Si, C, Mn, H_2O, sizing	2/week
Ferromanganese (medium C)	Si, C, Mn, H_2O, sizing	1/week
Nitrided ferromanganese	Si, C, Mn, H_2O, N, sizing	1/2 weeks
Ferrosilicon	Si, H_2O, Al, sizing	1/2 weeks
B. Nonroutine Bin Tests—Sample Size 13.6 to 22.7 kg (30 to 50 lb)		
Ferrophosphorus	P, H_2O	
Charge chrome	Cr, C, Si, H_2O	...
Ferrochrome-silicon	Cr, C, Si, H_2O	
Aluminum	all contaminants (Fe, Cu, etc.)	

Summary

In summary, selection of ferroalloys or other alloying materials is dependent upon the grade being produced, type of alloy addition system in the melt shop, melting practice, material handling and storage systems, and certainly economic considerations as well as the ability to meet customer specifications. The wide variety of HSLA requirements currently being demanded by the expanding HSLA marketplace has mandated more variations and restrictions in chemistry than were previously needed, and this in turn has placed more emphasis on steelmaking proficiency. The importance of consistent quality from the alloy supplier has become rather apparent, and, therefore, he has a major role in meeting this challenge.

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DISCUSSION

Perry Weston[1] (*written discussion*)—1. Do these shops have computer-controlled alloy addition systems, since your ability to use large-size material is apparently contrary to most computer-controlled systems designed for 5.08-cm (2 in.) maximum-size material.

2. Do you have any recovery data for bagged ferroalloys?

Jerry Silver (*author's closure*)—1. The Aliquippa Works BOF Shop and Pittsburgh Works Electric Furnace Shop have computers for calculating the quantities of the various ferroalloys required for each heat. Neither shop, however, has computer-controlled alloy weight addition systems.

2. Some time ago, both bagged ferrocolumbium and canned ferrocolumbium were used interchangeably at Cleveland Works' BOF Shop. The risk of igniting the bags during heavy slopping, requiring reweighing of the material, resulted in the use of only canned ferrocolumbium at that time.

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[1] SKW Alloys, Niagara Falls, N.Y.

P. H. Wright[1]

Alloy Additions for the Production of Fine-Grain Strand-Cast Special-Quality Steel Billets

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REFERENCE: Wright, P. H., "**Alloy Additions for the Production of Fine-Grain Strand-Cast Special-Quality Steel Billets,**" *Ferroalloys and Other Additives to Liquid Iron and Steel, ASTM STP 739,* J. R. Lampman and A. T. Peters, Eds., American Society for Testing and Materials, 1981, pp. 180–190.

ABSTRACT: The grain refinement of steel has traditionally been achieved by the addition of aluminum to the ingot mold.

In the production of fine-grain strand-cast billets it has been necessary for the steelmaker to develop alternative methods of grain refinement because of the detrimental effect of aluminum on surface quality.

Elements used for this purpose are columbium and vanadium, added in the form of ferroalloys.

This paper discusses the reasons for the development of these practices, the effect of these additions on the finished product, and asks the question, "Why fine grain"?

KEY WORDS: ferroalloys, alloy additions, steelmaking, grain refining, columbium, vanadium

Commercial strand-casting of steel, first performed in the middle 60's, is now a mature and acceptable process route.

Table 1 shows the production of strand-cast semifinished products in the Western World for 1975 [*1*].[2]

The International Iron and Steel Institute (IISI) forecasts a Western World application rate of 41.4 percent of all steel cast by 1985.

Figure 1 shows past trends and forecast maximum growth; this projection made in 1977 is already outdated because of the accelerating energy crisis and consequently greater incentive to install strand-casting machines.

The Japanese steel industry strand-cast 53 percent of its total production in 1979 [*2*].

Table 2 shows the equivalent alloy additions necessary to replace the hardenability lost when grain size is refined from 3 to 8.

The ideal diameter as defined by Grossman [*3*] is frequently used to com-

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

TABLE 1—*Production of strand cast semifinished products, 1975.*

Area	Crude Steel Production, $\times 10^6$ tons	% Strand Cast
Western Europe	155.3	17.9
North America	119.0	10.1
Asia	114.3	28.9
Rest of Western World	33.7	11.0

AISI forecast for United States shows 22 to 25 percent by 1985 (from IISI, 1977) [*1*].
1 U.S. (short) ton = 0.9 metric ton.

pare the hardenability characteristics of different steels. If this system is used to calculate the ideal diameter (DI) of a coarse-grained electric furnace 1050 with total residuals of 0.63 and a fine-grained 4130, the results are 6.47 and 7.49 cm (2.55 and 2.95 in.), respectively. The similarity of these numbers should suggest to design engineers that the relevance of grain size be examined for each application. The cost differential between a 1050 and a 4130 is 34 percent at the hot-rolled bar stage.

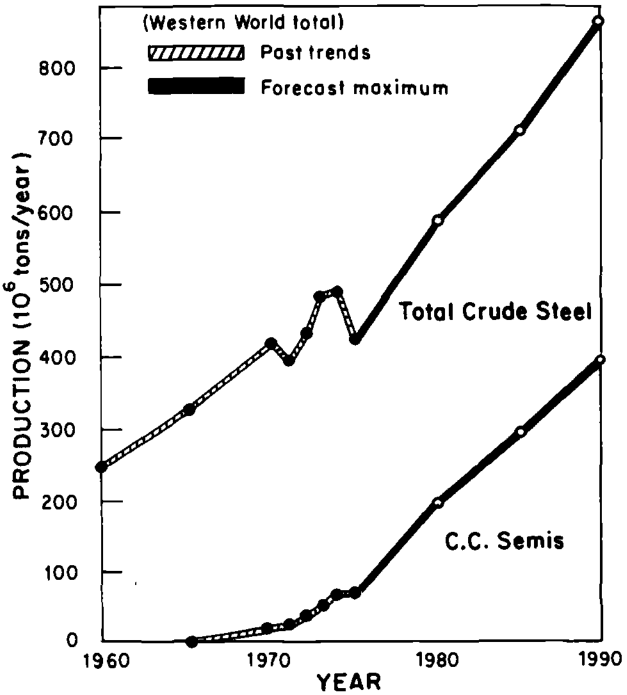
There are many applications where grain size as defined by the McQuaid-Ehn method is irrelevant. This method determines the austenitic grain size at 927°C (1700°F), a temperature which has relevance to heat treatment but not to a steel in the hot-worked condition. McQuaid himself reported that "the test indicates the structure only at the test temperature and does not necessarily indicate the grain size at any other temperature" [*4*].

Virtually all hot-working occurs over 1100°C (~2000°F). At this temperature the austenitic grain size of all steel is coarse and in fact at such temperatures steels classified as fine grain have a coarser grain than those classified as coarse grain [*5*]. There seems to be no relevance therefore to austenitic grain size measurements on steel to be used in the hot-forged or hot-rolled condition.

The Japanese report [*2*] that they have developed steel grades specifically for strand-casting. The U.S. steel industry should be fully aware of these developments since Japanese steel quality is invariably classified as excellent! It is the author's experience that there is a greater acceptance in Europe of the

TABLE 2—*Equivalent alloy addition.*

To Achieve the Same Increase in Hardenability	
Requires	0.25% carbon
	or 0.24% chromium
	or 0.18% molybdenum
	or 1.44% nickel
Or grain size increased from 8 to 3	



(From IISI, 1977)

FIG 1—*Possible future extrapolation of the continuous casting process; growth of tonnages of continuously cast semis.*

relative merits of coarse- and fine-grain steels than there is in the United States.

The potential alloy cost savings and the political instability in many of the alloy-producing areas of the world should induce end users to examine their real requirements.

Discussion

By using columbium or vanadium as a grain refiner in carbon and low-alloy steel, the strand-cast billet producers have developed a detailed picture of the effect of these elements on the finished product. Significant cost savings are available to all areas of the steel bar consuming sector. These include

1. improved strength-to-weight ratio, resulting in material cost savings of up to 20 percent,
2. reduced energy consumption in moving equipment,
3. improved machinability with possible substitution of hot-rolled columbium grain-refined steel for cold-drawn bar as a screw machine feedstock,
4. improved surface quality, and

5. elimination of heat treatment for some applications, resulting in energy, capital, and labor savings.

The original Society of Automotive Engineers (SAE) steel specifications were developed to simplify a complex situation in which thousands of different combinations of chemical elements were being manufactured. Undoubtedly this system achieved its objective and has served the steel industry well for many years.

At the present time this steel specification system does not recognize the metallurgical developments of the past decade applicable to bar products, and is effectively suppressing these developments at great cost to the national economy.

In its 1977 study of strand-casting the IISI listed eight reasons for this continued growth. These are given in Table 3.

At the present time there is one major quality disadvantage of strand-casting carbon and low-alloy fine-grained steel. This is that the traditional practice of using an aluminum mold addition to produce fine-grain steel also causes severe surface defects when applied to strand-casting. The steelmaker has therefore sought alternative grain-refining techniques, and has increasingly turned to the use of vanadium or columbium for this purpose.

In October 1979, *Metal Progress,* which is a monthly publication of the American Society of Metals (ASM) published the results of a survey entitled "User Experience With Strand Cast Steels" [*6*]. This survey was limited to experience with bars, rods, and semifinished. One of the subjects of this survey was user preference in grain refinement practice. Table 4 shows the results of this survey.

A more detailed analysis of the *Metal Progress* survey indicates that the users of rod are more discriminating than those of bar. Of the rod users who specified fine grain, 63 percent had a preference in grain-refining element; this figure was only 48 percent of bar users.

These results tend to indicate that the bar consumers in particular have, in many cases, a lack of awareness of the effects of various grain-refining practices.

TABLE 3—*Reasons for continued growth of strand-casting.*

Greater uniformity of cast structure
Improved quality of hot-worked structure
Increased yield
Reduced capital and depreciation costs
Reduced manning and labor costs
Reduced conversion costs and improved working conditions
Reduced energy consumption
Fewer processing steps

From IISI, 1977 [*1*].

TABLE 4—*User preference of grain-refining practice.*

No preference	44%
Prefer aluminum	42%
Prefer columbium	4%
No response to this question	10%

From *Metal Progress Survey*, Oct. 1979 [3] for rod, bar, and semis.

The use of columbium or vanadium in place of aluminum significantly changes the mechanical properties of hot-worked steel, affects heat-treatment response, and generally improves machinability. It would seem appropriate therefore for the steel industry to describe what it is doing in terms of grain-refining practice, why it is doing it, and what effect these practices have on the end user.

The following observations and results are directed primarily at bar products, used by the hot-forging and cold-finishing industries.

Practices

Traditionally, steel has been poured into ingots, and small pieces of aluminum have been added to the ingot mold during teeming. The total aluminum added is about 0.03 percent. This is sufficient both to complete deoxidation and to produce an inherently fine-grained austenite. This practice is inexpensive, presents no quality problems, and is universally applied.

As strand-casting developed, the steel producers attempted to duplicate this practice by continuously feeding an aluminum wire into the mold at a constant rate.

During the cooling and solidification of liquid steel, oxygen which dissolved in the metal during refining is continuously rejected from solution. This oxygen reacts to form liquid manganese silicate inclusions which mostly float to the top of the ingot or to the top of the mold in strand-casting. The addition of aluminum to the liquid metal causes the deoxidation product to be a solid manganese-alumino-silicate. In both types of casting practice these inclusions float to the top of the ingot or mold. In ingot practice this change in state of inclusion is insignificant because the process is static and the inclusions are cropped off with the top of the ingot during rolling. In strand-casting, however, as the billet is continuously moving downward, the inclusions are continuously floating upward and accumulating at the meniscus. Liquid inclusions dissipate as a thin film between the billet and mold and are never detectable in the cold billet. Solid inclusions, however, accumulate into lumps of slag up to half an inch in diameter. These pieces of slag also gravitate to the mold-metal interface, are trapped, and appear on the surface of the finished billet as defects. In many cases these defects are gross and in all cases render the as-cast product unsuitable for special applications. Extensive surface grinding is necessary to remove these defects. This is a slow labor-intensive process, is often incomplete, and when so results in surface defects in the finished product.

To overcome the surface slag problem, the strand-cast billet producers have increasingly turned to the use of columbium or vanadium for grain refinement. Though initially more expensive than a comparable aluminum addition, these alloys are cost-effective. They have no tendency to produce solid deoxidation products and result in a superior billet surface quality free of slag.

As stated in the foregoing, the effect of columbium and vanadium is mainly noticeable in the hot-worked mechanical properties and heat-treatment response. We will now consider these effects.

The strengthening mechanisms of columbium and vanadium are well understood. Vanadium carbonitrides are fully "solutionized" at hot-working temperature and on cooling they reprecipitate both before and during transformation. Strengthening occurs by grain refinement and by precipitation. Columbium in the form of carbides is much less soluble at hot-working temperatures and its degree of solution depends on both temperature and time. The extent to which columbium carbides dissolve affects the resulting mechanical properties. Consequently, the strengthening effects of columbium are less predictable than those of vanadium and will depend on reheat practice and hot-working technique; that is, induction heating, gas heating, rolling, pressing, etc.

Multiple-regression analysis of hundreds of test results at Chaparral Steel Co. has shown that mechanical properties change as shown in Table 5. The results are similar for each element except that by having much less effect on the ultimate tensile strength, columbium significantly raises the yield-tensile ratio. For this reason, columbium grain-refined steel has been found to have superior machinability, comparable to cold-drawn bar.

It can be seen from Table 4 that a typical grain-refining addition of 0.03 percent columbium will increase the yield strength of a hot-rolled bar by over 71 MPa (10 000 psi) with almost no effect on elongation.

A change of this magnitude is very significant. Much has been written about microalloy additions to high-strength low-alloy steels and this technology is widely used in flat-rolled products. However, from the point of view of the steel producer supplying forging bar products to the automotive, commercial hardware, and oil industries, there appears to be no appreciation of the potential benefits. This is confirmed by the Metals Products Survey [*6*] where only 4 percent of respondents preferred columbium as a grain refiner and almost 50 percent had no preference.

In the final analysis, the chemistry of a steel product is secondary to its ability to be formed to a final shape and then to perform in hostile environments involving stress, abrasion, heat, corrosion, etc. The basic steel grades

TABLE 5—*Effect of 0.01% of columbium or vanadium on hot-rolled mechanical properties.*

	Yield, ksi	Ultimate Tensile Strength, ksi[a]	Elongation, %
V	+3.16	+2.23	−0.1
Cb	+3.66	+0.20	+0.1

[a] 1 ksi = 6.8948 MPa.

For electric furnace plain carbon silicon-killed steels in the ranges 0.25 to 0.50C, 0.60 to 1.00Mn.

were developed to meet combinations of these environments. In many cases moving equipment is involved where energy consumed is proportional to weight. With established microalloying techniques, the strength of a hot-worked steel can be increased by 20 percent for about a 1 percent cost increase. See Table 6.

Why then are the known metallurgical benefits of columbium or vanadium not being more widely adopted? Part of the answer lies in the inertia of the steel specifying institutions. Most bar products are ordered to the American Iron and Steel Institute (AISI)-SAE steel numbering system. There is no way to order an enhanced-yield-strength 1040.

AISI has recently developed a "High Strength Sheet Steel Source Guide." Sixteen producers were offering 355-MPa (50 000 psi) yield strength steel under 20 trade names or designations. The aim of the new "Source Guide" is to break a communication barrier in selection and specification [*7*]. We need a similar guide for bar products. SAE specification J410C makes a start in this direction, but how well known is this standard?

We should also ask ourselves: To what extent can heat treatment be replaced by microalloying with vanadium or columbium?

In 1973 at Sheerness Steel in England the author investigated the effect of vanadium on hot-rolled strand-cast bars in conjunction with Highveld Steel and Vanadium Corp. [*8*]. The steel used was 0.23 percent carbon 1.25 percent manganese silicon killed. The vanadium content was varied up to 0.17 percent. Results are shown on Fig. 2 and it can be seen that 567-MPa (80 000

TABLE 6—*Strengthening cost-effectiveness columbium in Grade 1040.*

As-rolled yield strength-60 000 psi
To increase yield 20% requires 0.033Cb
Requires 0.66 lb of Cb/ton at $6.20/lb
= $4.1/ton raw steel
or $4.6/ton hot-rolled bar

1 psi = 6.8948 kPa.
1 lb = 0.45 kg.
1 U.S. (short) ton = 0.9 metric ton.

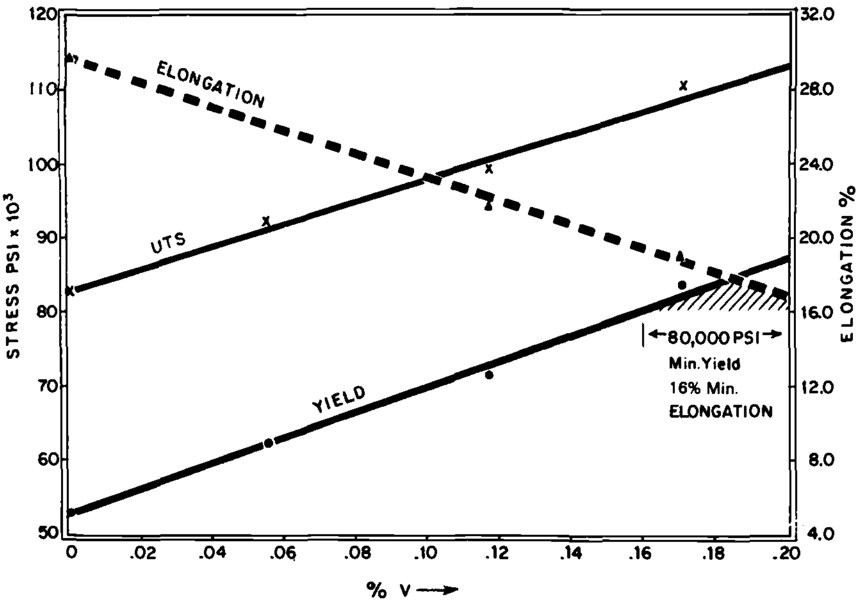


FIG 2—*Grade 1526 effect of vanadium mechanical properties.*

psi) yield strength with good ductility is readily achievable. These mechanical properties are typical of the lower end of the quenched-and-tempered ranges and can be achieved without the energy, capital, and labor costs associated with heat treatment.

Figure 3 is a typical tempering curve. This is for a 1050 and shows the similarity in approach of optimizing mechanical properties by heat treatment and by the use of vanadium [Figs. 3 and 4 elongation in 20.32-cm (8 in.) gage length].

The problem is how to sell these possibilities to the end user. We need the support of ASTM and AISI. The potential economies in materials and energy are tremendous.

Influence of Columbium and Vanadium on Heat-Treatment Response

Vanadium has long been known to retard the tempering of martensite and has been specifically used in some grades for this purpose. Columbium is reported to have a similar effect. The *Metal Progress,* users' survey [*6*] indicated some awareness of this phenomenon. The steel industry should therefore provide its customers with details of the magnitude of this effect if it wishes to adopt the vanadium or columbium grain-refining practice.

At Chaparral we searched the literature unsuccessfully for information on the effect of columbium and vanadium at low concentrations. The American Society for Metals (ASM) Metxadex computerized data base system was then commissioned to examine all abstracts on file since 1966. Again the

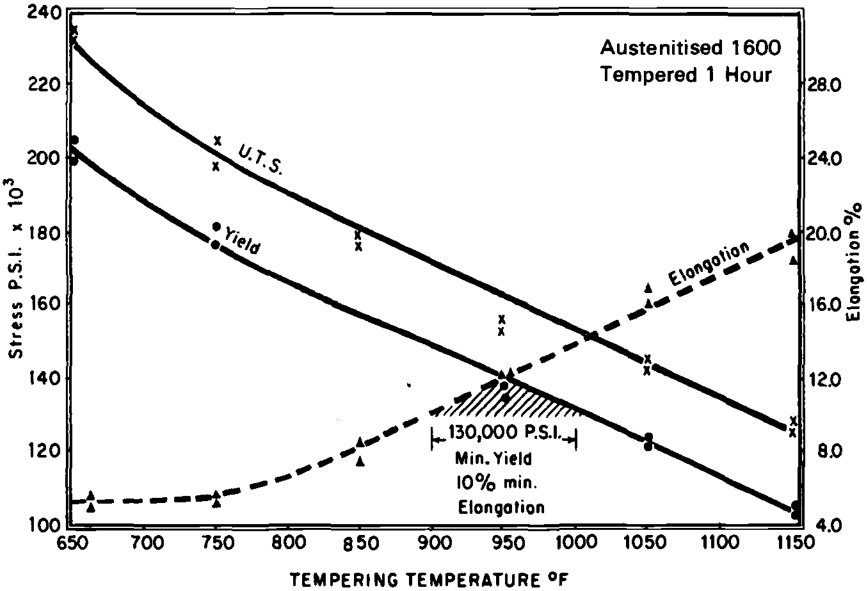


FIG 3—*Grade 1050 quenched-and-tempered properties.*

only information available related to much higher concentrations than are necessary for grain refinement. We therefore decided to investigate Grades 1045 and 4140, each grain refined with either aluminum, columbium, or vanadium.

Duplicate specimens of bars from each type of steel were quenched from (843°C) (1550°F) and tempered for 45 min at 56 deg C (100 deg F) intervals between 149 and 538°C (300 and 1000°F). The process of martensite decomposition was determined by hardness testing. Correlation coefficients of between 0.937 and 0.970 were obtained from simple regression analyses of the hardness results plotted against tempering temperature. A typical tempering curve is shown in Fig. 4.

The equations given in Table 7 were developed to predict the progress of tempering. The tempering temperatures necessary to achieve 40 HRC in 45 min are given in Table 8 for the six steels examined. The difference between steel of the same grade but different grain refiner is very significant.

Heat treaters in the United States have been processing columbium and vanadium steels for at least five years, often without knowing which type of steel they were dealing with. The use of equations such as these will simplify the process of achieving a specified hardness level.

The Relevance of Grain Size

There is a second solution to the problem of aluminum in strand-cast products.

At a symposium concerned partly with the availability of ferroalloys we

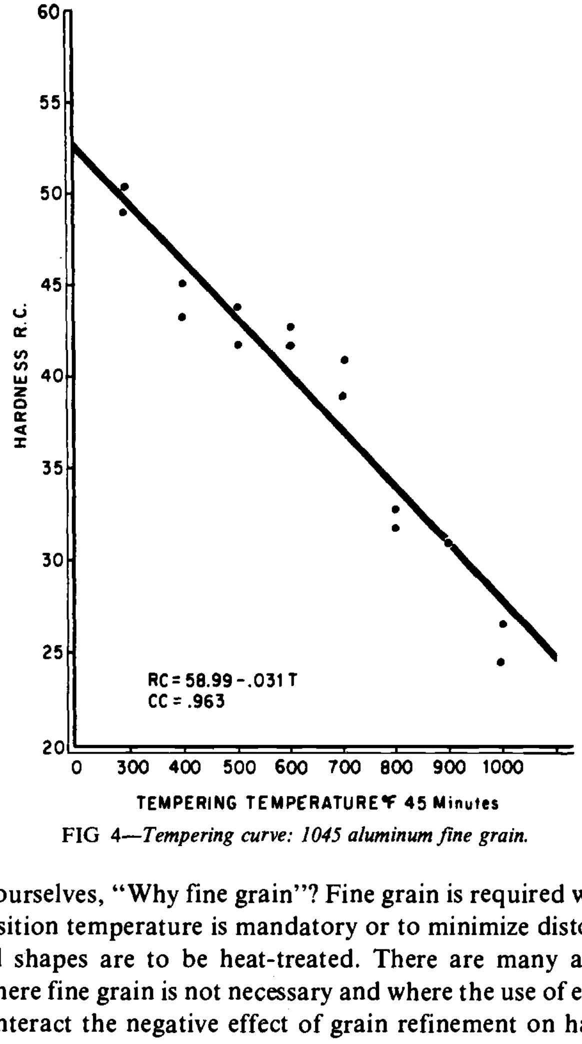


FIG 4—*Tempering curve: 1045 aluminum fine grain.*

should ask ourselves, "Why fine grain"? Fine grain is required where a low-impact transition temperature is mandatory or to minimize distortion when complicated shapes are to be heat-treated. There are many applications, however, where fine grain is not necessary and where the use of expensive alloys to counteract the negative effect of grain refinement on hardenability may be required.

TABLE 7—*Tempering equations for various grain refiners.*

1045	0.044V	HRC = 57.2 to 0.021 T
	0.021Cb	HRC = 58.8 to 0.025 T
	0.030Al	HRC = 59.0 to 0.031 T
4140	0.034V	HRC = 55.7 to 0.02 T
	0.028Cb	HRC = 57.0 to 0.023 T
	0.026Al	HRC = 56.0 to 0.03 T

T = Tempering temperature in deg F. Tempering time 45 min in all cases.
°C = (5/9) (°F −32).

TABLE 8—*Tempering temperature necessary to achieve 40 HRC in 45 min.*

Grain Refiner	1045	1040
Vanadium	819°F	785°F
Columbium	752°F	739°F
Aluminum	613°F	533°F

°C = (5/9) (°F −32).

I quote from the *1979 SAE Handbook:* "Steel compositions included in the SAE Handbook are considered ***adequate*** for practically all parts made of wrought ferrous materials, etc."

Adequacy is no longer enough.

Institutions such as the ASTM, AISI, and SAE must recognize developing metallurgical technology and play a leading part in encouraging the implementation of these developments.

Conclusion

The major problem identified in the Metal Product Survey [*6*] with the use of columbium or vanadium as a grain refiner is in the change in heat-treatment response. A solution to this problem has been offered by providing equations that can be used to predict the rate of tempering for each grain-refining element.

An alternative solution is to examine the relevance of grain size in each application. Significant reductions in the alloy content of quenched-and-tempered steel can be made when coarse-grain steels are utilized.

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A. T. Peters[1]

Additives to Steel and Iron for Improved Machinability

REFERENCE: Peters, A. T., "**Additives to Steel and Iron for Improved Machinability,**" *Ferroalloys and Other Additives to Liquid Iron and Steel, ASTM STP 739,* J. R. Lampman and A. T. Peters, Eds., American Society for Testing and Materials, *1981*, pp. *191–198.*

ABSTRACT: The properties required from free machining steels are machinability and surface finish; detrimental effects are the products of deoxidation. This paper describes the difficulties involved in producing high-carbon or continuously cast free machining steels, and the reasons for the virtual absence of free machining irons. Sulfur and lead as machinability promoters of steels, and the importance of the manganese/sulfur ratio, are considered, along with the forms available, manner of usage, recoveries, and recoveries from remelting scrap. The following topics are also discussed: ASTM specifications; phosphorus and nitrogen as chiefly surface finish promoters; manner of manufacture of ferrophosphorus and its properties and trends as affecting the steelmaker; products available, manner of usage, and recoveries from remelting scrap; nitrided alloys and their ASTM standards, manner of usage, recoveries, and recoveries from remelting scrap; selenium and tellurium as machinability enhancers; and possible future trends in the development of alloys for free machining steels.

KEY WORDS: free machining steels, ferroalloys, steel deoxidation, sulfur in steel, lead in steel, nitrogen in steel, phosphorus in steel, selenium in steel, tellurium in steel

The elements sulfur, lead, phosphorus, nitrogen, tellurium, and selenium—especially the first four—are vital in the production of steels used by high-speed automatic machine tools—the free machining steels. In addition to improved cutting and drilling properties, among others, the smoothness of the resulting surface finish is often important, especially if the machining is the final operation prior to polishing or plating. Hence free machining steels always incorporate alloying elements predominantly intended for improvement of cutting rates—sulfur and lead—singly or in combination; sometimes with machinability-enhancing tellurium or selenium, but often also elements which essentially contribute more to the better surface finish than to machinability—phosphorus and nitrogen.

Free machining steels are often a compromise between other mechanical properties or their surface quality and the cutting behavior. For instance, the very best machining steels, American Iron and Steel Institute (AISI) Series

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11XX and 12XX, should be completely undeoxidized (unkilled) for best machinability, with no silicon, aluminum, or titanium present because of the highly abrasive oxides resulting from the addition of these elements. However, this results in the ingots developing subsurface blowholes which lead to seam-type surface defects in the product. As a result, either the steelmaking and semifinished yields suffer when machinability is the supreme aim, and in the long term the product price responds to the high manufacturing cost, or the surface of the bar becomes a little less than perfect or its machinability is not at the very top theoretically possible.

To use higher-carbon steels as another example: They are harder and thus more difficult to machine, but for a variety of metallurgical reasons must be made killed, that means deoxidized with silicon and sometimes with aluminum or titanium—all elements that are detrimental to machinability as mentioned in the foregoing. High amounts of sulfur are beneficial for cutting properties but increase the in-process losses and may promote quench cracks during subsequent heat treatment. Fine-grained steels, necessary for some applications, are grain refined with aluminum, which, as mentioned, is strongly detrimental to machinability. Since sulfur is detrimental for many applications, lead is often used in high-carbon steels.

Hence steelmakers with major interests in the free machining bars area developed a number of proprietary steel grades, using as additives the uncommon and expensive tellurium and selenium, thus tending to improve their product machinability without affecting its other properties. The availability and cost of each of these elements are dependent on the ups and downs of the copper industry—an item completely beyond the control of the steel producer. A new additive is bismuth.

Much has been said about the rapid growth of "mini-mills," producing bars by the electric-arc furnace/continuous-caster sequence. Yet continuous casting is not conducive to the development of the best machining properties because steel for continuous casting must be killed; thus only free machining grades normally sold as killed are castable. Furthermore, the development of best machinability using the most common and cheapest promoter, sulfur, depends on the formation of large sulfides by their precipitation and growth in the liquid steel. This implies slow solidification, such as that of ingots, while the solidification rate of a cast strand is very rapid. The high solidification rate also interferes with lead being taken up into solution in the liquid steel. Thus, obtaining truly fast machining steels via the otherwise attractive continuous-casting process appears to be questionable.

Cast irons are seldom extensively machined and their machining properties are usually fairly good. They are subject to "hot tearing" of all but the simplest castings and thus the machinability-promoting, but also hot strength reducing, sulfur is seldom, if ever, added to iron melts. The presence of graphite in cast irons promotes machinability.

Since lead does not give hot shortness, it is sometimes added for this purpose. In the presence of large amounts of carbon, nitrogen is not effective and phosphorus increases the brittleness of iron castings. The expensive additives are not economically attractive in irons except for a few uncommon specific applications.

Sulfur

Sulfur is the oldest additive used for improving machinability in steels, in amounts up to 0.35 percent or infrequently higher. Since the sulfide inclusions which promote breaking off of the chips under the tool tip affect detrimentally the hot workability of steel, that is, its rolling or forging, highly resulfurized steel must be toughened by increased manganese contents—a manganese/sulfur ratio of 3.0. Unfortunately, manganese toughens the ferrite and thus is detrimental to machinability, and its control at low-carbon levels may be difficult.

Sulfur is usually added to the ladle early, during, or just before the tap. Lump iron pyrites are sometimes used in Europe, adding them to the furnace before tap or to the ladle. Neither is covered by an ASTM standard.

Sulfur is usually 99 percent pure, moisture being the principal impurity. Both platelets obtained from melting the sulfur out of underground deposits by superheated steam, the Frasch process, and flowers of sulfur obtained from desulfurization of gases or during refining of "sour" oil crudes are equally usable, preferably bagged, with recoveries of 80 to 90 percent. A new source is molten sulfur obtained from modern coke batteries which convert high-sulfur coals. Hence it might be expected that integrated steel mills may become self-sufficient, but the cost of processing a few tons per day of low-value material may make this unattractive and the entire output may be sold to a bulk processor.

Additions to individual ingots or castings as sulfur or iron pyrites are possible but inconvenient.

It might appear that, due to its low cost, the recovery of sulfur from remelted scrap may be unimportant, but this is not the case. Recovery of sulfur under the usual oxidizing remelting conditions is high, probably about 70 percent. A heat charged with sulfur-bearing scrap may melt too high in sulfur for the intended application if it is not to be a resulfurized grade. Remelting under nonoxidizing conditions, in electric-arc or induction furnaces, using strongly basic slag, gives very low sulfur recoveries.

The United States and Canada produce all of the sulfur consumed in steelmaking in these countries.

Lead

Lead improves machinability strongly, probably acting as a tool tip lubricant whether attached to the sulfide particles, as it usually appears, or dissolved in ferrite, but does not affect other mechanical properties. It is fairly often added to steel or iron, usually aiming for about 0.25 percent and almost invariably to the ladle stream using a pneumatic gun for uniformity of addition. No lead should be added to the ingot or casting bottom to compensate for its sinking properties. Recovery is about 70 percent.

The chemistry of the shot is covered by the ASTM Specification, Common Desulfurized Lead (B 29-79), but up to 0.1 percent of arsenic and antimony are often permitted. These improve the shotting characteristics of the molten lead and also allow the use of cheap scrap batteries for the production of the shot. Its grain size is usually specified in accordance with ASTM Specification for Wire-Cloth Sieves for Testing Purposes (E 11-70) as 20 to 40 or 60 mesh (0.85 to 0.42 or 0.25 mm). Finer shot exhibits lower recoveries, and grains coarser than 18 mesh (1.00 mm) tend to sink into the ingot or casting before dissolving, resulting in inclusions that do not promote machinability and may be actually detrimental by introducing tool "chatter."

Recovery of lead when remelting lead-bearing scrap is low, but some may collect on the furnace bottom and in extreme cases seep through the hearth refractory.

All lead shot used by the ferrous industry in the United States and Canada is produced domestically.

Phosphorus

Phosphorus improves steel machinability only indirectly; about 0.1 percent or less stiffens the ferrite in low-carbon steels, hence giving chips that break off easier at the tool tip. Also, the part surface finish is usually better. In the past, acid Bessemer steels were preferred over the open-hearth grades because of their slightly higher residual phosphorus (and nitrogen) content. Then the rephosphorized grades were developed in the 1920's and 1930's, the AISI 12XX Series. It should be noted that the ferrite strengthening effects of phosphorus are used in several modern High Strength Low Alloy Steels and also in steel for components of electrical motors. This alternate use may result in some supply and storage problems, as discussed later.

Additions of phosphorus to liquid steel are invariably made to the ladle, using ferrophosphorus. The alloy contains 24 to 26 percent phosphorus and 1 to 3 percent silicon. Their sum is constant at 26 to 27 percent phosphorus plus silicon. The recoveries are generally 80 to 85 percent. The phosphorus content of the alloy is inconveniently low, leading to high addition weights and thus significant chilling of the steel. But handling of metallic phosphorus is not possible on account of its pyrophoric properties.

Ferrophosphorus is a by-product of the production of phosphorus in submerged-arc furnaces. This is due to the fact that all iron impurities in the phosphate rock and fluxes collect at the furnace bottom and give iron saturated with phosphorus; its content is affected only by the quite constant temperature and silicon content. Improvements in phosphorus production lowered the yield of ferrophosphorus. Also, several producers went out of business in recent years on account of economic impracticability of installing pollution controls on their furnaces.

As mentioned, any element which gives abrasive inclusions is undesirable in free machining steels. Hence the silicon content of ferrophosphorus should be as low as possible, but the trend is in the opposite direction with some casts reaching as high as 4 and 5 percent silicon. For the same reason, formation of hard inclusions, chromium and vanadium, should be low. This requirement makes much Western phosphate rock unsuitable for the production of ferrophosphorus because chromium-plus-vanadium contents may reach 6 percent. Either element is also undesirable for steels for electrical applications. However, at least one producer developed a process for extraction of vanadium from ferrophosphorus produced from Western rock. If chromium could be eliminated as well, we could gain a new important source of ferrophosphorus.

Ferrophosphorus is fairly friable. Fines should be briquetted if high and consistent recoveries are to be obtained. Since the phosphorus content of the fines is diluted by the binder used for briquetting, the two materials, lumps and briquetted fines, may have to be stocked separately and care used when making the addition on account of the apparent different recoveries from gross addition weights.

The fines are also often higher in silicon and thus a little lower in phosphorus. However, higher-silicon ferrophosphorus, whether fine size or not, may be made "low effective silicon" by using an oxidizing binder such as phosphoric acid or calcium superphosphate at a significant cost increase. The apparent recovery of phosphorus from gross addition weight is lower than that from ferrophosphorus due to the dilution of the alloy by the binder, usually lower starting phosphorus content, and nonrecovery of any phosphorus from the binders. Thus the self-oxidizing, low-effective silicon briquettes must be stored and used separately if a shop is making both free machining and other rephosphorized grades and if alloy costs are to be kept as low as possible.

All ferrophosphorus used in the United States is produced domestically.

Under oxidizing remelting conditions, recovery of phosphorus in basic processes is negligible at high oxygen levels, that is, in low-carbon steels. This is significant, and, like sulfur, phosphorus may become troublesome in steel to be tapped above 0.4 percent carbon. Acid or nonoxidizing remelting gives very high recoveries.

Ferrophosphorus is not covered by an ASTM standard, and an old trade classification which included phosphorus and silicon contents is no longer in use.

Nitrogen

Nitrogen acts in steel like phosphorus, strengthening the ferrite. Thus it is often added to free machining, structural, and High Strength Low Alloy Steels, aiming for 0.01 to 0.02 percent. It is added to the ladle either as broken platelets of nitrogenized electrolytic manganese metal covered by the ASTM Specification for Electrolytic Manganese Metal (A 601-69) or as nitrided medium-carbon ferromanganese [ASTM Specification for Ferromanganese (A99-76)]. The former contains either 4 to 4 1/2 percent or, less commonly, 6 percent nitrogen. The latter is made by grinding the alloy and nitriding the fines to 4 to 4 1/2 percent nitrogen and briquetting the product because fines give low and erratic recoveries of nitrogen and manganese. This is due to floating on the steel surface in the ladle when the nitrogen is readily given off to the atmosphere, the manganese nitride being apparently metastable. For the same reason it is preferable to use the nitrided metal bagged or even canned. Recoveries are about 60 percent for either material and a little lower for the 6 percent grade.

Only minimum amounts of clay or carbonaceous binders, such as molasses, should be used, because steel inclusions originating from clay are detrimental to machinability if retained in the steel, and carbon input is undesirable in low-carbon steels, as most free machining grades are. The latter reason made calcium cyanamid unattractive to use as it contained much carbon, was consequently very smoky in use, and the nitrogen recoveries were erratic, due apparently to its high reactivity when added to the liquid steel. It was generally replaced by the nitrided medium-carbon ferromanganese after it was developed in the 1960's.

The low nitrogen content of either material makes additions to individual ingots impractical.

Recovery of nitrogen from scrap is not measurable but probably quite low, at least under oxidizing conditions.

Tellurium

Tellurium in amounts of about 0.05 percent increases the machinability of steels, especially enhancing the action of lead. It is used as the metal, adding it to the ladle stream when pouring ingots; recovery is about 70 percent. It is possible to use an alloy of lead and tellurium, but not if a tellurium-bearing, nonleaded grade is to be made. An alloy of manganese and tellurium is in use in Europe, reputedly giving slightly higher recoveries. Additions of tellurium to the ladle give lower and variable recoveries.

High contents of tellurium result in hot shortness of steels. Compensating for this by raising the manganese level is detrimental to machinability.

Tellurium cannot be used in the presence of nickel because it forms very low melting films of nickel telluride in the grain boundaries with resultant catastrophic deterioration of hot strength. This makes rolling or forging impossible. Thus stainless steels cannot benefit from tellurium additions.

Under oxidizing remelting conditions, the recovery of tellurium is negligible and probably low due to its evaporation, when scrap is remelted without access of oxygen.

Tellurium is a by-product of copper refining and thus its availability and price are strongly affected by the condition of the copper industry. A large share of the tellurium used in the United States is imported, partly from Canada. It is not standardized by ASTM.

Selenium

Selenium in amounts resembling those of tellurium is used apparently for the same purpose. It may be added to the ladle as ferroselenium or as the element to the ladle stream, with similar recoveries.

Much higher amounts of selenium, over 0.15 percent, are added to a few stainless steel grades, as shown in AISI specifications, for the purpose of improving their machinability. Obviously, selenium, in contrast to tellurium, does not promote hot shortness in the presence of nickel. Actually, additions of a nickel-selenium alloy especially developed for this purpose were reported from Europe, with recoveries higher than those when adding the elemental form.

Recovery of selenium under oxidizing remelting conditions is low.

Selenium is a by-product of copper refining and thus depends on the level of this industry. Some selenium is recovered from lead residues. None of its forms is covered by an ASTM standard.

Conclusion

Some predictions regarding future developments in additives for free machining steels may be as follows.

Sulfur will certainly remain as the mainstay. A better ferrophosphorus may be developed in the future, where cheap power is available, perhaps by using low-quality phosphate rock or phosphorus-rich mining or smelting residues, adding cheap scrap to the charge and making ferrophosphorus as the main product and phosphorus as the by-product; or perhaps iron could be dissolved in phosphorus, making it safe to handle in air. A higher-nitrogen true manganese-nitrogen alloy obtained from the liquid state, rather than the not very stable absorption-type alloy used at present, is being developed and this may give higher and more consistent recoveries of nitrogen.

The cost of the other additives, tellurium and selenium, is a function of copper and lead refining economics and thus the materials will not be plentiful and will remain expensive; unless the U.S. copper industry recovers strongly, they will continue to be imported.

Further improvements in high-speed machining may continue to make the expensive steels containing these additives attractive to users whose equipment is capable of full utilization of the enhanced free machining properties and production volume high enough to install such machinery. However, further developments in processes which manufacture parts requiring little or no machining, such as steel extrusion, cold forming, and perhaps powder metallurgy, may cut down the tonnages of all free machining steels. Thus the direction of progress of the part manufacturers will strongly affect the trends of free machining steels and hence the trends of additives used for their production.

APPENDIX I

Additives to liquid metals and alloys.[a]

Additive	Ferrous Industries		Nonferrous Industries	
	Form Used	ASTM Standard No.	Form Used	ASTM Standard No.
Aluminum	Al	B37	Al	B37
	FeAl		MnAl, CuAl	
Boron	FeB	A323^b	NiB, MnB,	
			CuB, AlB	
Calcium	CaC_2	...$^{(1)}$	Ca	
	CaSi	A495^b		
Cobalt	Co			
Columbium (niobium)	FeCb	A550^b	Cb, NiCb	
Copper	Cu		Cu	
Chromium	FeCr	A101^b	Cr	A481^b
	FeCrSi	A482^b	AlCr, CuCr	
Lead	Pb	B29$^{(1)}$		
			Pb	B29$^{(1)}$
Manganese	FeMn	A98^b	Mn	A601^b
		A99^b	MnTi	
	SiMn	A483^b	MnSi	A701^b
Magnesium	FeSiMg		NiMg	
	Mg,MgAl	...$^{(1)}$		
Molybdenum	FeMo	A132^b	Mo	
	MoO_3	A146^b		
Nickel	Ni	A494	Ni	A494
	NiO	A636^b		
	FeNi			
Nitrogen	FeMnN	A99^b		
	FeCrN	A101^b		
Phosphorus	FeP			
Rare earths	RE, RESi			
Selenium	FeSe, Se			
Silicon	FeSi	A100^b	Si	
	SiMn	A493^b	SiCu	B53
Sulfur	S			
Tellurium	Te			
Titanium	FeTi	A324^b		
	Ti	B367	Ti	B367
Vanadium	FeV	A102^b		
	FeVC			
Tungsten	FeW	A144^b		
	$CaWO_3$			
Zirconium	SiZr			
	FeZr			

[a] Contributed by Committee A-9.

[b] Under the jurisdiction of Committee A-9, contained in Vol. II, ASTM Standards.

(1) Particle size usually specified per ASTM Standard E11.

NOTE:. FeX or YX denotes a ferroalloy or masteralloy, not a compound.

APPENDIX II

Approximate Properties of Ferroalloys

Alloy	Size (Note 1)		Bulk Density (Note 1)		Friability Rating (Note 2)	Melting Range (Note 3)				Thermal Effect of 1 lb/ton (1/2 kg/ton). Added to Steel (Note 4)	
						°F		°C			
	in.	mm	lb/ft³	kg/m³		Liquidus	Solidus	Liquidus	Solidus	°F	°C
Al (95Al)	3/8	10	90	1440	...	1220	1220	659	659	+0.2	+0.1
FeAl (38Al)	5 × 2	102 × 51	205	3285	...	2318	2246	1270	1230	−1.4	−0.8
FeB (17B)	1 × D	25 × D	275	4405	...	2730	2600	1500	1427	−3.7	−2.1
CaSi (32Ca-61Si)	2 × D	51 × D	110	1760	6	2030	1800	1110	982	−2.6	−1.4
CaSi (16Ca-61Si)	3 × D	76 × D	140	2245	6	...	1795	...	980	−1.4	−0.8
C (98C)	...	...	...	...	...	...	...	...	...	−5.4	−3.0
Cu (99Cu)	...	...	...	...	...	1981	1981	1083	1083	−1.8	−1.0
FeCb (74Cb)	...	...	...	...	4	2800	2700	1538	1482	−1.1	−0.6
FeCb (54Cb)	1/2 × D	13 × D	300	4805	4	2720	2650	1493	1454	−1.3	−0.7
Cr (99Cr)	...	...	...	...	2	3300	3300	1805	1805	−1.7	−0.9
FeCr (69Cr-0.1C)	4 × D	102 × D	...	...	1	2920	2450	1604	1343	−1.7	−0.9
FeCr (69Cr-0.1C)	1 × D	25 × D	240	4165	1	2920	2450	1805	1343	−1.7	−0.9
FeCr (68Cr-5C)	...	...	...	...	4	2730	2670	1499	1465	−2.1	−1.2
FeCr (64Cr-3C)	8 × 4	203 × 102	240	3845	4	...	...	...	...	−2.0	−1.1
FeCr (56Cr-6C)	8 × 4	203 × 102	210	3365	4	2720	2660	1493	1460	−2.2	−1.2
FeCr (56Cr-6C)	1 × D	25 × D	250	4005	4	2720	2660	1493	1660	−2.2	−1.2
FeCrSi (60Cr-12Si-6C)	8 × 4	203 × 102	...	...	...	2800	2650	1538	1454	−1.8	−1.0
FeCrSi (40Cr-44Si)	...	...	...	...	...	2560	2540	1404	1393	−0.6	−0.3
FeCrSi (38Cr-40Si)	4 × 2	102 × 51	165	2645	...	2530	2480	1388	1360	−0.8	−0.4
FeCrSi (36Cr-40Si)	1 × D	25 × D	180	2885	...	2530	2480	1388	1360	−0.8	−0.4
Co	...	...	...	...	...	2696	2696	1480	1480	−1.5	−0.8
Mn (99Mn)	1 × 1/16	25 × 2	...	...	6	2300	2300	1260	1260	−1.8	−1.0
FeMn (88Mn-0.1C)	4 × 2	102 × 51	270	4325	...	2200	2190	1205	1200	−1.8	−1.0
FeMn (82Mn-1C)	4 × D	102 × D	270	4325	...	2230	2200	1221	1204	−1.8	−1.0
FeMn (78Mn-7C)	4 × 2	102 × 51	240	3820	...	2310	2100	1265	1149	−2.1	−1.2
FeMn (78Mn-7C)	2 × D	51 × D	260	4165	...	2310	2100	1265	1149	−2.1	−1.2
SiMn (67Mn-17Si)	8 × 4	203 × 102	200	3205	...	2360	2125	1293	1162	−1.4	−0.8
SiMn (67Mn-17Si)	2 × D	51 × D	245	3925	...	2360	2125	1293	1162	−1.4	−0.8
SiMn (67Mn-30Si)	2 × D	51 × D	235	3765	...	...	2272	...	1244	−1.2	−0.7
FeMo (60Mo)	3/4 × 1/4	19 × 6	290	4645	...	3308	2732	1820	1500	−1.8	−1.0
MoO_3 (56Mo)	...	...	110	1760	...	...	...	...	...	−2.1	−1.2

Ni (98Ni)	...	...	...	...	...	2650	2650	1455	1455	−1.2	−0.7
NiO (75Ni)	...	...	...	...	...	...	...	...	...	−2.9	−1.6
MnN (95Mn-4N)	1 × 1/16	25 × 2	...	...	5	...	...	...	...	−2.2	−1.2
FeMnN (75Mn-4N)	2 × 1	51 × 25	...	...	...	...	...	...	...	−2.4	−1.3
FeCrN (62Cr-5N)	...	...	...	...	...	...	...	...	...	...	...
VCN (80V-11C-6N)	1/2	13	120	1920	...	4400	3930	2430	2165	−3.4	−1.9
FeP (24P-3Si)	1 × D	25 × D	220	3530	...	2450	2305	1343	1262	−3.1	−1.7
RE (48Ce)	...	...	...	...	...	...	1450	...	2462	−0.5	−0.3
RESi (17Ce-33Si)	1 × D	...	130	...	...	2600	...	1427	...	−0.1	−0.1
S (99S)	...	...	...	...	...	240	240	115	115	+1.4	+0.8
FeSi (95Si)	2 × D	51 × D	90	1440	4	2560	2450	1404	1343	+1.4	+0.8
FeSi (75Si)	4 × D	102 × D	100	1600	4	2430	2310	1332	1266	+0.4	+0.2
FeSi (75Si)	2 × D	51 × D	110	1760	4	2430	2310	1332	1266	+0.4	+0.2
FeSi (65Si)	...	...	...	...	4	2320	2200	1270	1205	−0.1	−0.1
FeSi (49Si)	4 × D	102 × D	160	2565	5	2240	2210	1227	1210	−0.8	−0.4
FeSi (49Si)	2 × D	51 × D	170	2725	5	2240	2210	1227	1210	−0.8	−0.4
FeSi (15Si)	...	...	...	...	2	2280	2240	1249	1227	−1.6	−0.9
FeTa (55Ta)	...	...	...	...	...	...	...	...	...	−1.1	−0.6
Ti (90Ti-6V-4Al)	...	...	...	...	...	...	3100	...	1704	−0.1	−0.1
FeTi (70Ti)	...	...	...	...	3	...	...	...	...	−0.5	−0.3
FeTi (40Ti-3Al)	1/2 × D	13 × D	240	3845	3	2550	2400	1400	1316	−1.0	−0.6
FeTi (20Ti-8Al)	...	...	...	...	3	...	...	...	...	−1.4	−0.8
FeTi (30Ti)	1 × D	25 × D	280	4485	...	...	...	...	...	−1.1	−0.6
FeV (74V)	2 × D	51 × D	200	3205	1	2800	2700	1538	1483	−1.0	−0.6
FeV (54V)	4 × D	102 × D	230	3685	1	2720	2650	1493	1454	−1.3	−0.7
FeV (54V)	2 × D	51 × D	270	4325	1	2720	2650	1493	1454	−1.3	−0.7
FeV (42V-7Si)	...	...	...	...	1	2600	...	1427	...	−1.5	−0.8
FeVC (68V-14C)	1 × 1/2	25 × 13	...	...	...	2910	...	1600	...	−3.1	−1.7
VC (84V-13C)	1/2	13	120	1920	...	4400	3930	2430	2165	−2.8	−1.6
W	...	...	...	...	...	6170	6170	3410	3410	−0.5	−0.3
FeW (70W)	1/4	6	450	7200	...	5200	2850	2925	1570	−0.8	−0.4
FeZr (83Zr)	...	...	...	...	...	...	1750	...	954	−0.4	−0.2
FeSiZr (40Si-36Zr)	...	...	...	...	...	2450	2300	1343	1260	−0.1	−0.1

NOTE 1: " × D": "by Down," no lower size limit. Bulk density is affected by manner of manufacture of the material, especially porosity and friability, by particle shape, manner of handling, etc.

NOTE 2: Friability ratings are numbers expressing the tendency of the material toward attrition during handling, proceeding from "1" for very tough materials (for example, low C FeCr) to "6" for most friable alloys (for example, CaSi). For details, consult respective ASTM Standards. A quantitative test for friability is not available.

NOTE 3: Liquidus and solidus temperatures may be strongly affected by impurities.

NOTE 4: Solution temperature change, disregarding gains due to oxidation (that is, 100 percent recovery). Aluminum reacting with 0.01 percent oxygen (100 ppm) dissolved in the steel (deoxidizing) raises the steel temperature by approximately 5 deg F (3 deg C), while silicon raises it by approximately 4 deg F (2 deg C). These are additive to the solution effect as is the (variable) effect of oxidation of the main element.

These numbers were calculated by R. J. King and W. R. Chilcott, Jr., Research Laboratory, United States Steel Corp., Monroeville, Pa., from thermodynamic data in a consistent manner and are used in practice by a number of steelmaking shops in the United States and abroad.

Summary

As explained in the Introduction, this is a state-of-the-art review of less-well-known aspects of ferroalloys and other additives and less-common materials. As such, it should serve well as a review and source of thought for those engaged in the production and control of ferrous materials.

The initial paper by Huhn outlines in detail the background history, scope, and evolution of ferroalloy specifications as developed by ASTM Committee A-9. This paper points out that the ferroalloy industry is basically a service industry to the steel and nonferrous industries and is constantly undergoing changes in the products produced as a result of technological advances that have taken place in these industries.

Weston's paper reviews the current status of the International Standards Organization and how it is structured. Emphasis is placed on the necessity of involvement by ASTM to insure that the United States has a forum for asserting her influence on the international standards being published.

The seldom-mentioned subject of the Government's role as purchaser of ferroalloys for stockpiling is presented by Corder—who tactfully understates the pitiful state of financing of the program passed by Congress in July 1979. The paper was, of course, written before the change of the government in the United States in January 1981. It remains to be seen if this program as outlined is funded and implemented.

The recent decline, and prospects, of the ferroalloys industry in the United States is the subject of Gate, who highlights the problem in chromium and manganese products, while Deeley reviews in some detail the recent past and probably the future of the usage of ferroalloys, stressing the thermal aspects, and the possibilities of usage as powders injected into the liquid metal; a valuable list of references follows Deeley's text.

The intriguing possibilities of covering a large part of U.S. needs for a number of ferroalloys by the mining of ocean nodules is presented by one of the participants in the original exploration, U.S. Steel Corp. But the author, Balash, only alludes to the possibly severe political complications, the "underdeveloped countries," often major producers of ferroalloys or at least their ores, strongly objecting to the development of ocean mining, even within territorial waters defined recently, at their insistence, as extending to 200 nautical miles [230 miles (360 km)] from a shore.

Two steel producers discuss the control of purchasing and quality of incoming materials: Peters presents the case of a large nonalloy steel mill while Stryker states the problems of a high-alloy steel producer. There are significant differences in the two approaches based on the diverse needs of the plants and the markets served.

The second half of the symposium dealt with the less-well-known "modifiers" of properties, rare earths and titanium, followed by a discussion of aluminum and its replacement in continuous casting. The usage trends and addition mechanics of rare earths are covered by Trethewey and Jackman in some detail with particular emphasis on the growth in usage of rare-earth metals. A description of the role of these elements in modifying graphite cast iron shapes, by Cornell and Lalich, extends this discussion to complex additives. Demos and Kremin outline the leading titanium alloy sources for the lowest-cost titanium additions to iron and steel.

Silver of the Jones and Laughlin Steel Corp. gives an extensive discussion of alloy practices and relative costs of alloys and methods used to produce high-strength low-alloy steels, most of which are deoxidized with aluminum. The role of aluminum and aluminum recovery in steelmaking and the various forms available are covered by Larsen, followed by a paper by Deeley reviewing aluminum deoxidation practices and the use and properties of ferroaluminum as an alternative to metallic aluminum. Wright discusses the production of fine-grained steel using vanadium or columbium as the necessary substitutes for aluminum in open-stream continuous casting.

The last paper, by Peters, describes the additives used to produce free machining steels, their forms, conditions of use, and the reasons why a majority of these steels are not likely to be made in the future via the continuous casting process.

Appendix I broadly lists the alloys and other additives used in the ferrous and nonferrous industries, indicating their coverage by ASTM. Appendix II lists densities and thermal effects of the addition of a number of common ferroalloys, these having been calculated by R. J. King and W. R. Chilcott, Jr., U.S. Steel on a consistent basis. While the numbers may serve only as a guide, they represent a unique assembly of data not available in a condensed form.

A thread common to all presentations is their practicability. No theoretical considerations are given, the symposium having been designed as a forum for the exchange of ideas between the practitioners of the art and producers of the alloys and additives. It is hoped that the present *Special Technical Publication* will serve a similar purpose.

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