Refractory Metals and Their Industrial Applications

Robert E. Smallwood, editor

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Foreword

The Symposium on Refractory Metals and Their Industrial Applications, held in New Orleans, Louisiana, on 23-24 September 1982, was sponsored by ASTM Committee B-10 on Reactive and Refractory Metals and Alloys. Robert E. Smallwood, Allied Corporation, served as symposium chairman and has edited this publication.

Related
ASTM Publications

Industrial Applications of Titanium and Zirconium: Third Conference, STP 830 (1984), 04-830000-05

Industrial Applications of Titanium and Zirconium, STP 728 (1981), 04-728000-05

Applications-Related Phenomena in Titanium Alloys, STP 432 (1968), 04-432000-05

A Note of Appreciation to Reviewers

The quality of the papers that appear in this publication reflects not only the obvious efforts of the authors but also the unheralded, though essential, work of the reviewers. On behalf of ASTM we acknowledge with appreciation their dedication to high professional standards and their sacrifice of time and effort.

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Introduction

The Symposium on Refractory Metals and Their Industrial Applications, held on 23-24 September 1982 in New Orleans, Louisiana, was sponsored by ASTM Committee B-10 on Reactive and Refractory Metals and Alloys. Although Committee B-10 has for some time written standards used for commercial applications of refractory metals and has sponsored previous symposia on *reactive* metals, this conference was its first devoted to the *refractory* metals (molybdenum, niobium, tantalum, and tungsten). It was energetically supported by suppliers and fabricators and was intended to provide a comprehensive description of these four metals for the industrial user.

Indeed, the symposium was conceived and based on the premise that no publication exists for the industrial user on the various properties and end uses of these metals. While most engineers and designers are familiar with tungsten lamp filaments, the large marjority are only vaguely acquainted with the other three metals and their applications. Refractory metal use to date has primarily been in high temperature applications. The uses discussed at this meeting included electrical, electronic, and corrosion-resistant applications at ambient temperatures.

All the refractory metals have certain properties found in no other materials. This volume is directed towards providing a broad base of information in order for engineers and designers to compare the refractory metals with other candidate materials.

Robert E. Smallwood

Project Manager
Allied Corporation, Hopewell, Virginia;
symposium chairman and editor

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Russ Burman[1]

Properties and Applications of Molybdenum

REFERENCE: Burman, R., **"Properties and Applications of Molybdenum,"** *Refractory Metals and Their Industrial Applications, ASTM STP 849,* R. E. Smallwood, Ed., American Society for Testing and Materials, Philadelphia, 1984, pp. 3-17.

ABSTRACT: Molybdenum ("Moly") is the most readily available and least expensive refractory metal. Massive ore reserves and many refinement facilities are located within the United States. The major application for Moly, over 80% of total markets, is that of alloy additions to irons and steels.

Metallic Moly is consolidated into commercial products by the powder-metallurgy process (P/M) and by the consumable electrode vacuum-arc casting process (VAC). Moly's high melting point and low vapor pressure at extreme temperatures justify its applications to cold wall vacuum or inert atmosphere furnace equipment. These properties, as well as Moly's high thermal conductivity and good electrical and chemical properties, lead to applications in glass-making manufacture of fibers and containers. Moly is also widely used in electronics, solid-state devices, X-ray tubes, crystal growing, heat pipes, photo-etched masks, etc.

TZM Moly Alloy is the best commercial high strength, high temperature material for hot-work tool applications such as die casting (even ferrous metals), hot extrusion (nonferrous and ferrous metals), hot piercing stainless steel tubes, isothermal forging tools, isothermal shape rolling, hot gas valves and seals, and hot turbine components. The Moly-30% tungsten alloy (Mo-30W) is commercially employed for its high melting temperature of 2829°C (5125°F) and its chemical inertness in corrosive molten zinc, especially the high purity grades. Moly and Moly-base alloys are commercially used for principally high temperature applications in hot equipment, hot working tools, and hot operating machines.

KEY WORDS: TZM Moly Alloy, Mo-30W, molybdenum, applications, properties

Molybdenum ("Moly") is the most readily available and least expensive refractory metal. Major ore bodies and many refinement facilities are situated in the United States. In addition, Moly has seen ambient and high temperature service to 1649°C (3000°F) and even higher.

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The most common application for Moly remains that of alloy additions to irons and steels. It is also applied to heat- and corrosion-resistant alloys, magnetic alloys, and many high temperature, high strength alloys that can tolerate less refined ferro-molybdenum or molybdic oxide for alloy additions. Certain heat- and corrosion-resistant alloys and virtually all present day vacuum-melted superalloys, however, require the extreme purity of metallic Moly powder or one of the consolidated powder-metallurgy (P/M) forms—pellets, corrugates, or briquettes. Molybdenum as an alloy addition generally imparts improved hardenability to steels, good toughness at low temperatures, enhanced strength and toughness at elevated temperatures, better abrasion resistance, and improved chemical corrosion resistance, and is a common alloy to most superalloy compositions for similar product benefits.

The latest annual figures available for Moly use in the Free World confirm that alloying of irons and steels is by far the most common application for Moly (Table 1).

Metallic Moly

Metallic Moly has many unusual and useful properties. The vast majority of engineering applications utilize this metal's high melting temperature, high strength and stiffness especially at elevated temperatures, resistance to chemical corrosion in many media, and its excellent thermal, nuclear, and electrical properties. This combination of properties makes available new design concepts for higher operating efficiency and improved service performance than are possible with other more common materials.

Moly can be consolidated by the established P/M method. High purity powder is pressed into a compact, sintered at high temperature (generally in pure hydrogen), and the resulting billet warm-cold worked into a useful product. Moly can also be consolidated by the consumable electrode vacuum-arc casting (VAC) process. Extreme purity powder is pressed into a hexagonal electrode, sintered at high temperature, and continuously melted to fill a wa-

TABLE 1—*Moly use in the Free World.*

Alloy steels	45%	
Stainless steels	21%	
Tool steels	9%	
Cast iron and rolls	6%	
	81%	subtotal
Chemicals (including MoS_2-lube additive)	9%	
Metallic Moly	5%	
Superalloys and specialties	4%	
Miscellaneous	1%	
	100%	total

ter cooled copper ingot mold, all three operations occurring simultaneously within a high vacuum chamber. The resulting ingot is warm-cold worked in several stages into useful products. For both P/M and VAC Moly products, the warm-cold working refines the grain structure as it strengthens and toughens the product. These molybdenum products, however, are not identical in chemical, physical, or mechanical features; each is distinctive and exhibits particular advantages.

Properties and Applications

Moly's high melting point of 2610°C (4730°F), nearly 1093°C (2000°F) higher than most high temperature metals, and low vapor pressure at extreme temperatures are the major reasons for the widespread application to cold-wall vacuum or inert atmosphere furnace equipment. Reflective heat shields and diverse furnace hardware, such as boats, trays, skids, racks, etc., perform well under these extreme processing temperatures and environmental conditions. Furthermore, since molybdenum exhibits high thermal conductivity (81 Btu/ft^2/ft/h/°F at 70°F and 58 Btu/ft^2/ft/h/°F at 2000°F, values several times those for steel, especially at elevated temperatures), has good electrical conductivity (34% IACS at 32°F, about one third that of the pure copper conductivity standard), and is chemically inert to most molten glasses (molybdenum oxides do not discolor glass), it is widely employed for electrical heating or heat booster electrodes in many commercial continuous glassmaking operations for manufacture of glass fibers and glass containers (Figs. 1 and 2).

Many of the abundant applications of metallic molybdenum involve electronic, solid-state, and thermionic devices (Fig. 3). Besides numerous components for high-power vacuum tubes, magnetrons, heat pipes, X-ray tubes, and thyristors, Moly is widely used for crystal-growing devices, glass-metal joints in electronic tubes, and chemical or photo etched masks, screens, and gratings (Fig. 4).

In addition to Moly's good thermal and electrical characteristics, it provides excellent dimensional stability during outgassing, has low vapor pressure and electron emissivity, is easy to fabricate and clean, and has good thermal expansion match with the common electronic tube borosilicate glasses. Moly also displays good electrical contact properties and high arc resistance in applications such as resistance weld electrodes, tips, or welding rolls in the toughest weld service conditions.

In the search for a "superbattery" to smooth out electric power production by energy storage at the utility site and also as a possible power source for pollution-free passenger vehicle service, Moly is a principal material contender in two of the four superbattery front-runners—the lithium-iron-sulfide and the sodium-sulfur systems. In both systems metallic Moly would serve as the current collection components by reason of good thermal and electrical

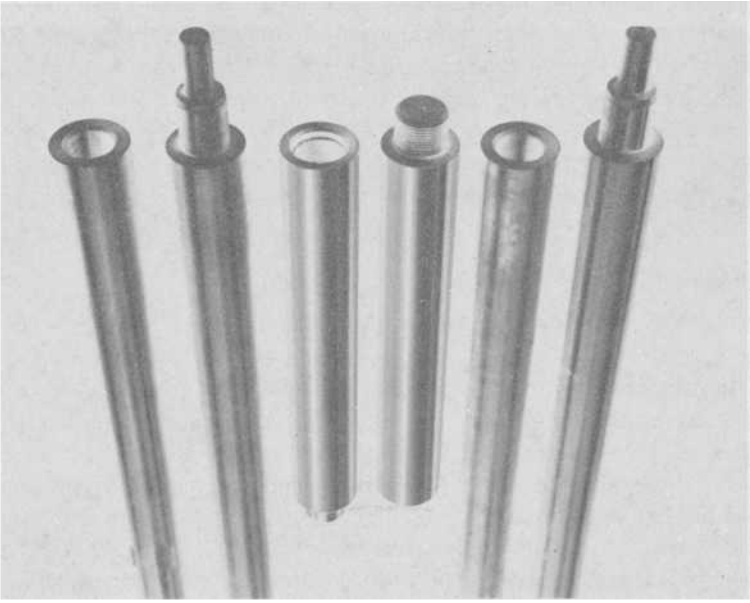

FIG. 1—*Several styles of Moly glass-melting electrodes.*

FIG. 2—*Various glass containers made using Moly glass-melting electrodes.*

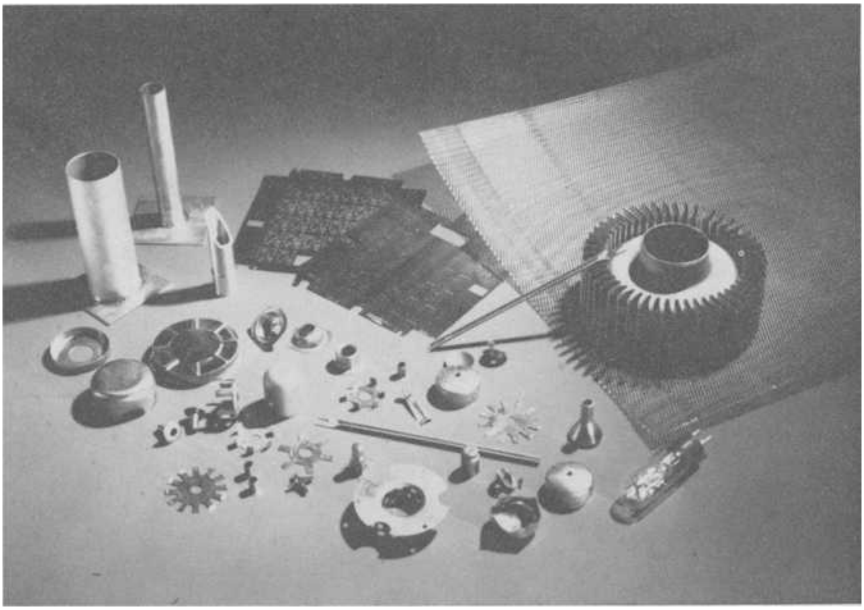

FIG. 3—*Miscellaneous electronic, thermionic, and hot gas components (expanded Moly mesh product).*

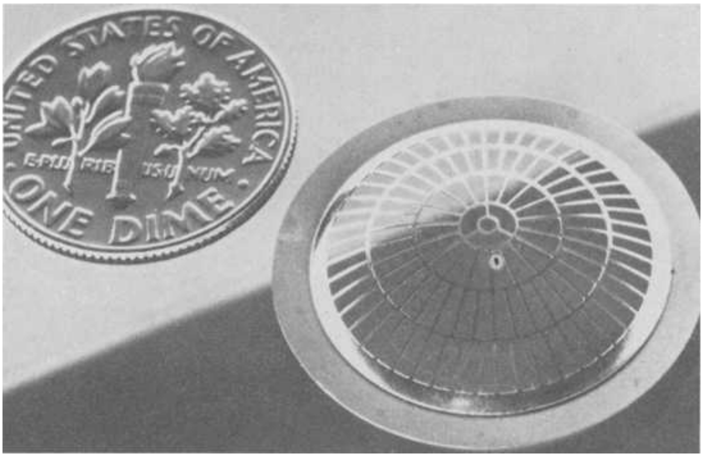

FIG. 4—*Photochemical etched-and-drawn component.*

properties, high stiffness, and adequate corrosion resistance to the aggressive electrolyte, a liquid in the Li-Fe-S system and a solid in the Na-S system.

Moly displays high rigidity or stiffness, as reflected by a modulus of elasticity of about 324 million kPa (47 million psi) at 21.1°C (70°F), and it retains good rigidity at high temperatures as well. Its stiffness at 1093°C (2000°F), a modulus of elasticity of 200 million kPa (29 million psi), is as great as that of steel at room temperature. "Chatter-free" Moly boring bars offer high damping capacity for deep hole machining (Fig. 5), and Moly grinding quills for precision-grinding operations are in widespread use, generally for high-speed, large-volume grinding processes.

Moly has certain characteristics, such as low thermal expansion (only about half the thermal expansion of most steels), high stiffness, and good polishability to optical finish surfaces, necessary for high energy output, high surface temperature laser mirror components. Energy-concentrating Moly laser mirrors show good dimensional stability under the intense thermal pulse gradients generated during laser operations. Some of these laser applications relate to our national defense; other Moly laser mirrors will likely play an important role in the controlled thermonuclear reactor (CTR) for fusion power commercial systems in the 21st century.

Moly-base alloys offer many advantages over unalloyed Moly by providing physical, chemical, and mechanical property benefits. The two principal Moly alloys commercially available today were developed some years ago for applications in the missile and aerospace fields. These fields demanded stronger refractory materials at ever higher stagnation or service temperatures and also alloys that could withstand erosion or melting at ever higher propellant combustion temperatures.

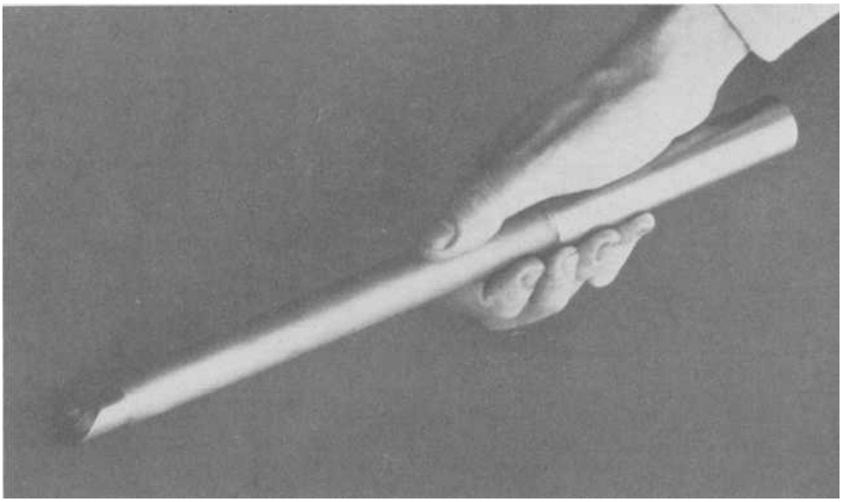

FIG. 5—*Typical 356 mm (14 in.) Moly boring bar.*

TZM Moly Alloy

"TZM Moly" Alloy having about 0.5% titanium and 0.08% zirconium has assumed the workhorse role for higher temperature performance components that must show superior hot strength or creep resistance, or resistance to recrystallization and softening, compared with pure Moly. Witness the long-term creep resistance superiority of TZM Moly to commercial nickel-base superalloys (Fig. 6) that can extend the service temperature regime to much higher turbine efficiency levels.

These high-temperature, high-strength improvements for TZM Moly derive from solid solution strengthening by dissolution of the alloying elements and from dispersion strengthening by formation of complex Mo-Ti-Zr spheroidal carbides. TZM Moly also exhibits superior high temperature strength and creep resistance to pure Moly (Fig. 7), while at the same time resisting recrystallization, softening, and loss of strength to some 260°C (500°F) higher service temperatures than for unalloyed Moly. Consequently, the principal applications for TZM Moly usually involve service temperatures of 1093°C (2000°F) and above.

Since TZM Moly has excellent high temperature properties and outstanding thermal diffusivity, it has found extensive application to die casting and permanent molding tools, such as critical cores and die inserts used in the die casting of aluminum, copper, and zinc alloys. Even the ferrous die casting

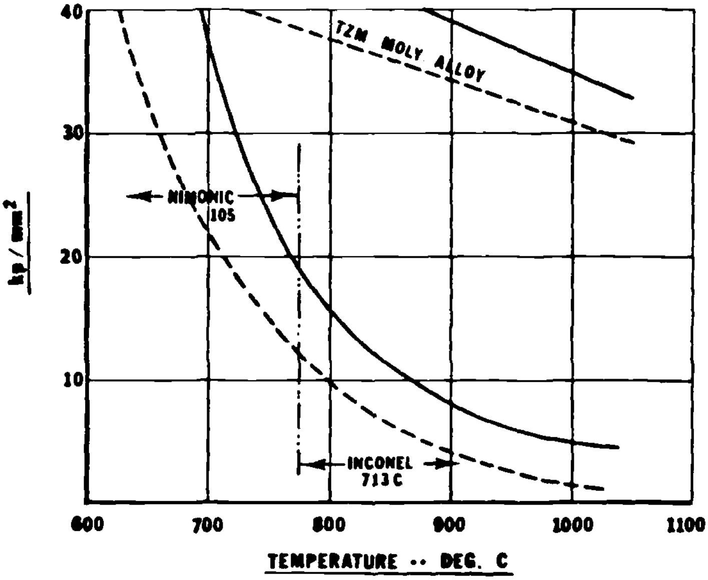

FIG. 6—*Average stress rupture strength of TZM Moly versus commercial superalloys (solid line = 10 000 h; dashed line = 100 000 h).*

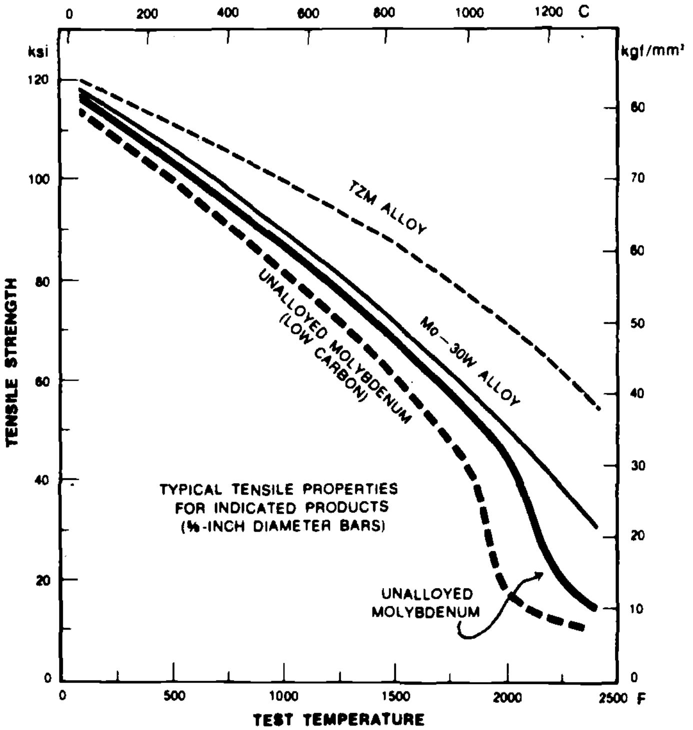

FIG. 7—*Tensile strength versus temperature for TZM Moly, unalloyed Moly, and Mo-30W alloy.*

process has become practical with heavy reliance upon TZM Moly die inserts and projection cores.

The U.S. automotive industry has been a particularly strong proponent of TZM Moly for aluminum die casting tools. A large aluminum compressor die casting has utilized 58 TZM Moly uncooled cores to cast a complex housing (Fig. 8).

In typical applications, the TZM Moly cores virtually eliminate solder and heat checking, and there is a dramatic reduction of required tool maintenance. TZM Moly also sees service in a host of hot work tool applications, in which the tools function at even higher temperatures.

In the hot extrusion of principally copper-base alloys, small TZM Moly extrusion die inserts or nibs are commonly employed for commercial production of barstock. Complex steel shapes also have been successfully extruded using TZM Moly working die inserts with a tool steel backing.

Bullet-shaped TZM Moly piercer points are used for the economic production of very long stainless steel tubes or for the most difficult-to-pierce stainless steel grades. TZM Moly high strength and hardness at the intense "red hot" tool temperatures and good resistance to thermal shock from pierce-to-

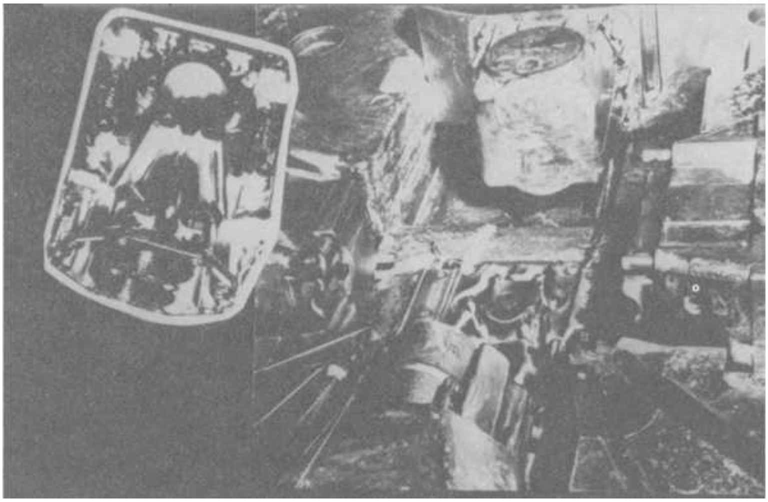

FIG. 8—*58 TZM Moly cores used to die cast aluminum compressor housing* (inset).

pierce often allow over 50 stainless steel tubes of uniform size to be made before reworking the point to the next smaller size.

A very significant hot-work tool application for TZM Moly is the isothermal forging process developed by Pratt & Whitney and designated the Gatorize™ process. In this process, large complex turbine disks are forged under vacuum in the superplastic range, where recrystallization and solutionizing occur simultaneously (Fig. 9). Usually difficult or impossible-to-fabricate two-phase nickel-base alloys and titanium alloys of high purity P/M origin are fabricated into near net shape turbine parts by employing TZM Moly heated dies. Dies nearly 1.2 m (4 ft) in diameter have been fabricated by conventional forging to produce these larger turbine disks for some of our most advanced aircraft engines. The principal attributes for the TZM Moly tools include high strength and creep resistance at service temperatures around 1093°C (2000°F) as well as a high level of resistance to recrystallization (and the accompanying marked reduction of strength) under this prolonged high temperature exposure.

The most critical Gatorize tool components were found to require unusual forged strength and hardness for practical service life. A unique fabrication technique ("Black Fabrication") was developed and patented to achieve ultra high strength TZM Moly knockout pins that improved tool component performance dramatically.

Another innovative process development that uses TZM Moly for hot-work tools is the Isothermal Shape Rolling™ (ISR) Process by Solar-Division of Caterpillar (Fig. 10). TZM Moly ring- or disk-shape rolls have been employed to form-roll "near net shapes" in difficult-to-work metals such as titanium

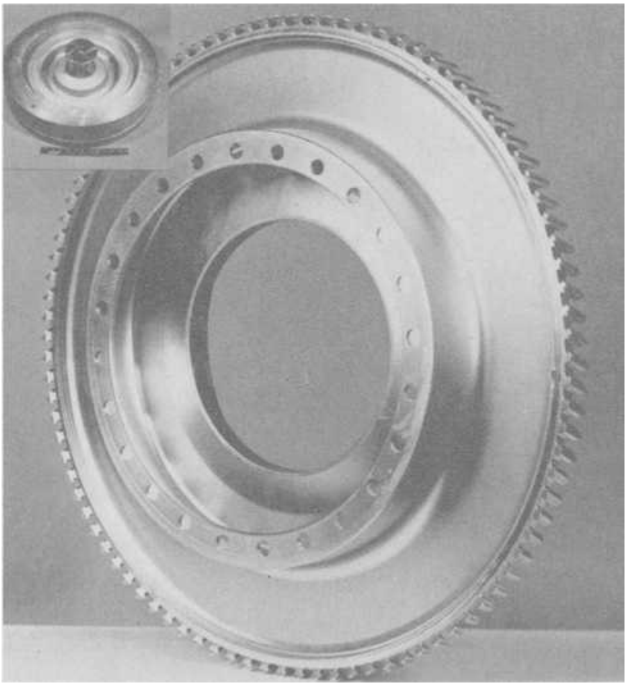

FIG. 9—*TZM Moly tools* (inset) *used to process (Gatorize method) large turbine disks.*

and the superalloys by resistance heating the workpiece through the electrically conductive shaping rolls. This process is reported to eliminate chill of the workpiece by the shaping tools as well as surface scale or subsurface contamination effects. Both the high temperature strength and the favorable electrical characteristics of TZM Moly are of value in this hot-work tool service.

The nuclear applications for Moly or TZM Moly have greatly fluctuated over the years—from the early potential fuel pin cladding material, to turbine components in a potassium-vapor turboalternator, to the SNAP-50/SPUR power conversion system, to nuclear fuel refinement equipment for the fast breeder reactor, to the latest fusion power reactor development for the CTR planned for commercial power generation in the 21st century.

The two containment methods for the fusion reaction of CTR being pursued are the magnetic and the inertial confinement. But the three-fold common goal for fusion remains: (1) creating sunlike temperatures, at least 100 million degrees C, in an ionized gas plasma, (2) then *densifying* by squeezing together more than 10^{14} particles/cm^3, (3) for a time period sufficient to obtain more energy output than input to heat the plasma. Either containment method may require TZM Moly or other refractory metals to serve for damage

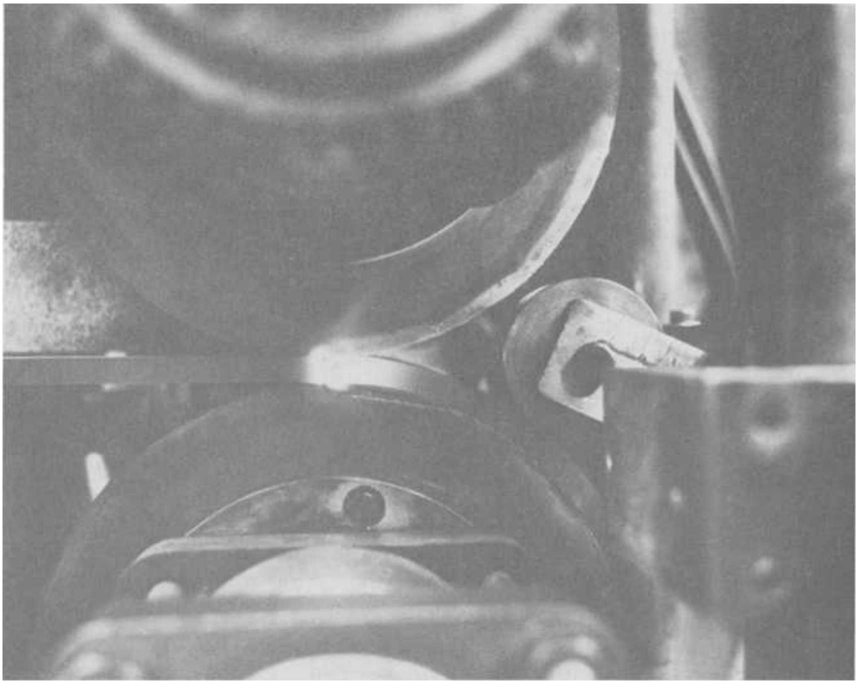

FIG. 10—*TZM Moly rolls used to heat and deform ISR near-net-shape superalloy.*

limiters, neutral beam injection, first wall structures to contain the plasma, high temperature ducts, or energy-concentrating laser mirror components. The low thermal expansion and good dimensional stability, low neutron capture power, chemical resistance to alkali metals, and excellent hot strength and creep resistance of TZM Moly are the properties of real concern for such diverse nuclear applications. The world's largest fusion test reactor, the Tokamak Fusion Test Reactor at Princeton, New Jersey, was scheduled for completion in late 1982. This torodial fusion reactor will consist of ten 72-ton modules and cost about one-third billion dollars.

There are many other TZM Moly uses. For instance, it is finding application for a variety of high inlet temperature, high pressure turbine engine components such as retainer rings, supports, hot gas seals and valves, and "special fabricated" turbine wheels or wheel blades. One special fabricated TZM Moly disk hub was electron-beam welded to a cast TZM blade ring and successfully spin tested as a 152-mm (6-in.)-diameter turbine wheel assembly for brief periods at turbine inlet temperatures approaching 1093°C (2000°F) and at speeds of well over 40 000 rpm!

A relatively recent market application for TZM Moly is that of hot gas valves and seals for high temperature gas systems, for purposes of control, proportional gas flow, diversion, or by-pass. The average 260°C (500°F) increased recrystallization temperature (softening temperature) for TZM Moly wrought products permits useful service at higher gas temperatures without the serious reduction of strength and hardness and the accompanying embrittlement of pure Molybdenum at high fuel combustion temperatures, usually above 1370°C (2500°F). The improved weldability of TZM Moly Alloy is an additional asset for such pressure-tight, plumbing-type hot gas control systems, often of complex design and with many, many joints. Of special interest are the numerous TZM Moly mechanical hot gas Gamah seals produced by Stanley Aviation Corporation that develop positive pressure sealing while maintaining good high temperature strength and resistance to creep or thermal shock in the new Trident submarine missile system.

Mo-30W Alloy

Another commercial molybdenum-base alloy, Mo-30W alloy, has gained some prominence beyond the initial higher melting temperature sought for missile and aerospace applications. The original Mo-30W solid-solution alloy (molybdenum and tungsten exhibit complete liquid solubility in all proportions) was developed to withstand erosion or incipient melting of rocket nozzles at higher propellant combustion temperatures. The 2832°C (5125°F) melting point of Mo-30W, 204°C (400°F) higher than Moly, satisfied this criterion in several applications. However, the most significant markets developed afterward because of the alloy's physical and chemical properties and adequate fabricability features.

The chemical inertness of Mo-30W in the presence of corrosive molten zinc, especially high purity grades such as special high grade zinc (99.99 Zn), was the key discovery that opened new markets to this refractory metal alloy. Although metallic tungsten also provides outstanding resistance to chemical attack by molten zinc, the Mo-30W alloy is readily machinable and capable of manufacture into a variety of wrought shapes including round bars, tubes, sheet, and plate, as well as simple assemblies. In addition to the basic metal properties of high strength and rigidity, Mo-30W wrought products exhibit useful ductility, especially if hot or unnotched. These products are readily fabricable into equipment components to function in aggressive molten zinc or even zinc vapors.

The earliest and most widespread use of Mo-30W in the zinc industry was for pump equipment, used to transfer or agitate molten metal with some control. Critical Mo-30W pump elements are employed in various type liquid-metal pumps with outstanding service records; in fact, the earliest known pump components have seen a decade of dependable pumping service in high purity molten zinc.

Centrifugal impeller-type pumps are widely employed for molten metal pumping, and the impeller shaft has proven the most crucial pump component in molten zinc service. The 63.5-mm (2½-in.)-diameter steel-reinforced impregnated graphite shaft for a commercial pump has been replaced with a 19.05 mm (¾-in.)-diameter Mo-30W alloy shaft in many installations and has provided several years of useful service. A bonus for the shaft conversion is the dramatic reduction of detrimental zinc dross formation resulting from the smaller-size Mo-30W shaft and the consequently much slower peripheral rotation speeds. A complete Mo-30W centrifugal-impeller pump comprising shaft, impeller, collector body, riser, discharge tube, and the required rod supports was fabricated for zinc pump development at a prominent zinc refinery (Fig. 11).

Simple propeller or paddle type mixers of various size have been fabricated from Mo-30W alloy, with good service reports in refining processes, preparation of zinc alloys, and reprocessing of spent nuclear fuels.

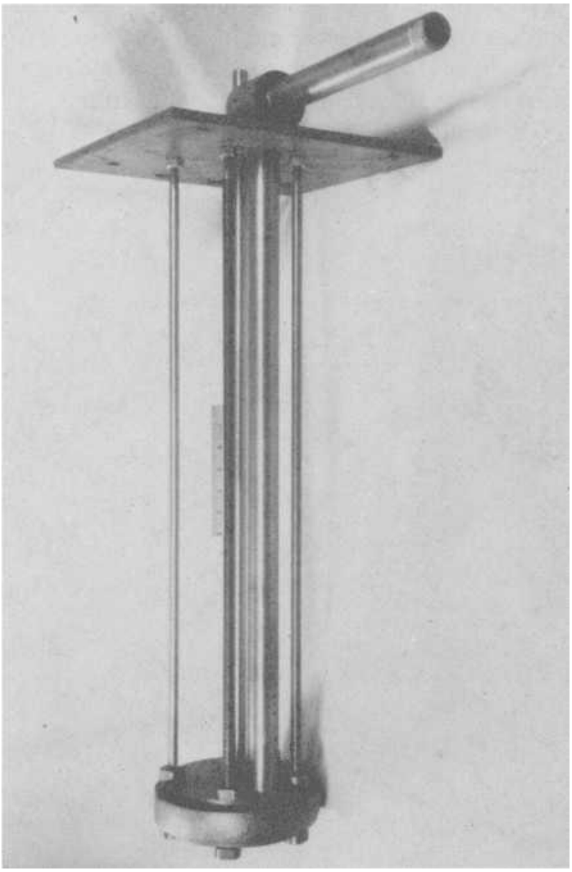

FIG. 11—*Complete impeller-type zinc pump constructed of Mo-30W; the pump diameter is 102 mm (4 in.).*

Several types of valves for the precision metering of zinc have been fabricated from Mo-30W. The major success for Mo-30W alloy is a three-piece needle valve (metering needle–delivery tube–valve chamber) used to precisely control the flow of molten zinc to a Properzi continuous casting wirebar machine (Fig. 12). The highly erratic performance of the original porcelainized steel valve assembly averaged some 11 340 kg (25 000 lb) of zinc wirebar product, whereas the Mo-30W assembly had accounted for nearly 4 535 900 kg (10 million pounds) of product at last check.

Up to 50.8-mm (2-in.)-diameter Mo-30W conductor tubes and thermocouple protection tubes (thermotubes) have been used in the development of vapor deposition processes for zinc, in the remote transfer of nuclear fuel refining metal mixtures, and in various galvanizing operations. In addition to the high resistance to chemical attack by corrosive zinc for Mo-30W alloy, the higher thermal conductivity and low specific heat of the metal make for more precise temperature sensing and much faster response to temperature change for such thermotubes than for common refractory silicon carbide or steel protection tubes. Another advantage of metallic Mo-30W thermotubes is the greatly enhanced mechanical and thermal shock resistance. This resistance is useful because detrimental conditions are prevalent where solids are charged into the molten zinc bath.

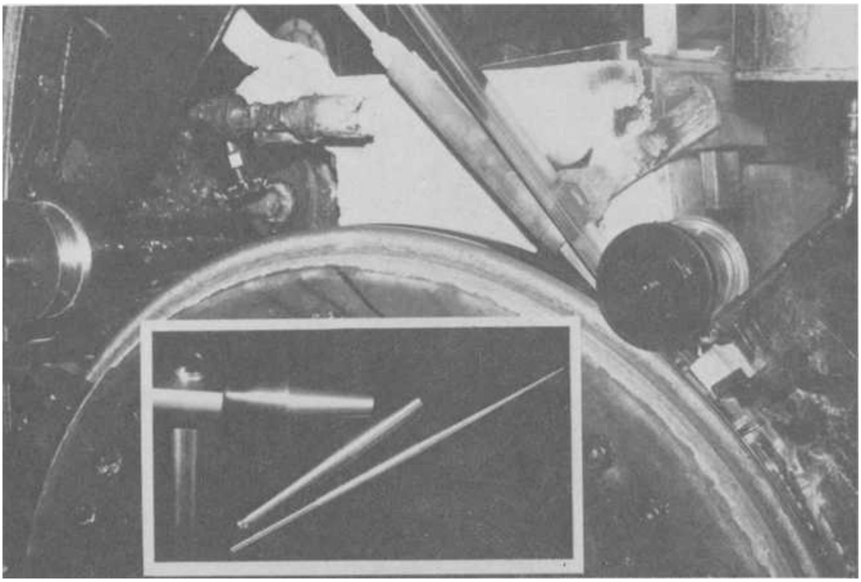

FIG. 12—*Properzi continuous casting wirebar machine showing metering valve assembly and Mo-30W components* (inset).

Summary

Moly and several Moly-base alloys produced by either the vacuum-arc casting method or the powder/metallurgy method of consolidation have been commercially used for principally high temperature applications in hot equipment, hot working tools, and hot operating machines. This refractory metal possesses the unique combination of physical, chemical, and mechanical properties required for such high temperature, high stress service.

Further information on molybdenum can be found in the author's "Molybdenum—A Super Superalloy," *Journal of Metals*, December 1977.

R. T. Webster[1]

Niobium in Industrial Applications

REFERENCE: Webster, R. T., **"Niobium in Industrial Applications,"** *Refractory Metals and Their Industrial Applications, ASTM STP 849*, R. E. Smallwood, Ed., American Society for Testing and Materials, Philadelphia, 1984, pp. 18-27.

ABSTRACT: This paper discusses niobium in industrial applications. Niobium is principally used as an alloying element in specialty steels and superalloys and as a carbide in cutting tools for machinery. Niobium alloys containing tin or titanium have become the primary materials used in superconducting applications.

KEY WORDS: niobium, applications, fabrication, welding, corrosion resistance

Niobium, a refractory metal with properties resembling tantalum, has been used in industrial applications for several decades. Niobium ore is often found in mineral deposits that also contain tantalum, such as the tin ores from Malaysia. On the other hand, many mineral formations contain significant quantities of niobium with little associated tantalum; these formations are found in Brazil, Canada, and many African countries.

Niobium is principally used as an alloying element in specialty steels and superalloys and as a carbide in cutting tools for machinery.

Niobium, as a metal, had its first major application in nuclear reactors because of its excellent corrosion resistance in the containment of liquid metals. The next major application was in aerospace rocket motors because of its high temperature properties. It is also used in the skin and structural members of space vehicles. Niobium is increasingly being used in chemical corrosion-resistant applications because it has a corrosion resistance to most media similar to that of tantalum. Because of its high corrosion resistance to liquid sodium, niobium is used in sodium vapor lights.

Niobium alloys containing tin or titanium have become the primary materials used in superconducting applications.

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Physical Properties

Niobium is a soft, ductile primary metal. It is silvery gray in appearance, something like stainless steel. Its density of 8.6 g/cm^3 is somewhat greater than steel but considerably less than the majority of high melting point metals such as tungsten and tantalum. Table 1 lists the physical properties of niobium.

Mechanical Properties

The mechanical properties of niobium are comparable to those of metals such as titanium, vanadium, and tantalum. Table 2 lists the mechanical properties of niobium.

Corrosion Resistance

General Corrosion Data

Niobium, like other refractory metals, owes its corrosion resistance to a readily formed, adherent, passive oxide film. Because the corrosion properties of niobium resemble those of tantalum and because it is less expensive, niobium should be considered in all applications requiring tantalum.

TABLE 1—*Physical properties of niobium.*

Melting point, °C	2468
Boiling point, °C	5127
Density, g/cm^3	8.66
Crystal structure	body centered cubic
Lattice constant, Å	3.30
Covalent radius, Å	1.34
Thermal neutron absorption cross section, barns	1.1
Electronegativity, Paulings	1.6
Thermal conductivity	
0°C, J (s cm °C)	0.523
1600°C, J (s cm °C)	0.691
Coefficient of thermal expansion at 20°C ($\times 10^{-6}$/°C)	7.1
Electrical resistivity, $\mu\Omega$	15
Temperature coefficient ($\times 10^{-3}$/°C)	3.95
Volume electrical conductivity, %IACS[a]	13.3
Special heat	
15°C, J/g	0.268
1227°C, J/g	0.320
Heat capacity (Cp), J/mol °C	
0°C	24.9
1200°C	29.7
2700°C	33.5

[a] International Annealed Copper Standard.

TABLE 2—*Mechanical properties of niobium.*

Modulus of elasticity, GPa	1.034
Poisson's ratio	0.38
Hardness (VHN)	77 to 170
Ultimate tensile strength, MPa	170 to 550
Yield strength, MPa	100 to 275
Elongation, % in 51 mm	15 to 40

Niobium is slightly less resistant than tantalum in aggressive media (for example, in hot concentrated mineral acids). Table 3 gives some typical corrosion data for niobium. Like tantalum, niobium is susceptible to hydrogen embrittlement if cathodically polarized by galvanic coupling or by impressed potential. In addition to being very stable, the anodic niobium oxide film has a high dielectric constant and a high breakdown potential. These properties, coupled with its good electrical conductivity, have led to niobium's use as a substrate for platinum-group metals in impressed-current cathodic-protection anodes.

Acid Solutions

Niobium is resistant to most organic acids and mineral acids at all concentrations below 100°C except hydrofluoric acid. This list of acids includes the halogen acids (hydrochloric, hydroiodic, and hydrobromic), nitric acid, sulfuric acid, and phosphoric acid. Niobium is especially resistant under oxidizing conditions (for example, concentrated sulfuric acid and ferric chloride or cupric chloride solutions). Niobium is completely resistant in nitric acid, having a corrosion rate of 0.025 mm/year (1 mpy) in 70% nitric acid at 250°C. It is completely resistant in dilute sulfurous acid at 100°C. In concentrated acid, at the same temperature, niobium has a corrosion rate of 0.25 mm/year (10 mpy). In chrome-plating solutions, niobium experiences only a slight weight change, and in the presence of small amounts of fluoride catalyst, it exceeds the corrosion resistance of tantalum.

Niobium is inert in mixtures of nitric acid and hydrochloric acid. It has a corrosion rate of less than 0.025 mm/year (1 mpy) in aqua regia at 55°C. In boiling 40 and 50% phosphoric acid with small amounts of fluoride ion impurity (5 ppm), niobium has a corrosion rate of 0.25 mm/year (10 mpy). In mixtures of nitric acid and sulfuric acid, niobium dissolves readily.

Alkaline Solutions

In ambient aqueous alkaline solutions, niobium has corrosion rates of less than 0.025 mm/year (1 mpy). At higher temperatures, even though the corrosion rate does not seem excessive, niobium is embrittled even at low concentrations (5%) of sodium hydroxide and potassium hydroxide. Like tantalum, niobium is embrittled in salts that hydrolyze to form alkaline solutions. These salts include sodium and potassium carbonates and phosphates.

Salt Solutions

Niobium has excellent corrosion resistance in salt solutions, except those that hydrolyze to form alkalis. It is resistant to chloride solutions even with oxidizing agents present. It does not corrode in 10% ferric chloride at room temperature, and it is resistant to attack in seawater. Niobium exhibits resistance similar to tantalum in salt solutions.

Gases

Niobium is easily oxidized. It will oxidize in air above 200°C. The reaction, however, does not become rapid until above red heat (about 500°C). At 980°C, the oxidation rate is 0.05 mm/year (17 000 mpy). In pure oxygen, the attack is catastrophic at 390°C. Oxygen freely diffuses through the metal causing embrittlement. Niobium reacts with nitrogen above 350°C; with water vapor above 300°C; with chlorine above 200°C; and with carbon dioxide, carbon monoxide, and hydrogen above 250°C. At temperatures of 100°C, niobium is inert in most common gases (for example, bromine, chlorine, nitrogen, hydrogen, oxygen, carbon dioxide, carbon monoxide, and wet or dry sulfur dioxide.

Liquid Metals

Niobium is resistant to attack in many liquid metals to relatively high temperatures. These include bismuth below 510°C; gallium below 400°C; lead below 850°C; lithium below 1000°C; mercury below 600°C; sodium, potassium, and sodium-potassium alloys below 1000°C; thorium-magnesium eutectic below 850°C; uranium below 1400°C; and zinc below 450°C. The presence of oxygen in excess of 700 ppm in liquid metals may reduce niobium's resistance to these liquid metals.

Galvanic Effects

If niobium is polarized cathodically by galvanic coupling or chemical attack, it can be destroyed by hydrogen embrittlement. For this reason niobium cannot be protected from these processes by cathodic protection. If niobium is polarized anodically, however, it forms a very stable, passive film which protects the metal from corrosion. This property, combined with good electrical conductivity (13% that of copper) and good mechanical properties, has lead to the use of niobium as a substrate metal for platinum in impressed-

TABLE 3—*Corrosion data for niobium in aqueous media.*

	Concentration, wt%	Temperature, °C	Corrosion Rate, mm/year (mpy)
	Acid Solutions		
Hydrochloric acid	1	boiling	nil
Hydrochloric acid (aerated)	15	RT-60	nil
Hydrochloric acid (aerated)	15	100	0.025 (1.0)
Hydrochloric acid (aerated)	30	35	0.025 (1.0)
Hydrochloric acid (aerated)	30	60	0.05 (2.0)
Hydrochloric acid (aerated)	30	100	0.125 (5.0)
Hydrochloric acid	37	RT	0.025 (1.0)
Hydrochloric acid	37	60	0.25 (10)
Hydrochloric acid	37% with Cl_2	60	0.5 (20)
Hydrochloric acid	10% with 0.1% $FeCl_3$	boiling	0.025 (1.0)
Hydrochloric acid	10% with 0.6% $FeCl_3$	boiling	0.125 (5.0)
Hydrochloric acid	10% with 35% $FeCl_2$ and 2% $FeCl_3$	boiling	0.05 (2.0)
Nitric acid	65	RT	nil
Nitric acid	70	250	0.025 (1.0)
Phosphoric acid	60	boiling	0.5 (20)
Phosphoric acid	85	RT	0.0025 (0.1)
Phosphoric acid	85	88	0.05 (2.0)
Phosphoric acid	85	100	0.125 (5.0)
Phosphoric acid	85	boiling	3.75 (150)
Phosphoric acid	85% with 4% HNO_3	88	0.025 (1.0)
Phosphoric acid	40-50% with 5 ppm F^-	boiling	0.25 (10)
Sulfuric acid	5-40	RT	nil
Sulfuric acid	98	RT	embrittle
Sulfuric acid	10	boiling	0.125 (5.0)
Sulfuric acid	25	boiling	0.25 (10)
Sulfuric acid	40	boiling	0.5 (20)
Sulfuric acid	40% with 2% $FeCl_3$	boiling	0.25 (10)
Sulfuric acid	60	boiling	1.25 (50)
Sulfuric acid	60% with 0.1-1% $FeCl_3$	boiling	0.5 (20)
Sulfuric acid	20% with 7% HCl and 100 ppm F^-	boiling	0.25 (10)
Sulfuric acid	50% with 20% HNO_3	50 to 80	nil
Sulfuric acid	50% with 20% HNO_3	boiling	0.25 (10)
	Organic Acids		
Acetic acid	5-99.7	boiling	nil
Citric acid	10	boiling	0.025 (1.0)
Formaldehyde	37	boiling	0.0025 (0.1)
Formic acid	10	boiling	nil
Lactic acid	10-85	boiling	0.025 (1.0)
Oxalic acid	10	boiling	1.25 (50)
Tartaric acid	20	RT to boiling	nil
Trichloroacetic	50	boiling	nil
Trichloroethylene	99	boiling	nil

TABLE 3—*(continued)*.

	Concentration, wt%	Temperature, °C	Corrosion Rate, mm/year (mpy)
	Alkalines		
NaOH	1-40	RT	0.125 (5.0)
NaOH	1-10	98	embrittle
KOH	5-40	RT	embrittle
KOH	1-5	98	embrittle
NH_4OH		RT	nil
	Salts		
$AlCl_3$	25	boiling	0.005 (0.2)
$Al_2(SO_4)_3$	25	boiling	nil
$AlK(SO_4)_2$	10	boiling	nil
$CaCl_2$	70	boiling	nil
$Cu(NO_3)_2$	40	boiling	nil
$FeCl_3$	10	RT-boiling	nil
$HgCl_2$	saturated	boiling	0.0025 (0.1)
K_2CO_3	1-10	RT	0.025 (1.0)
K_2CO_3	10-20	98	embrittle
K_3PO_4	10	RT	0.025 (1.0)
$MgCl_2$	47	boiling	0.025 (1.0)
$NaCl_2$	saturated and pH=1	boiling	0.025 (1.0)
Na_2CO_3	10	RT	0.025 (1.0)
Na_2CO_3	10	boiling	0.5 (20)
Na_2HSO_4	40	boiling	0.125 (5.0)
NaOCl	6	50	1.25 (50)
Na_3PO_4	5-10	RT	0.025 (1.0)
Na_3PO_4	2.5	98	embrittle
NH_2SO_3H	10	boiling	0.025 (1.0)
$NiCl_3$	30	boiling	nil
$ZnCl_2$	40-70	boiling	nil
	Miscellaneous		
Bromine	liquid	20	nil
Bromine	vapor	20	0.025 (1.0)
Chrome plating Solution	25% CrO_3, 12% H_2SO_4 H_2O	92	0.125 (5.0)
Chrome plating Solution	17% CrO_3, 2% Na_2SiF_6, trace H_2SO_4 H_2O	92	0.125 (5.0)
H_2O_2	30	RT	0.025 (1.0)
H_2O_2	30	boiling	0.5 (20)

current cathodic-protection anodes. Its anodic breakdown potential in chloride solutions is about 115 V compared with 10 V for titanium. Niobium platinized anodes are used in high resistivity waters and other environments requiring high driving potential to obtain good current spread. In this application, niobium has an advantage over tantalum, because it is less expensive. The cost can be further decreased by using a composite electrode with a copper core, which increases the conductivity of the anodes.

Fabrication

General Working Characteristics

Two features affect the working characteristics of niobium. First, because of its high melting temperature (approximately 2400 °C) no appreciable softening occurs below 400 °C (the temperature at which niobium reacts vigorously with the atmosphere). Secondly, sheathing for protection is not practical, because the sheathing material is likely to be softer than the metal to be worked.

Niobium's cold-working properties are excellent, since the metal can be easily forged, rolled, or swaged directly from the ingot at room temperature. After the cross-sectional area has been reduced by about 90%, annealing is necessary. Heat treatment at 1200 °C for 1 h causes complete recrystallization of material cold-worked over 50%. The annealing process must be performed in a high purity inert gas or in a high vacuum at pressures below 1×10^{-4} torr. The use of a vacuum is preferred, because it is difficult to ensure the purity of inert gas. It is also less expensive to use vacuum furnaces for these operations.

Niobium is well suited to deep drawing, and the metal may be cupped and drawn to tube, although special care must be taken with lubrication. The sheet metal can be easily formed by general sheet metal working techniques. The low rate of work hardening facilitates these operations by reducing springback.

Machining

Niobium may be machined by the usual techniques, although owing to the tendency of the material to gall, special attention should be paid to tool angles and lubrication. Recommended tool angles and speeds are given in Table 4.

Turning

Lathe turning is best carried out with high speed steel tools, using air, soluble oil, or other suitable products for cooling and lubricating. This material turns very much like lead or soft copper; it must be sheared and the chip

TABLE 4—*Recommended tool angles and speeds.*

Approach angle	15 to 20 deg
Side rake	30 to 35 deg
Side and end clearance	5 deg
Cutting speed	3 to 4 m/s with high-speed steel 13 to 15 m/s with carbide

allowed to slide off the tool surface. If any buildup of the material is allowed, the pressure will break the cutting edge and ruin the tool. Carbide tooling should be used only for fast, light cuts, with a depth of 0.25 to 0.38 mm (0.010 to 0.015 in.), to work efficiently.

Drilling

Standard high speed drills, ground to normal angles, may be used, but the peripheral lands wear badly and care must be taken to see that the drill has not worn undersize.

Screw Cutting

Provided that plenty of lubricant is used, niobium may be screw-cut using a standard die-cutting head. The use of ample lubricant prevents galling on the die and consequent tearing of the thread. Roll threading is the preferred method.

Spinning

Normal techniques of metal spinning may be applied successfully to niobium, with minor modifications. It is generally better to work the metal in stages; for instance, when spinning a right-angled cup from flat sheet, several formers should be used to give steps of approximately 10 deg. Wooden formers may be used for rough spinning, but a brass or bronze former is essential for finishing because the metal is soft and takes up the contour of the former. For small work, aluminum, bronze, or Narite tools should be used with a radius of approximately 9.5 mm (3/8 in.). (If sharp angles are required, the tool must be shaped accordingly.) Yellow soap, or tallow, is suitable for lubricating the material, which must be cold worked continually. The peripheral speed of the work-piece should be about 152 m/min (500 ft/min). When spinning, niobium is prone to "thinning" and care must be taken to avoid this. The tool should be worked in many long sweeping strokes using a light pressure rather than a few heavy strokes.

Welding

Because niobium is a reactive metal, proper precautions must be exercised to avoid contamination during welding. Most of the common electric welding techniques can be employed in welding niobium and its alloys, provided that this high reactivity with the elements found in air and dirt, grease, and other contaminants its taken into account. Fluxes cannot be used, since they will form brittle compounds with niobium.

Arc Welding

The most common weld method is gas tungsten arc welding (GTAW) using direct current, straight polarity, and high frequency arc initiation.

Welding may be performed in air with proper inert gas shielding. The front and back sides of the welds, as well as the heat-affected zone near the weld, must be protected from the atmosphere. Shielding can be accomplished by constructing a gas passage for the back side of the weld and using the shielding gas from the torch and a trailing shield. For welds that are difficult to completely cover with inert gas, a flush chamber can be constructed of metal or plastic to completely enclose the weld area.

For critical welds where the best mechanical properties must be achieved, the use of vacuum weld chambers is recommended. The air can be removed from the chamber and backfilled with inert gas to completely eliminate contamination from air.

Evidence of contamination of the weld is readily observed, since any discoloration of the normal silver, bright appearance of niobium weldments is an indication of absorbed oxygen. Adverse amounts of contamination can be checked by performing hardness and bend ductility tests.

Resistance Welding

While tungsten-inert-gas (TIG) welding is the preferred method for welding niobium sheet in thicknesses of 0.51 mm (0.020 in.) or greater, the method is somewhat limited for thinner sheet. It is possible to weld sheet as thin as 0.30 mm (0.012 in.) or even thinner, but special attention must be paid to the shape of the electrode tip. Extremely careful jigging is essential for accurate alignment and prevention of distortion and misalignment during welding. For sheet thinner than 0.51 mm (0.200 in.), it is generally better to use the resistance method of welding.

The problem of contamination during resistance welding is not as great as in TIG welding, because the duration of the weld can be kept short. Spot welding may be carried out in air, provided the weld time is restricted to one or two cycles, but seam welding should be carried out under water. The water does not protect the weld from contamination in the same way as the argon shield does during arc welding. Its function is to remove heat from the weld as quickly as possible, thus keeping the time that the metal is hot to a minimum.

Transformer or stored energy type equipment can be used, but the welding heads should be of the low-inertia type so that, as the welds are made, proper pressure will be maintained throughout the welding cycle. The surfaces to be welded should be cleaned and degreased before welding. Any copper pick-up from the electrode that contaminates the sheet after welding may be removed by pickling in nitric acid.

Other Welding Methods

Niobium can be welded by electron beam and laser beam methods.

F. J. Hunkeler[1]

Properties of Tantalum for Applications in the Chemical Process Industry

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REFERENCE: Hunkeler, F. J., **"Properties of Tantalum for Applications in the Chemical Process Industry,"** *Refractory Metals and Their Industrial Applications, ASTM STP 849,* R. E. Smallwood, Ed., American Society for Testing and Materials, Philadelphia, 1984, pp. 28-49.

ABSTRACT: A comparison of the basic properties of tantalum with other high-performance metals and alloys used in the chemical process industry (CPI) is given. It is pointed out that the electrochemically passivating oxide film that spontaneously forms on tantalum is responsible for its extraordinary performance. It is the premier example of this type of corrosion resistance and accounts for tantalum having the most effective resistance over the broadest range of acidic media conditions. The fabrication characteristics of tantalum and the variety of equipment available are described. Tantalum's performance characteristics and limitations in several CPI environments are discussed in relation to other commonly used metals.

KEY WORDS: tantalum, chemical process industry, corrosion resistance

Consideration of tantalum's position in the periodic table provides a reasonably good inference of its categorical properties (Fig. 1). It is typically one of the "reactive metals." Many of its prominent features resemble those of titanium and zirconium, and it is reasonably compatible and comparable with those metals as well as with molybdenum and tungsten. All these "reactive-refractory" metals have good strength, show considerable metallurgical and chemical interactivity with other elements, and each seems to have at least one outstanding attribute that makes it especially useful for some chemical, electronic, nuclear, or thermal application.

These metals combine strongly with oxygen, carbon, nitrogen, and other metals and nonmetals outside their group, and many of their properties are

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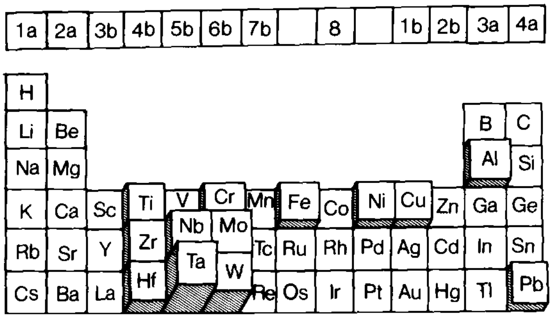

FIG. 1—*Periodic table.*

quite sensitive to relatively small amounts of other atomic species. Because of this reactivity these metals must be fabricated to finished products under closely controlled processing conditions. This behavior is also a very important source of their most useful attributes, however, and the strong oxide, carbide, and nitride formations are the bases of their most prominent uses. In particular, it is the special oxide characteristics that provide the chemical passivation responsible for high chemical resistances in certain chemical environments which can be almost equivalent to the inertness of the more noble metals.

Basic Pertinent Characteristics

Quantitative Physical Properties

Figures 2 to 7 can be used to compare the relative effectiveness to tantalum in engineering applications to the other most commonly used chemical process industry (CPI) metals. The values presented are those of the pertinent commercial grades of each metal and are the practical engineering values rather than scientific-pure element measurements. The thermal and electrical conductivities (Figs. 2 and 3) of tantalum are quite high relative to many of the other base metals and are considerably better than widely used alloys such as Hastelloys, stainless steels, and Monel.

Tantalum also has a usefully high value of elastic modulus (Fig. 4), a desirable characteristic for provision of structural rigidity of engineering components. Note that tantalum's value of elastic modulus is equivalent to those of nickels and steels and considerably more than those of brasses, aluminums, titanium, glasses, and graphite. In addition, this value does not decrease significantly when tantalum is heated to higher temperatures.

Figure 5 shows that tantalum's basic tensile strength properties also approach equivalency with other base metals used for structural chemical equipment. By yield strength criteria tantalum is actually more mechanically

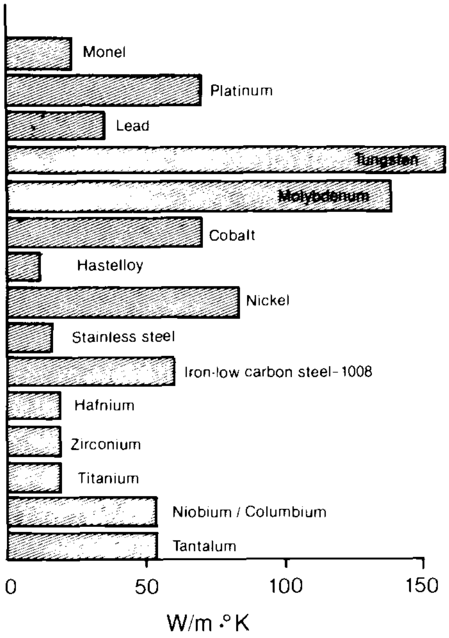

FIG. 2—*Thermal conductivity of commercially pure grades of commonly used metals for CPI equipment and for some of their derived alloys.*

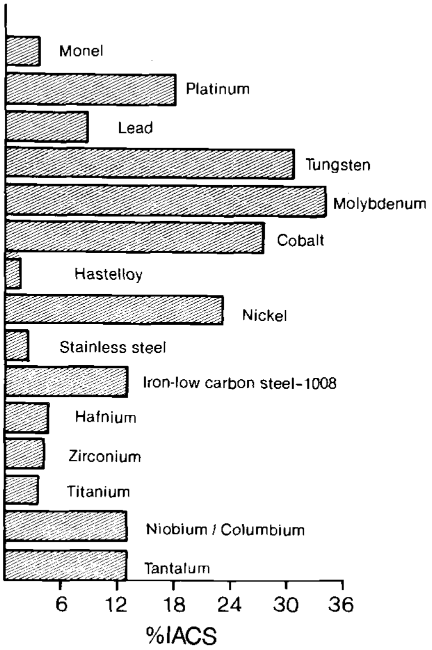

FIG. 3—*Electrical conductivity of commercially pure grades of commonly used metals for CPI equipment and for some of their derived alloys.*

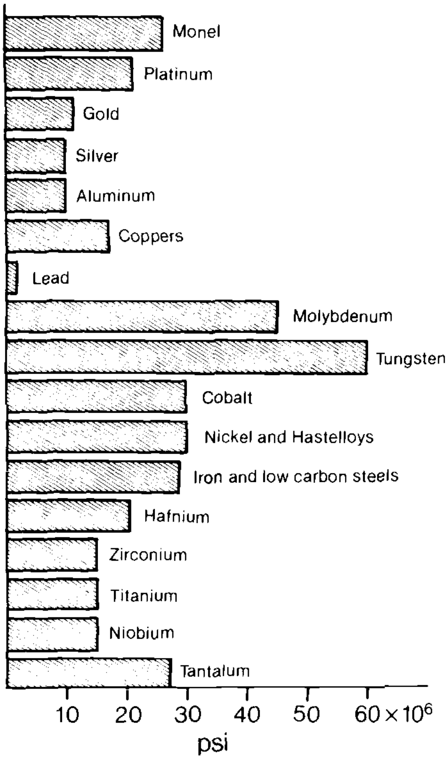

FIG. 4—*Tensile elastic modulus of commercially pure grades of commonly used metals for CPI equipment and for some of their derived alloys.*

deformation resistant than the unalloyed coppers and nickels and is comparable to the higher purity grades of titanium, zirconium, and steel. Like these, tantalum is also amenable to development of higher strength compositions by addition of modest amounts of solid-solution alloying species which do not seriously detract from corrosion performance. To date, however, enough serious demand has not arisen to require the practical development effort to make these higher strength compositions available beyond the moderate enhancement of strength levels provided by vacuum arc melting and alloying with 2.5% tungsten.

Figure 6 shows the strength levels of tantalum and other metals at temperatures up to 200°C (390°F). The values are given in ranges in order to include the various compositional grades of the metals. The slopes as well as the levels of the lines are significant. These data show that up to temperatures of 200°C or more tantalum strengths equivalent to the other (unalloyed) structural metals are maintained. The decrease in ductility of the tantalum at the higher strength and higher temperature levels is not enough to be of concern.

The economic aspect of tantalum usually requires that the price be considered a fundamental engineering property. Figure 7 shows some cost values in

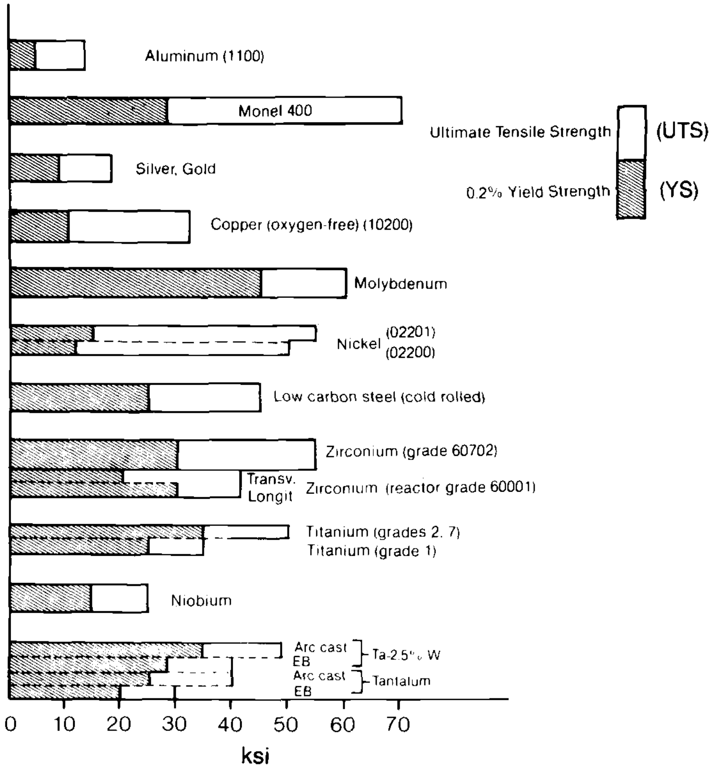

FIG. 5—*Tensile strength of commercially pure grades of commonly used metals for CPI equipment and for some of their derived alloys (ASTM minimum values).*

the same manner as the other properties in order to give a simplistic but reasonable comparative assessment of that factor. The fabricated item cost takes into account the not-more-expensive labor costs of fabricating out of tantalum. The cost of the tantalum equipment is still considerably greater than that of the other readily available high-performance metals, but the scale of comparison can be used to indicate whether other compensating trade-offs such as extended life, improved operating efficiencies, and thinner metal requirements with tantalum justify the initially higher cost. The ingot prices are compiled from commercial market data as of early 1982. The fabricated item prices are projected from average known labor and design data and from comparative quotes for equipment designed for the same service from each metal.

Chemical Aspects

Two basic chemical mechanisms determine the extent of reaction or nonreaction of metals with environments. One is the intrinsic chemical affinity of

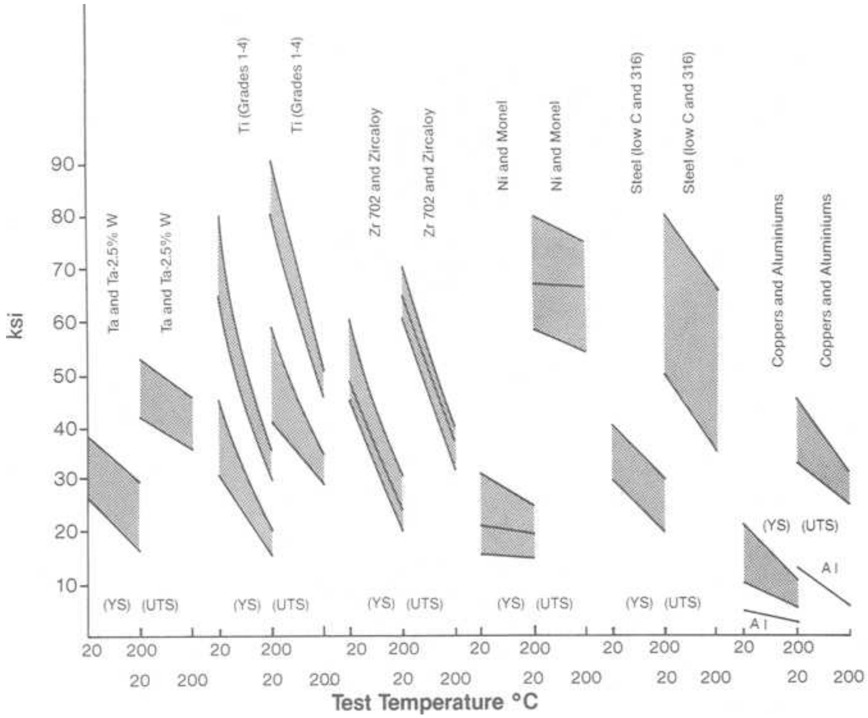

FIG. 6—*Comparison of typical ranges of tensile strength values at 20 and 200°C of metals and alloys commonly used for CPI equipment.*

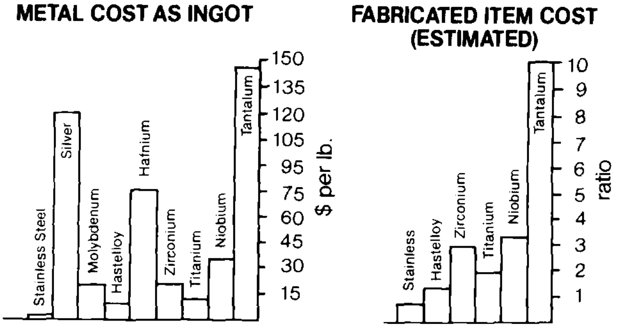

FIG. 7—*Estimated relative cost of metals at ingot stage and as finished fabricated equipment.*

the metal with the environmental species; the other is the formation of a protective passivating surface composition on initial or previous exposure to an oxygen-containing environment. The former accounts for the "noble" and "semi-inert" behavior of many of the common metals such as gold, silver, and copper in certain chemical media. Many of the most commonly used metals exhibit some degree of each type of response, depending on the specifics of the chemical conditions, and therefore are amenable to "tailoring" of their composition to particular circumstances by alloying. Hastelloys, bronze, and stainless steel are examples. The reactive-refractory metals depend entirely on the passivation mechanism. In particular, a spontaneously forming oxide is the determining factor in their corrosive response. Tantalum is not only characteristic of these in its behavior, it is probably the ideal example of this class of materials.

Oxides such as these do not necessarily have the same atomistic construction as the familiar bulk oxides but exist with a variety of structural forms and chemical compositions which account for various degrees of physicochemical behavior. Some of these films are apparently amorphous rather than crystalline. They are of just the correct density to exist on the metal surface without physical flaws and can deform with it without damage. The metal in a strict sense is a composite material with very special optimum electrical and chemical properties under certain situations. The primary reason for tantalum's commercial development is that the oxide film on the anodized metal exhibits such strong stable dielectric action that it is used for highly effective electronic capacitors. The oxide film is extremely thin (Angstrom dimensions), adherent, stable and durable, and is electrically rectifying. It so strongly inhibits the transfer of ions and electrons that it is essentially impervious to a wide range of electrochemical media, and is self-limiting of its own thickness growth.

These protective oxide films do have limitations in their susceptibility to certain chemical species and can be compromised beyond certain ranges of temperatures, concentration, and electrochemical potential. Tantalum's extraordinary corrosion immunity indicates that its passivating oxide has the broadest range of resistance with respect to chemical and thermal breakdown susceptibility. In addition, it forms and persists even in extremely oxygen-deficient environments. Under conditions where the immunity is lost, however, the metal will lose corrosive resistance dramatically. This occurrence has a positive aspect, since the limiting conditions for effective behavior can be relatively well defined.

Figure 8 compares the relatively wide range of acidic electrochemical conditions over which tantalum is highly effective with the ranges of the other most effective corrosion-resistant materials employed in the chemical industry. The analogy to the conditions over which glass is effective is a good one. Actually, this chart somewhat understates the relative capabilities of tantalum since it does not indicate the temperature ranges of effectiveness and be-

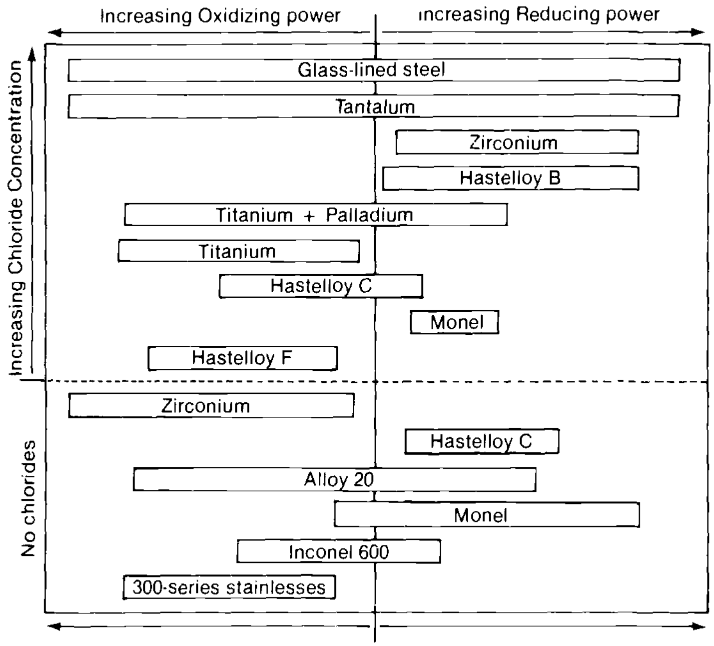

FIG. 8—Comparative general corrosion resistance of several metals and alloys in various acid environments. The figure illustrates the range of conditions of oxidizing and reducing power and chloride concentration which the materials withstand effectively.

cause it only describes the resistances qualitatively. "Effectiveness" for most metals usually is based on 5, 10, or 20 mil per year (mpy) corrosion rates, whereas for tantalum it is defined more closely to zero or at 1 to 2 mpy.

The conditions under which tantalum is most appropriately used can generally be best defined as those for which these other materials have some critical degree of susceptibility to metal loss or damage, or in situations for which little or no metallic corrosion products can be tolerated. Tantalum's most widespread usage is generally associated with the higher concentrations and temperatures of sulfuric acid (H_2SO_4) processing. High-concentration, high-temperature hydrochloric acid (HCl) media also frequently require tantalum equipment. Tantalum is also used in nitration processes, processes involving organic chlorides, and in bromine production. Tantalum is particularly appropriate in these and other solutions wherein there are contaminants of species which are highly aggressive to the normally used materials, or in situations where there may be uncontrollable temperature or composition excursions. Flouride ions, sulfur trioxide, and a few uncommon complex ions must be avoided, however.

Applications

Tantalum's high degree of fabricability allows that almost any equipment design can be constructed with it. In view of the aforementioned favorable engineering properties, a wide range of both standard and custom design apparatus of tantalum is industrially appropriate. Also, because of tantalum's relatively high base metal price, there is a considerable amount of lined equipment construction wherein other materials are mechanically surface clad with tantalum. Figure 9 shows a tantalum patch kit assembly used for the repair of damages which regularly occur in glass-lined equipment, and Fig. 10 shows a standard thermowell widely used in the process industry. These two items are probably the most common simple examples of the utilization of the metal's high durability. The duplex stainless steel/tantalum expansion joint bellows (Fig. 11), the packing support screen (Fig. 12), and the lined shell (Fig. 13) are good illustrations of tantalum equipment components where the high degree of fabricability allows considerable economic benefit.

Tantalum's essentially zero metal loss due to corrosion in most applications

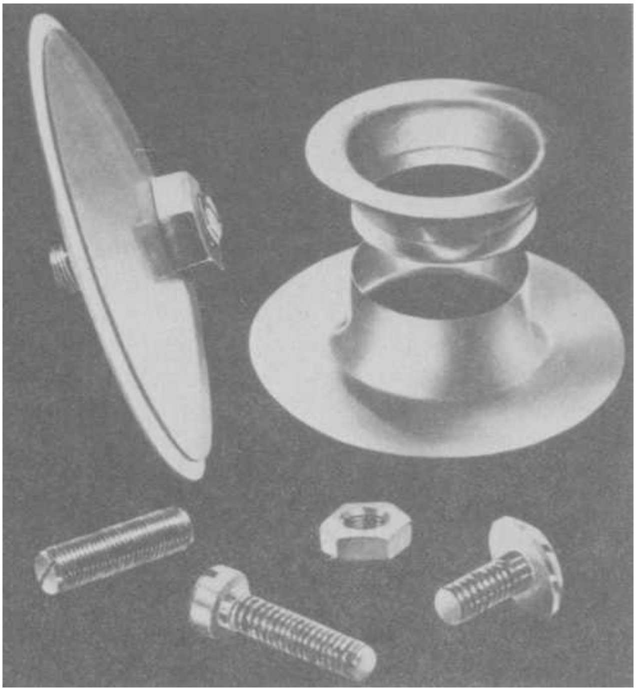

FIG. 9—*Tantalum patch kit assembly.*

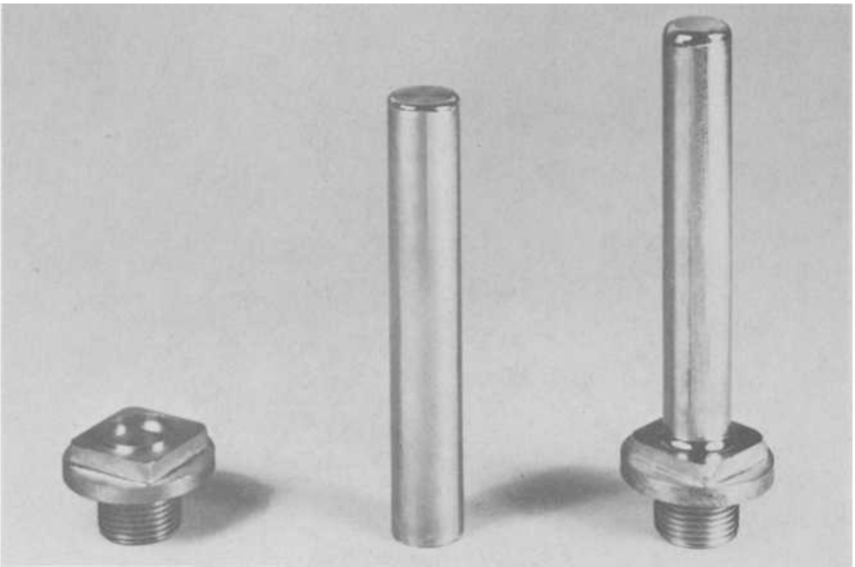

FIG. 10—*Tantalum thermowells.*

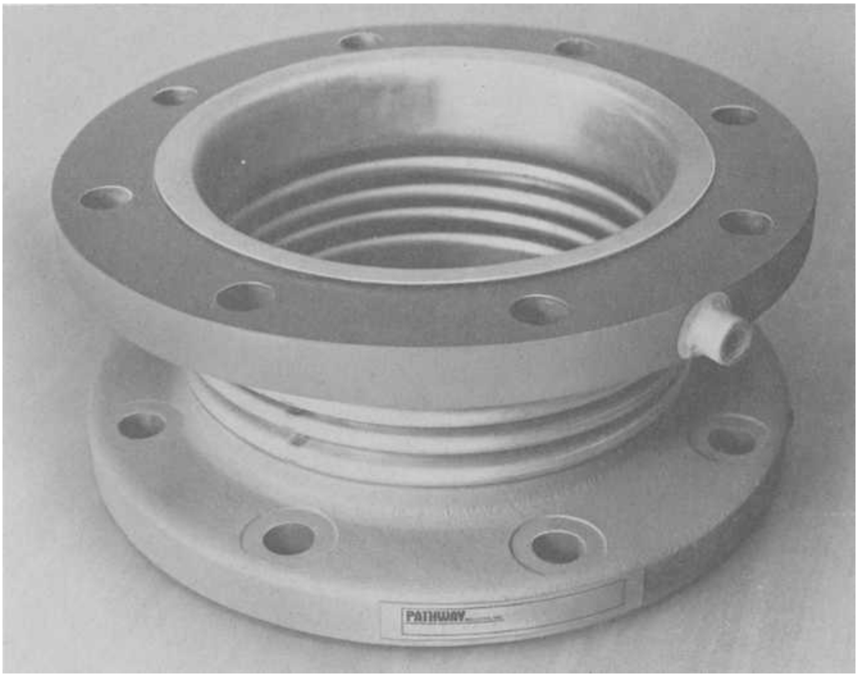

FIG. 11—*Duplex stainless steel/tantalum expansion joint bellows.*

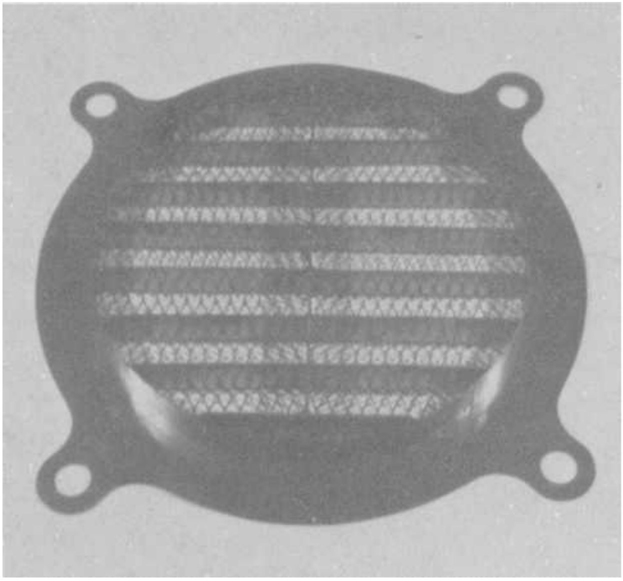

FIG. 12—*Tantalum packing support screen.*

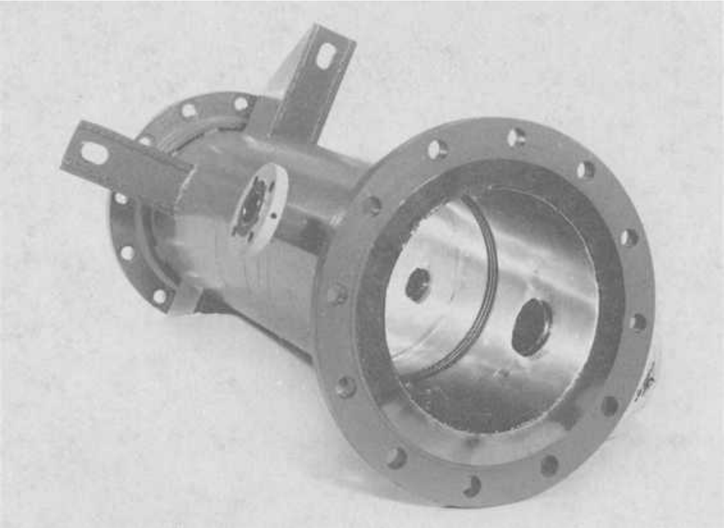

FIG. 13—*Tantalum-lined heat exchanger shell.*

contributes importantly to some further very desirable features in its use as heat transfer equipment:

1. It allows the use of absolute minimum thickness metal. In conjunction with its favorable modulus of elasticity good component rigidity is realized.
2. Absence of scaling and fouling avoids diminution of heat transfer effectiveness by conduction and convection, and hindrance of flow by obstruction.

The next group of photos shows equipment manufactured to take maximum advantage of these characteristics. Bayonet heaters (Figs. 14 and 15) and heat exchangers (Fig. 16) of tantalum with metal tube and sheet thicknesses in the range of 0.3 to 1.0 mm (0.013 to 0.040 in.) are indicative of its good formability, weldability, and adaptability to precision fit. The use of thin wall tubing also contributes an economic advantage by making possible the predominant use of seam-welded tubing formed from sheet. The ball valve (Fig. 17) might be the best illustration of a construction making highly effective use of these characteristics.

Limitations

Tantalum has some well defined and recognized limitations. It also has some potentials and prospects which may expand its utilization. It is not the best choice of material for use in strongly alkaline environments or where flu-

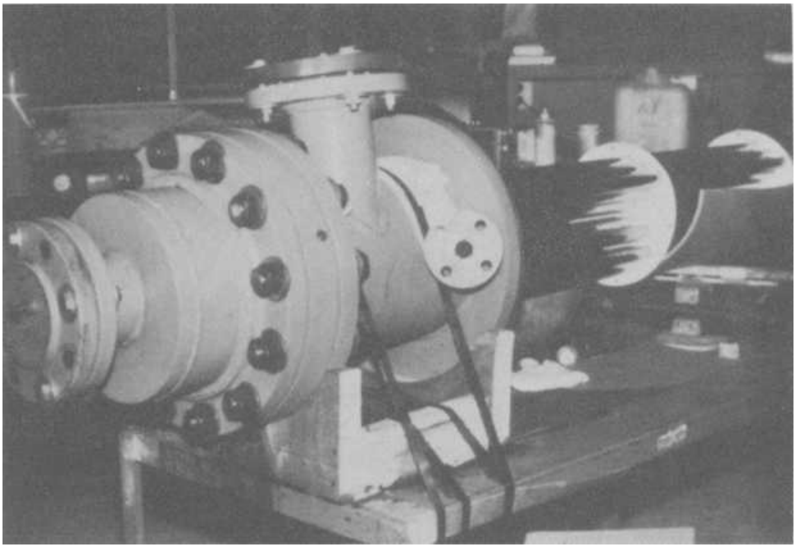

FIG. 14—*Tantalum bayonet heater.*

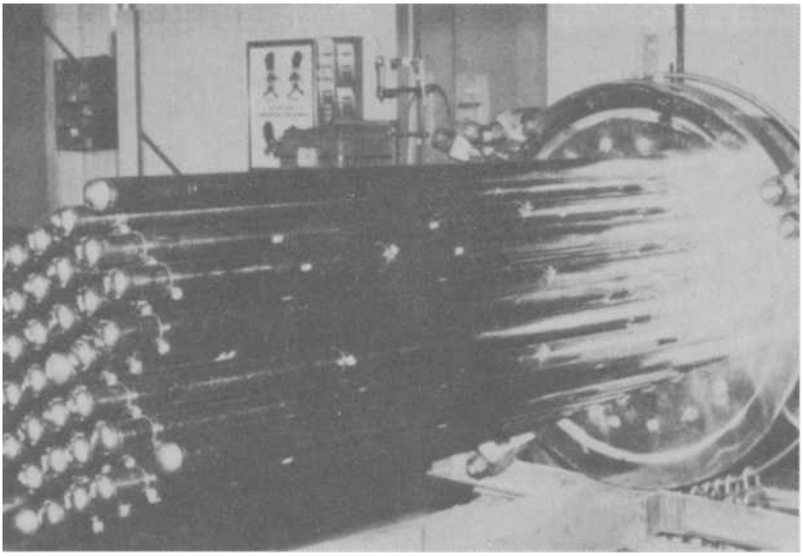

FIG. 15—*Tantalum bayonet heater tube bundle.*

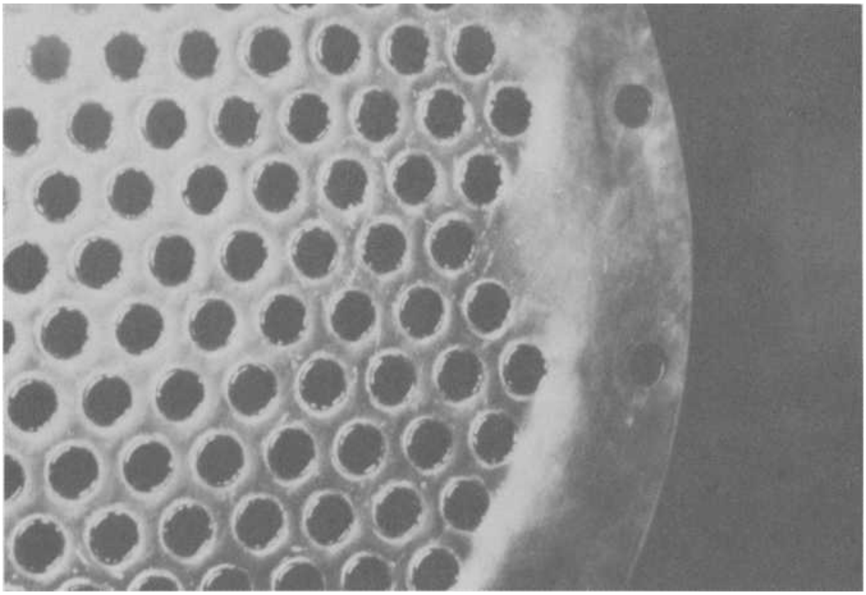

FIG. 16—*Heat exchanger showing tantalum tube/tube sheet welds.*

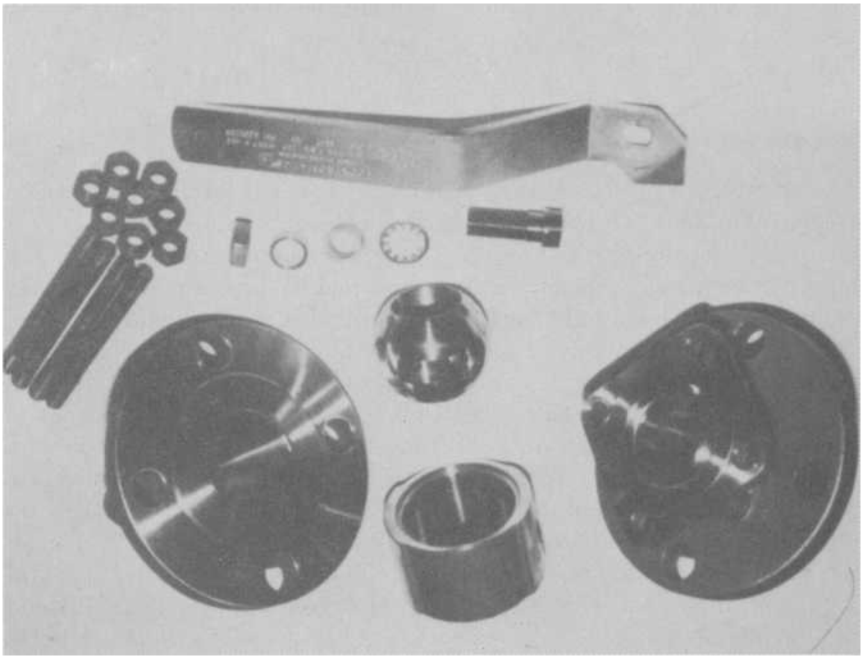

FIG. 17—*Tantalum-lined ball valve assembly.*

orides are present. Generally, in highly aggressive acidic solutions tantalum loses its inertness and becomes reactive or contaminable at temperatures of approximately 200 to 250°C (390 to 480°F). It is not immune to hydrogen embrittlement; on the other hand, it is not so sensitive in this respect that it should be shunned. Experience has indicated that tantalum has withstood many hydrogen prone and cathodic situations without serious effect. The practices of platinum spotting and the deliberate formation of a thicker oxide by thermal or electrochemical anodization are considered to lessen hydrogen take-up.

Exposure of tantalum during processing or use in air or other chemically active surroundings at temperatures above 427 to 538°C (800 to 1000°F) gives a high likelihood of permanent contamination and degradation of the metal. Sometimes, such as in welding, meticulous protective practice is able to compensate, but in other situations it is necessary to preclude exposure. Compatibility with other engineering materials is only a problem when elevated temperatures (> 538°C) are attained. Especially in welding situations it is necessary to employ appropriate precautionary practices because of tantalum's very high reactivity and fusion temperature. However, tantalum has some reasonable tolerance for association with titanium, zirconium, tungsten, molybdenum, and niobium, is essentially nonreactive with copper and lead.

Developments

Some metallurgically enhancing practices that can extend the specific strength of tantalum without detracting from chemical or mechanical performance are (1) alloying with between 2 to 3% tungsten, and (2) oxygen and impurity composition control by refining and melting practices. The tungsten addition does not impart any significantly noticeable microstructural features and accordingly has not exhibited any detectable chemical or metallurgical problems in performance. It does raise the strength by 30 to 50% by solid solution strengthening. Controlling the levels of oxygen and impurities in amounts less than 0.1 wt% provides strengthening effects in tantalum to an even greater extent than it does in titanium and zirconium, and the decrease in ductility is not sufficient to be detrimental for practical purposes. The Table 1 data are indicative of the strength levels of tantalum mill products materials that can be and are produced. Observations have not indicated that tantalum with these somewhat higher levels of oxygen and impurities in solid solution has any subsequent proneness to welding porosity such as can occur when powder-metallurgy consolidated tantalum is welded. Also, these oxygen-impurity enhanced compositions do not exhibit any significant microstructural features or effects which would be detrimental to in-service performance.

A large portion of the tantalum mill products and fabrications produced for the electronics industry is processed from powder-metallurgy consolidated metal. Conversely, most of these product forms to be used for CPI applications are initially consolidated in high vacuum to ingot either by electron beam or consummable arc melting in which compositional purity levels are very closely controlled. Subsequent mechanical processing is primarily done without heating or with only moderate warming. The high level of purity and natural malleability allows cold reductions in area well in excess of 95% without annealing. This high degree of formability also allows extensive upsetting, drawing, deep drawing, spinning, stretching, etc., into a wide variety of mill shapes and fabricated items. In Fig. 18 the shells are capacitor cases which are deep drawn from sheet; other machined and formed small parts can be manufactured into a variety of equipment components.

Composite fabrications of tantalum with steels, copper, and aluminum have frequently been made, and good bonding between pieces of tantalum with titanium and with zirconium has been obtained with welded and fabricated items. "Welds" of tantalum to the titanium and zirconium do not involve macroscopic fusion of the tantalum, but the joint integrity is excellent.

TABLE 1—*Tensile strength values of electron beam, alloyed, and oxygen/impurity enhanced grades of tantalum.*

	Electron-Beam Tantalum at Room Temperature (ASTM Minimum Value)	Arc-cast Tantalum at Room Temperature (Minimum Value)	Electron-Beam Ta + 2.5W at Room Temperature (ASTM Minimum Value)	Arc-cast Ta + 2.5W at Room Temperature (Minimum Value)	O_2-enhanced Tantalum (0.02 to 0.04%) at Room Temperature (Typical Value)	O_2-enhanced Ta + 2.5W (0.02 to 0.04%) at Room Temperature (Typical Value)
Ultimate tensile strength, psi[a]	30 000	40 000	40 000	53 000	55 000	70 000
0.2% yield strength, psi	20 000	25 000	28 000	37 000	45 000	60 000
% elongation, total	25	32	20	27	22	18
		200°C (390°F) Range of Values		200°C (390°F) Range of Values		
Ultimate tensile strength, psi		34 000 to 38 000		48 000 to 52 000		
0.2% yield strength, psi		16 000 to 22 000		33 000 to 39 000		
% elongation, total		20 to 25%		17 to 20%		

[a] 1 psi = 6.89 kPa.

FIG. 18—*Tantalum capacitor cases (deep drawn).*

Performance Characteristics

Perhaps tantalum's most useful attribute is the wide spectrum of chemical compositions and concentrations over which it exhibits almost a total absence of susceptibility to corrosion (Fig. 8). Zirconium, titanium, Hastelloys, etc., often show increases in general corrosion rate or become susceptible to pitting attack or stress corrosion cracking (SCC) as the electrochemical parameters change; that is, in certain combinations of oxidizing-reducing potentials and with particular anion (for example, chloride) or cation (for example, ferric or cupric) concentrations, their protective passivating capability is exceeded. In some anhydrous oxygen-deficient conditions the passivating oxide may be prevented from forming sufficiently to be effective enough. There have been no reports of limitations in these respects for tantalum. Except for some isolated instances the few observations of attack of tantalum have been a very uniform general corrosion or hydrogen embrittlement. Tantalum is not apparently susceptible to SCC or pitting in any media observed. Also, there does not appear to be any degree of oxygen depletion that can prevent passivation or allow crevice corrosion. It appears that the highly rectifying effect of the passivating film precludes the existence of local electrochemical cells despite any corresponding variations in the metal itself. Therefore there does not seem to be any differential corrosion effects associated with chemical inhomogeneities, welds and heat-affected zones, or intergranular areas.

The curves of the iso-corrosion charts (Figs. 19 and 20) approximate the concentration-temperature conditions under which a material's corrosion rates are above or below 5 mils per year (mpy). None of the alloys, except

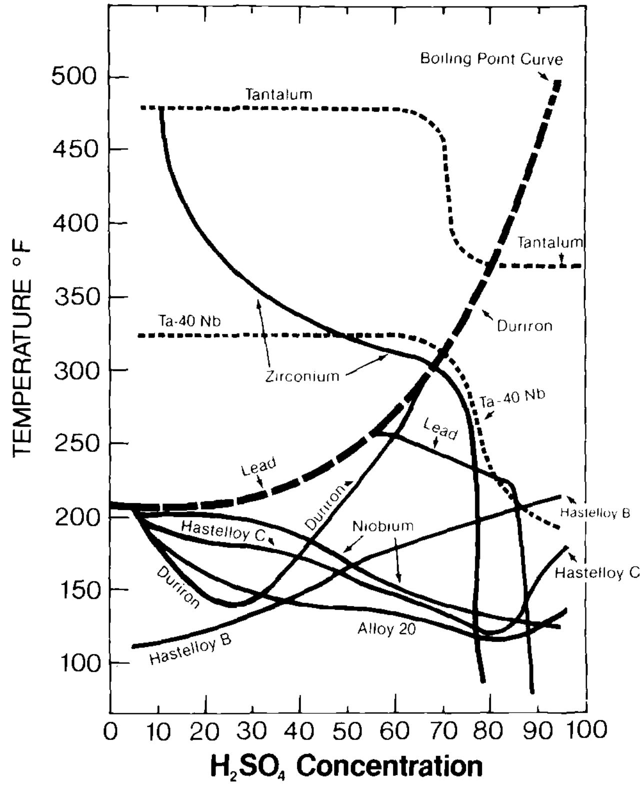

FIG. 19—*5 mpy H_2SO_4 iso-corrosion chart (compiled and interpolated from several sources).*

tantalum, spans the entire acid concentration range at temperatures greater than about 100°C (212°F). Actually the 5 mpy criterion is an understatement for tantalum, since experience has indicated 1 to 2 mpy as more representative at temperatures below about 190°C (375°F) and at the highest concentrations. Above about 200°C (390°F), however, tantalum does begin to corrode measurably at higher rates in a uniform attack; apparently the oxide's barrier quality is breached in that region. The precise mechanism(s) for the loss of protection has not been defined.

For H_2SO_4 (Fig. 19) the zone above about 60 to 70% concentration and 200°C (300°F) is especially aggressive for the other metals. Above about 66 to 77°C (150 to 170°F) and 50% concentration the options for long-service materials become quite limited other than the brittle materials Duriron, glass, and graphite. Recently there have been observations that the addition of nitrate ion (NO_3) to H_2SO_4 significantly diminishes the rate of corrosion of tantalum at temperatures up to 246°C (475°F).

For HCl (Fig. 20) it can be seen that there are even fewer candidate materi-

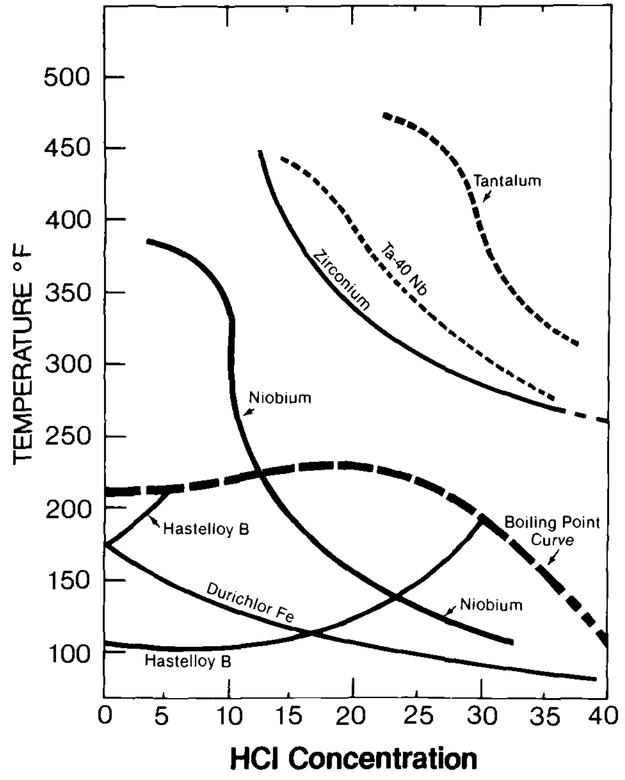

FIG. 20—*5 mpy HCl iso-corrosion chart (compiled and interpolated from several sources).*

als which withstand even half of the 40% concentration range at temperatures above about 66 °C (150 °F). Only zirconium and tantalum provide a high margin of assurance for long-term durability. Zirconium, however, is seriously susceptible to pitting attack in the presence of some oxidizing species such as ferric and cupric ions whereas tantalum is not. Tantalum is also resistant to both wet and dry chlorine.

Most of the passivating metals exhibit good resistance over a fairly wide range of concentrations and temperatures in nitric acid (HNO_3). All except tantalum, however, have susceptibility to stress corrosion cracking in certain regions. They are also prone to attack when other aggressive species such as chloride or ferric ions are present, even at contamination levels.

In general, alloying of tantalum with more than a few percent of another reactive metal will yield an alloy with corrosive properties between the two metals and significantly inferior to straight tantalum. This effect has been well demonstrated by work done with the alloys Ta-Ti, Ta-W, and Ta-Nb.

The considerable extent to which a mixed media of acid with other ions can be selectively corrosive to the different metals is particularly demonstrated in the results of exposure of several alloys to an environment of water, HCl, iron chloride, and aluminum chloride at 80 to 114°C. The order of decreasing resistance to attack was established in a recent experimental program as:

Ta; Ta-2.5W alloy
Nb-Ta alloy
Nb; Zr
Hastelloy B2

Other recent data, though obtained in boiling 70% and 75% H_2SO_4 at 165 and 185°C (330 and 365°F), indicate a similar sequence of corrosion resistance; that is,

Ta
Ta-Nb alloys; Hf
Zr; Nb

In both cases the tantalum had essentially nil corrosion, whereas corrosion was of measureable extent in the other metals.

In highly reducing media such as HCl and H_2SO_4 embrittlement may become the limiting factor in the performance of these metals, including tantalum. For tantalum the tendency for hydrogen absorption increases at higher pressures, temperatures, and concentrations. It becomes particularly likely at concentrations beyond about 20% HCl and 70% H_2SO_4 and temperatures greater than 176°C. Some inhibiting effect to this susceptibility has been demonstrated by the presence of additional oxide on the metal surface and by the introduction of minor amounts of platinum in electrical contact.

An experimental program evaluating tantalum for sour gas and oil service has yielded strong evidence that it is highly resistant to embrittlement or corrosion in hot acid-chloride-hydrogen sulfide environments. Tantalum specimens have withstood with no discernible effects the following exposures:

- 30 days at ambient temperature in NACE solution[2] at a yield stress of 172 MPa (25 000 psi).
- 10^{-6} in./in./s slow strain rate extension at ambient temperature in NACE solution to ductile fracture.
- 10^{-6} in./in./s slow strain rate extension at 176 to 243°C (350 to 470°F) in aqueous 25% NaCl + 689 kPa (100 psi) H_2S by ductile fracture.

Each condition was repeated for a welded tantalum piece and with galvanic coupling to steel.

Fabrication Characteristics

Formability

The variety of product forms manufactured of tantalum reflects the highly favorable fabrication characteristics of the metal. In simplistic terms its

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[2] NACE solution is aqueous 5% NaCl, 0.5% acetic acid, and H_2S (saturated, 1 atm).

workability might be described as having resemblances to both copper and titanium. The predominant limiting consideration in fabricating tantalum, which must be remembered and respected, is its strong interactive tendency with other metals, air, and many chemicals when its passivity is compromised. Accordingly, it is important (1) to avoid heating tantalum in air or in contact with other noninert materials for measureable time periods at temperatures above about 316 to 427°C (600 to 800°F), and (2) to avoid or minimize the degree of burnishing action in mechanical processing, because surface galling and sticking readily occurs. Neither of these precautions is highly restrictive in practice.

The rate and extent of work hardening of tantalum are not great relative to those of other structural metals. Therefore extensive shape changes can be accomplished without annealing and without high risk of fracture; the degree of springback (or "stay-put") also favorably compares to the other common metals. There appears to be little or no well-defined fatigue data, probably because in any relevant applications the metal has displayed good resistance. It has been definitively observed in recent years that alloyed tantalum or arc melted metal with enhanced oxygen and impurity composition levels respond to shop fabrication more favorably than very high purity electron-beam melted metal. The high purity metal work hardens so slowly that it exhibits a "mushy" characteristic and a tendency to locally "neck down" in severe forming operations.

Welding

High integrity welding of tantalum is routinely accomplished with standard tungsten-inert-gas (TIG) procedures and meticulous attention to prevention of contamination. Weld evaluation is relatively clear-cut because the bright shiny weld bead is indicative of the high quality requirement. Refer to the photographs of the tantalum thermowells (Fig. 10), heat exchanger and shell (Fig. 13), and pickling tank (Fig. 21). Any discoloration or dullness in the weld is reason to suspect the integrity and a hardness check should be made. Before welding it is advisable, if possible, to etch off any oxide and remove any other chemical films including residues from cleaning solvents or handling stains. Thorough inert gas purging and coverage are necessary.

Straight polarity (electrode negative) direct-current power is most appropriate for TIG welding. Extremely coarse grain size in the fusion zone of the weld and considerable grain growth in the heat-affected zone are characteristics of tantalum welds. Weld strength efficiencies of about 90% are usual, but occasionally harder, stronger welds than the base metal are obtained in sheet welds. This is primarily because of the high sensitivity to oxygen content in the weld and is not necessarily undesirable.

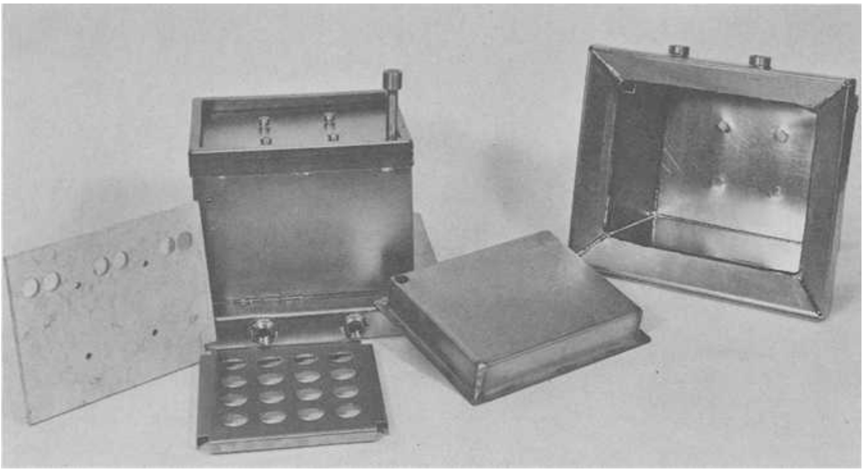

FIG. 21—*Solid tantalum pickling tank.*

TABLE 2—*Basic parameters of tantalum machining.*

Setup	rigid	. . .
Feed/cut depth	heavy	>0.4 mm (0.015 in.) IPR
Surface speed	slow	40 to 50 SEPM
Tooling	maintained sharp	5 to 10 deg side clearance
. . .	heavy lube flow	45 deg side rake
		5 deg back rake
		5 to 10 deg front clearance

Machining

High quality machined items are routinely produced when attention is devoted to the basic limiting parameters. These are listed in Table 2.

Grinding of tantalum is done but should be avoided or at least limited as much as practicable. The abrading medium is "loaded" and worn at a high rate, making a good surface and controlled metal removal difficult.

Robert H. Burns,[1] *Fred S. Shuker, Jr.,*[2] *and Paul E. Manning*[3]

Industrial Applications of Corrosion-Resistant Tantalum, Niobium, and Their Alloys

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REFERENCE: Burns, R. H., Shuker, F. S., Jr., and Manning, P. E., **"Industrial Applications of Corrosion-Resistant Tantalum, Niobium, and Their Alloys,"** *Refractory Metals and Their Industrial Applications, ASTM STP 849,* R. E. Smallwood, Ed., American Society for Testing and Materials, Philadelphia, 1984, pp. 50-69.

ABSTRACT: During the period 1960-1982, tantalum, niobium, and their alloys have become increasingly important in industrial applications where superior corrosion resistance is required. These materials are particularly attractive when selected on the basis of "life cycle costing". This takes into account initial cost, levels of product quality, length of trouble-free operation, and any increase in productivity due to reduced downtime and lower maintenance requirements. The chemical process industry, in particular, has taken advantage of these materials for processing mineral acids at temperatures and concentrations higher than can be withstood by any other materials.

Advances in electron-beam melting technology have also made it possible to manufacture larger and cleaner ingots, resulting in the availability to industry of larger sheets, tubes, and plates with improved property reliability.

KEY WORDS: tantalum, niobium, tantalum-base alloys, niobium-base alloys, service life, corrosion resistance, acid resistance tests, hydrogen embrittlement, anodic protection, heat exchangers, vessels, cathodic protection, platinized niobium, getters, furnace ware, surgical implants

Although the electronic industry still consumes the major share of U.S. tantalum production (for electronic capacitors), chemical process industry (CPI) usage and other industrial corrosion applications have increased to the point where the label "exotic" no longer applies to tantalum [*1*]. The excellent corrosion resistance of tantalum and its alloys makes them ideal for a wide range of chemical process equipment.

Niobium and its alloys possess corrosion resistance approaching that of

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[1] Cabot Corporation, Reading, Pa. 19603.
[2] KBI Division, Cabot Corporation, Reading, Pa. 19603.
[3] Cabot Corporation, Kokomo, Ind. 46901.

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tantalum and its alloys. Niobium continues to find principal use as an alloying element in steel and superalloys, but it is also of interest as a corrosion-resistant material either singly or in combination with tantalum or other alloying elements.

Tantalum, niobium, and their alloys also have high melting points and excellent elevated temperature mechanical properties; they are excellent materials for high temperature corrosion applications such as crucibles, furnace interiors, heat shields, and thermocouple sheaths in vacuum or inert atmosphere.

The long service life and reliability of these materials usually offset their higher initial construction and installation costs.

The purpose of this paper is to document recent data obtained in corrosion tests of tantalum, niobium, and their alloys in aqueous solutions, to demonstrate the advantages of a newly introduced Ta-Nb alloy (60 wt% Ta, 40 wt% Nb), and to highlight service experience with these materials at high temperatures and in surgical applications.

Corrosion Characteristics of Tantalum, Niobium, and Their Alloys

Positive Characteristics

The outstanding corrosion characteristics of tantalum and niobium are due to a naturally occurring amorphous surface oxide film which is approximately 10 to 40Å thick. On tantalum, the film is stable up to 260°C [*2*]. Tantalum is recognized as the most corrosion-resistant metal available for industrial corrosion applications, particularly for the chemical industry (Table 1). Niobium is less corrosion resistant than tantalum, but is still quite satisfactory in a large number of applications (Table 2).

Tantalum-base alloys such as Ta-2.5W and Ta-10W have been designed for increased mechanical properties over the parent metal with little or no loss in corrosion resistance. KBI® alloy 40, a Ta-40Nb alloy presently receiving extensive laboratory and field testing, exhibits corrosion resistance very near that of tantalum.[4]

Niobium and its alloys (such as Nb-1Zr) are used in many industrial applications, even though they are less corrosion resistant than tantalum or even KBI alloy 40. However, they are extremely resistant to corrosive attack when compared with other engineering materials such as titanium or nickel-base alloys.

Even when tantalum, niobium, and their alloys suffer corrosive attack in service, the problems are minimal because uniform dissolution is the typical form of attack. The passive oxide film on these alloys is extremely resistant to corrosive breakdown and repairs itself rapidly. This virtually prevents the oc-

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[4] KBI is a registered trademark of Cabot Corporation.

TABLE 1—*Corrosion resistance of tantalum.*

A = no attack up to about 150°C (302°F) or as specified
V = variable, depending on concentration and temperature; **X** = not resistant

Chemicals
A Acetic acid
A Acetic anhydride
A Air, below 300°C
X Air, above 300°C
A Aluminum chloride
A Aluminum sulfate
A Amines

V Ammonia
A Ammonium chloride
V Ammonium hydroxide
A Ammonium nitrate
A Ammonium phosphate
A Ammonium sulfate
A Amyl acetate or chloride

A Aqua regia
A Barium hydroxide
A Body fluids
A Bromine, dry, below 300°C
A Bromine, wet
A Calcium bisulfite
A Calcium chloride

A Hydrochloric acid
X Hydrofluoric acid
V Hydrogen
A Hydrogen bromide
A Hydrogen chloride
X Hydrogen fluoride
A Hydrogen iodide

A Hydrogen peroxide
A Hydrogen sulfide
A Hypochlorous acid
A Iodine, below 300°C
A Lactic acid
A Magnesium chloride
A Magnesium sulfate

A Mercury salts
A Methyl sulfuric acid
A Mixed acids (H_2SO_4-HNO_3)
A Nickel salts
A Nitric acid
A Nitric acid, fuming
A Nitric oxides

X Sodium bisulfate, molten
A Sodium bisulfate, solution
A Sodium bromide
V Sodium carbonate
A Sodium chlorate
A Sodium chloride
V Sodium hydroxide, dilute

X Sodium hydroxide, conc.
A Sodium hypochlorite
A Sodium nitrate
X Sodium pyrosulfate, molten
A Sodium sulfate
V Sodium sulfide
A Sodium sulfite

A Sulfamic acid
A Sulfur, below 500°C
A Sulfur chlorides
A Sulfur dioxide
X Sulfur trioxide
A Sulfuric acid, to 175°C
X Sulfuric acid, over 175°C

A Calcium hydroxide
A Calcium hypochlorite
A Chloric acid
A Chlorinated brine
A Chlorinated hydrocarbons
A Chlorine, dry, below 250°C
A Chlorine, wet

A Chlorine oxides
A Chloroacetic acid
A Chromic acid
A Chrome plating solutions
A Citric acid
A Cleaning solution
A Copper salts

A Ethylene dibromide
A Ethyl sulfate
A Fatty acids
A Ferric chloride
A Ferrous sulfate
V Fluoride salts
A Formic acid
A Hydriodic acid
A Hydrobromic acid

A Nitrogen, below 300°C
A Nitrous acid
A Nitrosyl chloride
X Oleum (fuming sulfuric acid)
A Organic chlorides
A Oxalic acid
A Oxygen, below 300°C

A Perchloric acid
A Phenol
A Phosphoric acid, <4 ppm F
A Phosphorous, below 700°C
A Phosphorous chlorides
A Phosphorous oxychloride
A Pickling acids, except HNO_3-HF

A Phthalic anhydride
V Potassium carbonate
A Potassium chloride
A Potassium dichromate
V Potassium hydroxide, dilute
X Potassium hydroxide, conc.
A Potassium iodide-iodine
X Potassium pyrosulfate, molten
A Silver nitrate

A Sulfurous acid
A Sulfuryl chloride
A Thionyl chloride
A Tin salts
A Zinc chloride
A Zinc sulfate

Liquid Metals
A Bismuth to 900°C
A Gallium to 450°C
A Lead to 1000°C
A Lithium to 1000°C
A Magnesium to 1150°C
A Mercury to 600°C

A Potassium to 900°C
A Sodium to 900°C
A Sodium-potassium alloys to 900°C
V Zinc to 500°C
V Tin
V Uranium

TABLE 2—*Corrosion resistance of niobium.*[a]

	Temperature				Temperature		
	20°C	60°C	100°C		20°C	60°C	100°C
Chemicals							
Acetic acid (10%)	A	A	A	Ketones	A	A	A
Acetic Acid (glac. and anh.)	A	A	A				
Acetone	A	A	A	Lactic acid (100%)	A	A	A
Acetylene	A	A	A				
Alcohols (most)	A	A	A	Maleic acid	A	A	A
Aliphatic esters				Mercuric chloride	A	V	V
Aliphatic halogen compounds-chloroform	A	A	A	Naphtha	A	A	A
Alum	A	A	A	Naphthalene	A	A	A
Aluminum chloride	A	A	A	Nickel salts	A	A	A
Ammonia anhydrous	A	A	A	Nitric acid (25%)	A	A	A
Ammonium chloride	A	A	A	Nitric acid (50%)	A	A	V
Amyl acetate and chloride	A	A	A	Nitric acid (95%)	V	V	X
Aniline and compounds	A	A	A				
Aqua regia	V	X	X	Oils, essential	A	A	A
				Oils, mineral	A	A	A
Bonzoic acid	A	A	A	Oils, vegetable and animal	A	A	A
Boric acid	A	A	A	Oxalic acid	X	X	X
Brines, saturated	A	A	A	Oxygen	A	A	V
Bromine, moist	A	A	V	Perchloric acid	A	A	A
Calcium chloride	A	A	A	Phenol	A	A	A
Carbon disulphide	A	A	A	Phosphoric acid (25%)	A	V	X
Carbonic acid	A	A	A	Phosphoric acid (50%)	A	V	X
Chlorine, dry	A	A	A	Phosphoric acid (95%)	V	V	X
Chlorine, wet	A	A	A	Potassium hydroxide	X	X	X
Chlorides of Na, K, Mg	A	A	A	Pyridine and compounds	A	A	A
Chromic acid (80%)	A	V	V				

Citric acid	A	A	A	Seawater	A	A	A
Copper salts (most)	A	A	A	Silicic acid	A	A	A
Cyclohexane	A	A	A	Silver nitrate	A	A	A
				Sodium carbonate	X	X	X
Detergent, synthetic	A	A	A	Sodium hydroxide	X	X	X
				Sodium hypochlorite	X	X	X
Emulsifiers	X	X	X	Sodium silicate	X	X	X
Ether	A	A	A	Sodium sulfide	A	A	A
				Starch	A	A	A
Fatty acids ($C = C_6$)	A	A	A	Sugar and syrups	A	A	A
Ferric chloride	A	A	A	Sulfates of Na, K, Mg, Ca	A	A	A
Ferric sulfate	A	A	A	Sulfites	A	A	A
Fluorine	X	X	X	Sulfonic acids	A	A	V
Formaldehyde	A	A	A	Sulfur	A	A	A
Formic acid	A	A	A	Sulfur dioxide, dry	A	A	A
				Sulfur dioxide, wet	A	A	V
Glycerine	A	A	A	Sulfur trioxide	X	X	X
Glycols	A	A	A	Sulfuric acid (20%)	A	A	A
				Sulfuric acid (50%)	V	X	X
Hexamine	A	A	A	Sulfuric acid (70%)	V	X	X
Hydrochloric acid (10%)	A	V	X	Sulfuric acid (95%)	X	X	X
Hydrochloric acid (conc.)	V	X	X				
Hydrofluoric acid	X	X	X	Tallow	A	A	A
Hydrogen peroxide (30%)	V	X	X	Tannic acid (10%)	A	A	A
Hydrogen sulfide	A	A	A	Tartaric acid	A	A	A
				Trichlorethylene	A	A	A
				Vinegar	A	A	A
				Yeast	A	A	A
				Zinc chloride	A	A	A

A = normally no attack
V = variable depending on purity
X = not resistant

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[a] These are general recommendations and are not to be interpreted as absolute values.

currence of pitting, crevice attack, intergranular corrosion, and stress corrosion cracking, thus eliminating the major causes of catastrophic failure common to other engineering materials. This translates into substantial savings since thinner sections can be used. These savings are clearly evidenced when these materials are selected on the basis of life cycle costing. In addition to initial cost, this takes into account levels of product quality, length of trouble-free operation, and any increase in productivity due to reduced downtime and lower maintenance requirements.

Limitations of Tantalum, Niobium, and Their Alloys

Hydrogen embrittlement is the single most important cause of failure of tantalum, niobium, and their alloys. These metals readily absorb hydrogen interstitially; as a result they become brittle although their physical appearance remains the same. Niobium is even more susceptible to hydrogen embrittlement than tantalum.

Tantalum and niobium absorb molecular hydrogen above 250°C and atomic hydrogen, more active than molecular hydrogen, at room temperature. In aqueous solutions, embrittlement by atomic hydrogen is by far the more serious problem. It can come about by any of the following mechanisms:

1. Dissolution of the metal in hydrofluoric acid.
2. Stray currents that cause the metal to become cathodic.
3. Galvanic coupling to a more active metal.

Tantalum and niobium react readily with almost all salt solutions and acids producing amorphous oxide films, as previously described. Therefore, even though bare tantalum would be at the active or anodic end of the electromotive series, similar to aluminum or zinc, the presence of this passive oxide film increases its potential and places tantalum at the more noble end of the electromotive series. As a result, when tantalum is connected to another metal such as aluminum or steel to form a galvanic couple, tantalum becomes cathodic. The more active metal, aluminum or steel, will dissolve; the cathodic reaction produces hydrogen, which embrittles the tantalum. The effect of hydrogen is cumulative and results in progressive loss of strength and eventual failure of the tantalum. Therefore it is essential that tantalum be maintained as the anode when connected to another metal. The foregoing considerations apply equally to tantalum alloys, niobium, and niobium alloys.

Anodic Protection of Tantalum, Niobium, and Their Alloys

Anodic protection of these refractory metals is generally accomplished by connecting them to the positive pole of a d-c source (about 15 V); the negative pole is connected to some other metallic part which is exposed either to the solution in the vessel or to ground, as schematically shown in Fig. 1. Obvi-

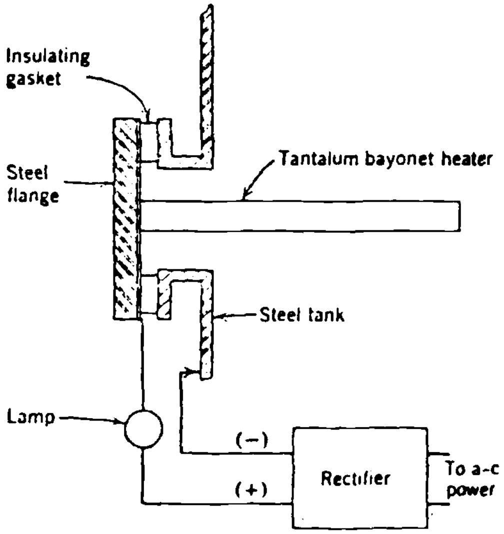

FIG. 1—*Protecting tantalum bayonet heaters from galvanic attack.*

ously, this arrangement is not possible if the electrolyte attacks the refractory metal.

Other methods of preventing hydrogen embrittlement are:

1. *Anodization of the refractory metals* to maintain their anodic character. As an additional precaution, however, the refractory metals should still be connected as the positive electrode.
2. *Attachment of another metal* which has a low hydrogen overvoltage and is electrochemically cathodic to the refractory metal in the particular electrolyte. Platinum has been used effectively in industry, particularly in hydrochloric acid, which does not significantly attack the naturally formed oxide film. Since these refractory metals are close to platinum and gold in the electromotive series, only these noble metals meet the low hydrogen overvoltage conditions of the method given above. Small areas of noble metal (that is, platinum foil) can be attached to the refractory metal by spot welding. Other methods include electroplating, and rubbing noble metal powder or wool on the surface of the refractory metals (tantalum, niobium, and their alloys).
3. *Addition of platinum salts to the solution* [*3*]. Adding small amounts of platinum chloride salts have been used successfully to prevent the embrittlement of tantalum (also niobium) in HCl.

Failure Due to Surface Inhomogeneities

In addition to hydrogen embrittlement, corrosive failure of refractory metals may result from surface inhomogeneities such as (1) differences in surface texture, (2) surface impurities due to machining, grinding, or forming, and (3) chemical inhomogeneities such as inclusions. These inhomogeneities cause failures by creating localized galvanic cells on the surface of the metal. They can only be prevented by careful surface preparation with inspection before installation. Whenever possible, cleaning by etching in a nitric acid-hydrofluoric acid mixture solution should precede actual use of the material.

Corrosion Resistance in Aqueous Environments

In aqueous environments, pure tantalum is the most corrosion resistant metal. It is resistant to corrosive attack by all chemicals, except fluorides, fuming sulfuric acid, and concentrated alkalies.

Niobium is inert to almost all salt solutions and acids at room temperature except fluorides, sulfuric acid containing free sulfuric trioxide, and alkalies. At or near room temperature, it is similar to tantalum in its corrosion characteristics. Its corrosion resistance is generally satisfactory up to about 100°C in most corrosive environments.

Specific data are given below for the corrosion resistance of tantalum, niobium, and their alloys in the most common aqueous environments.

Hydrochloric Acid—Tantalum is resistant to hydrochloric acid at nearly all concentrations, temperatures, and pressures. No significant attack has been observed up to 190°C and 4.1 MPa (600 psi) in concentrations less than 30%. Tantalum may, under the most severe conditions, suffer hydrogen embrittlement at high temperatures in HCl. Coupling the tantalum or niobium to a small piece of platinum can prevent hydrogen embrittlement [*3*].

Ta-2.5W and Ta-10W exhibit corrosion resistance similar to that of the base metal.

KBI alloy 40 demonstrated excellent resistance to hydrochloric acid in laboratory tests (Fig. 2). It can be seen that alloy 40 is resistant to HCl at all concentrations up to the boiling point. At 190°C, in 30% HCl, significant corrosion accompanied by hydrogen absorption was observed. This resistance is comparable to that of tantalum (Fig. 3). Additions of oxidizing, reducing, or neutral salts do not alter corrosion resistance (Table 3).

Niobium, as previously stated, is not as resistant to HCl as tantalum or alloy 40 (Table 3).

Sulfuric Acid—Tantalum is highly resistant to sulfuric acid (Fig. 4). Measurable slow uniform attack in high concentration sulfuric acid begins at about 175°C. At temperatures as high as 200°C, tantalum can be used successfully with 98% H_2SO_4 [*4*].

Ta-2.5W and Ta-10W exhibit corrosion resistance to H_2SO_4 similar to unalloyed tantalum.

KBI alloy 40 also possesses excellent corrosion resistance in sulfuric acid (Fig. 5). Recent tests show that measurable corrosion begins in boiling 70% H_2SO_4. The hydrogen pickup characteristics appear to be similar to tantalum (Table 3).

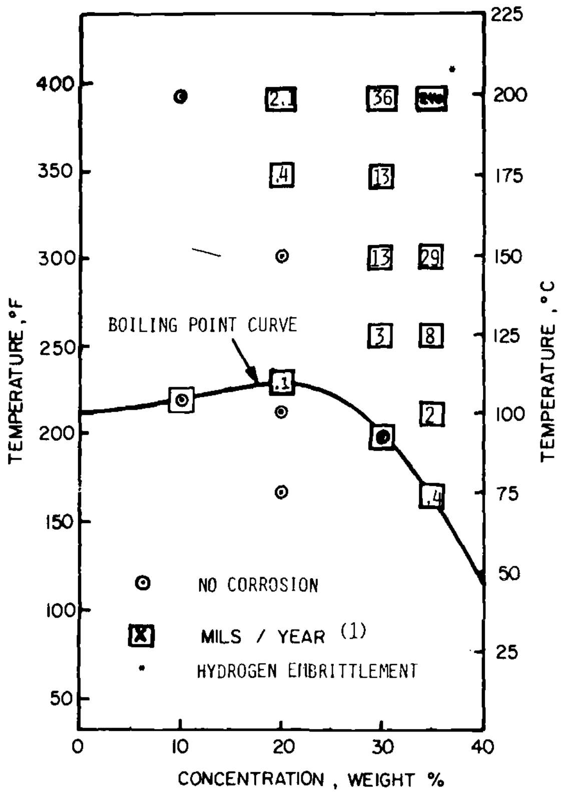

FIG. 2—*Corrosion resistance of KBI alloy 40 in hydrochloric acid* [13].

Nitric Acid—The corrosion resistance of tantalum is excellent in nitric acid and aqua regia. Tantalum is inert to nitric acid at all concentrations up to boiling. Chlorides in nitric acid do not reduce the corrosion resistance. In chemical processing equipment, tantalum successfully handles fuming nitric acid at services up to 5.6 MPa (800 psig) and 315°C for years [*4*].

Initial laboratory testing of KBI alloy 40 showed that it also possesses, as expected, excellent corrosion resistance in nitric acid. After one week in 65% HNO_3 at boiling, no corrosion resulted.

No niobium corrosion resulted from exposures in solutions up to 70% HNO_3 at temperatures up to 250°C [*5*]. Niobium is not adversely affected by oxidizing salts such as ferric chloride or cupric salts in nitric acid. Nitric acid processing is an area where niobium should find extensive use.

Phosphoric Acid—Tantalum is resistant to concentrated phosphoric acid (85%) when fluoride concentration is low (less than 4 ppm) at temperatures up to 200°C. In boiling 85% H_3PO_4 (165°C), the corrosion rates determined for tantalum, KBI alloy 40, and niobium were respectively 0.005 (0.2 mpy),

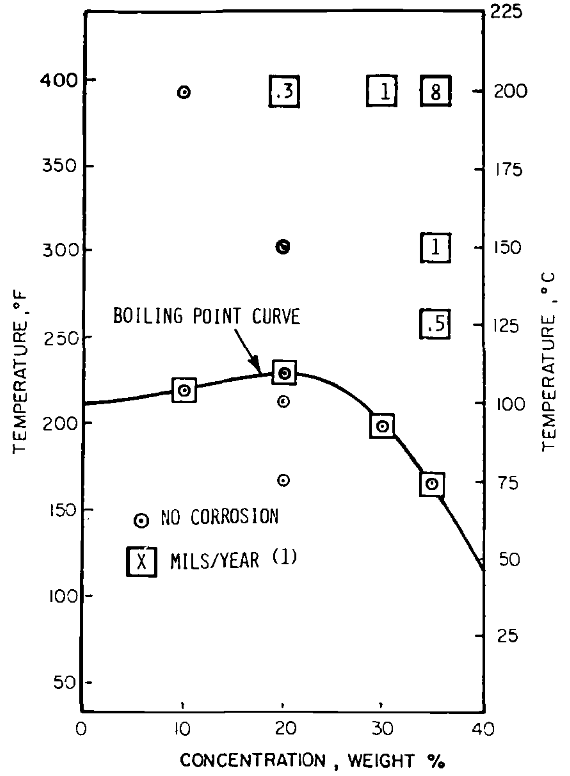

FIG. 3—*Corrosion resistance of tantalum in hydrochloric acid* [13].

0.063 (2.5 mpy), and 1.2 (48 mpy) mm/year.[5] Niobium is resistant to concentrated phosphoric acid (85%) up to 100°C [5].

Organics—In general, tantalum is completely resistant to most organic compounds; it is used in heat exchangers, spargers, and reaction vessels, particularly when corrosive inorganic chemicals are involved or low residual impurities are essential. These include solutions of acetic, lactic, monochloroacetic, formic, and oxalic acids up to their boiling points, as well as phenol. In addition, most organic salts, gases, alcohols, ketones, alkalies, and esters do not attack tantalum. Exceptions include fluoride-containing reagents or hydrolizable reagents that yield hydrofluoric acid or contain free sulfur trioxide or strong alkalies.

Tantalum is an excellent material where product contamination and undesirable side reactions must be avoided such as in food processing and some chemical industry applications [*4*].

Miscellaneous Chemicals—Tantalum is resistant to hydrogen peroxide, the

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[5] Original measurements were in English units.

TABLE 3—*Corrosion test results on tantalum, KBI alloy 40, and niobium at boiling in* $H_2SO_4 + AlCl_3$, $H_2SO_4 + NaCl$, $H_2SO_4 + FeCl_3$, $HCl + AlCl_3$, $HCl + NaCl$, *and* $HCl + FeCl_3$.

		Corrosion Results after Four 24-h Periods						
		Tantalum		KBI alloy 40		Niobium		Approximate Boiling Temperature, °C
Acid Concentration	% Salt	mpy[a]	H_2 ppm[b]	mpy	H_2 ppm	mpy	H_2 ppm	
10% H_2SO_4	5% $AlCl_3$	nil	<5	nil	15	2.2	50	101
10% H_2SO_4	15% $AlCl_3$	nil	5	nil	15	3.5	60	101
30% H_2SO_4	5% $AlCl_3$	nil	5	nil	10	6.9	125	107
30% H_2SO_4	15% $AlCl_3$	nil	<5	nil	20	6.7	90	107
60% H_2SO_4	5% $AlCl_3$	0.2	5	1.1	20	29	90	141
10% H_2SO_4	10% NaCl	...	...	nil	10	2.9	40	101
30% H_2SO_4	10% NaCl	...	...	0.1	<5	9.7	90	107
60% H_2SO_4	10% NaCl	nil	<5	1.1	5	49	85	141
70% H_2SO_4	10% NaCl	0.4	<5	8.0	10			165
10% H_2SO_4	0.01% $FeCl_3$	nil	...	nil	...	1	5	101
30% H_2SO_4	0.01% $FeCl_3$	nil	...	0.1	...	4	25	107
50% H_2SO_4	0.01% $FeCl_3$	nil	...	0.3	...	...	...	124
60% H_2SO_4	0.01% $FeCl_3$	0.1	<5	1.0	<5	40	110	143
10% HCl	5% $AlCl_3$	nil	<5	nil	<5	4.9	60	104
10% HCl	15% $AlCl_3$	nil	10	nil	<5	12	175	104
20% HCl	5% $AlCl_3$	nil	<5	nil	5	23	305	104
20% HCl	5% $AlCl_3$	nil	<5	nil	5	19	210	104
5% HCl	10% NaCl	nil	5	nil	<5	1.2	20	101
10% HCl	10% NaCl	nil	5	nil	10	7.4	175	104
15% HCl	10% NaCl	nil	<5	nil	<5	16	215	109
10% HCl	0.005% $FeCl_3$	nil	...	nil	...	1.6	...	104
20% HCl	0.005% $FeCl_3$	nil	5	0.1	5	32	5	110
30% HCl	0.005% $FeCl_3$	nil	<5	nil	5	...	...	92
36% HCl	0.005% $FeCl_3$	nil	...	nil	...	...	...	81

[a] mpy = corrosion rate in mils per year (one mil per year = 0.025 mm/year).

[b] H_2ppm = parts per million of hydrogen absorbed during test.

halogens chlorine, bromine, and iodine, the halogen-containing acids HBr and HI, and almost all salts that do not contain fluorine.

Fabrication Methods Applicable to Refractory Metals

In general, there are three types of construction used to fabricate tantalum, niobium, and their alloys into vessels and other components for the chemical process industry [6]. They are (1) loose-lined, (2) integrally clad, and (3) solid.

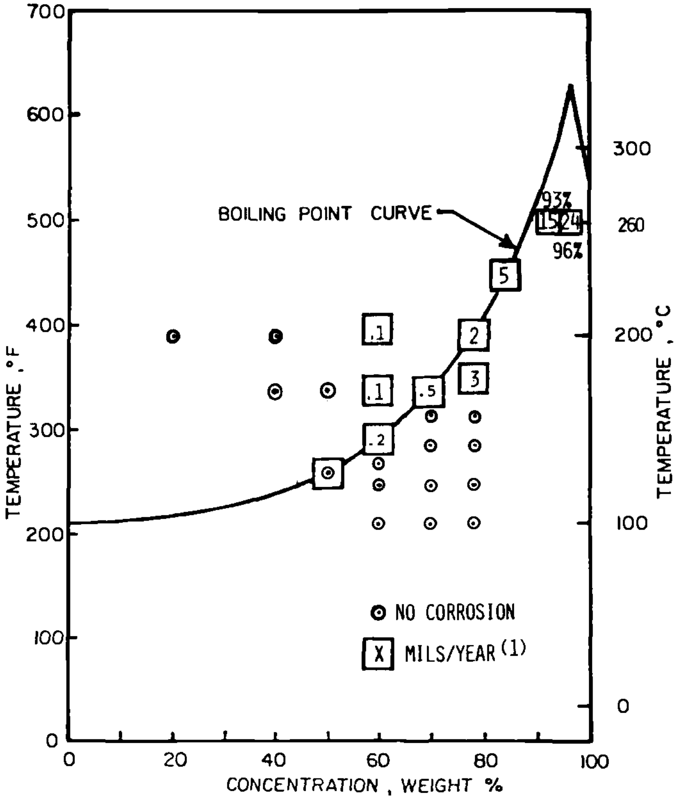

FIG. 4—*Corrosion resistance of tantalum in sulfuric acid* [13].

Loose-Lined Construction

Refractory metals may be fabricated separately as liners and inserted into shells without bonding. This "loose-lined construction" is the most economical and most widely used fabrication method. Liner thicknesses of 0.38 to 0.76 mm (0.015 to 0.030 in.) are satisfactory since corrosion will be uniform. Other corrosion-resistant metals such as titanium or zirconium require thicknesses of 1.0 to 3.2 mm (0.040 to 0.125 in.) to accommodate localized corrosion processes such as pitting, crevice corrosion, cracking by stress corrosion, and corrosion fatigue.

Although economical, the loose-lined type of construction has some intrinsic disadvantages: (1) unsuitability for use in vacuum, (2) limitations with regard to temperature and pressure, (3) poor heat transfer qualities due to air space between liner and shell, and (4) difficulty in repairing liner failures.

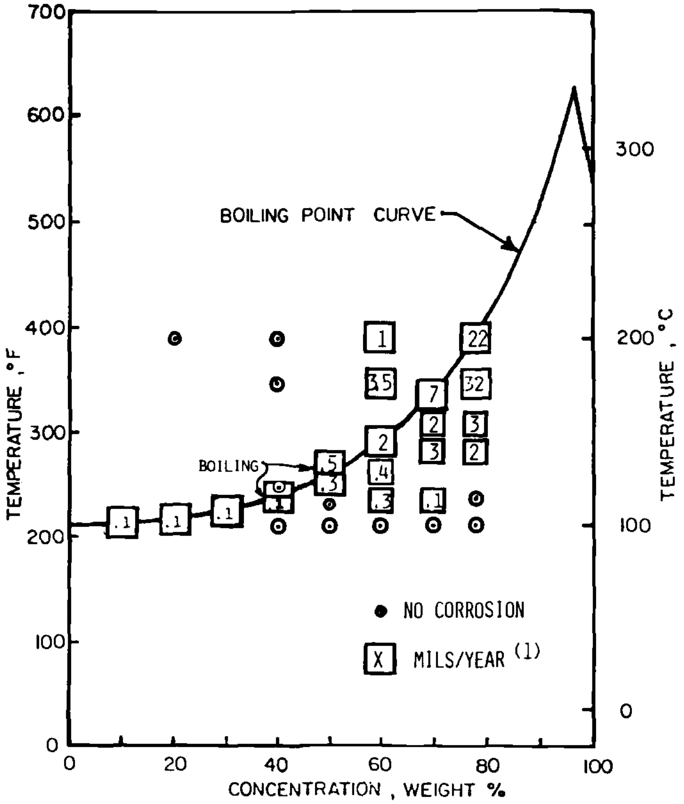

FIG. 5—*Corrosion resistance of KBI alloy 40 in sulfuric acid* [13].

Integrally Clad Construction

In this fabrication method, refractory metal sheet is explosively bonded to a substrate such as copper or steel. No heating is used so each material retains its initial properties. The resulting composite can be rolled, fabricated, or welded. This process has made it possible to construct large high pressure vessels and has contributed greatly to the cost-effectiveness of refractory materials.

Solid Construction

This construction applies to structures manufactured totally from the same corrosion-resistant material. This is the most expensive method of construction. It is only used in cases where no other method is satisfactory, for example, in the case of U-bundle condensers.

Industrial Applications of Tantalum, Niobium, and Their Alloys

There are substantially more corrosion resistance applications for pure tantalum than for any other refractory metal. Not only is tantalum the most corrosion resistant refractory metal, it is extremely easy to fabricate, both from the standpoint of the material supplier and the fabricator or end user.

CPI Reaction Vessels

Tantalum can be cost effective for most reaction vessels. Compared to less expensive materials, with accompanying poorer corrosion resistance, tantalum can be used at higher operating temperatures as well as at higher reactant concentrations, often permitting a reduction in the size of the reaction vessel. Tantalum is typically used as thin sheets explosively bonded to a substrate (usually steel) or used as loose liners. The wall thickness of the substrate is proportional to the pressure in the reaction chamber. For over 30 years, tantalum vessels have been used to produce HCl from hydrogen chloride gas by absorption [*2*]. Tantalum vessels have also been employed in the manufacture of insecticides, pharmaceuticals, fine chemicals, explosives, dyestuffs, and in the condensation of phosgene derivatives. These applications rely on tantalum to minimize product contamination.

Tantalum and niobium vessels have been used extensively in chromic acid plating applications such as tanks, heat exchangers, piping, thermowells, distillation and condensation columns, and anode baskets and bars. Small amounts of fluorides in these plating solutions have been reported not to attack tantalum [*7*].

Tantalum and Ta-10W sheet have been used extensively to repair defects in glass-lined vessels. Tantalum was chosen because of its chemical inertness, which is similar to glass. Disks of Ta-10W alloy, which have a higher yield strength than tantalum [410 MPa (60 000 psi) compared to 140 MPA (20 000 psi)] (Table 4), are often required to maintain more reliable seals when used to patch glass-lined vessels.

Heat Exchangers

Tantalum, niobium, and their alloys are ideal materials for heat exchangers because of their high thermal conductivity. This, coupled with their ability to be used in thin cross sections and their nonfouling character, further increases their ability to transfer heat rapidly [*8*]. By way of comparison, the thermal conductivity of tantalum and niobium is more than twice that of titanium, three times better than zirconium or stainless steels, and four times that of nickel-base alloys. The heat transfer rate does not change with time because the amorphous oxide layer does not become thicker. Heat transfer equipment components include heat exchangers, condensers, bayonet heaters, spiral coils, U-tubes, spargers, and side arm reboilers.

TABLE 4—*Physical and mechanical properties of tantalum, niobium, and selected corrosion-resistant alloys.*

	Tantalum	Ta-2.5W	Ta-10W	KBI alloy 40	Niobium	Nb-1Zr
Density						
g/cm^3	16.6	16.7	16.9	12.1	8.57	8.57
lb/in.^{3}	0.601	0.6	0.610	0.437	0.310	0.310
Melting point, °C	2996	3000	3035	2700	2468	2410
Avg. ASTM grain size, 0.76-mm (0.030-in.)-thick sheet[a]	6 to 7	7 to 8	8 to 9	8 to 9	6 to 7	8 to 9
Tensile strength (min.)[a]						
MPa	206	276	483	276	172	241
psi	30 000	40 000	70 000	40 000	25 000	35 000
0.2% yield strength (min.)[a]						
MPa	138	193	414	193	103	138
psi	20 000	28 000	60 000	28 000	15 000	20 000
Elongation % in 50.8 mm (2 in.) gage length (min.)[a]	25	25	15	25	25	20

[a] Annealed condition.

The Ta-2.5W alloy is also used extensively in heat exchanger applications because it provides increased hardness, strength, and abrasion resistance without sacrificing corrosion resistance.

Other Applications

Tantalum and its alloys (Ta-2.5W and Ta-10W) have been fabricated into intricate shapes such as impellers for sulfuric acid pumps and spinnerettes for the production of synthetic yarn [*2*]. Additional tantalum applications include thermowells, rupture diaphragms, orifices, tower internals, and valve liners.

Tantalum allows a processor to go to higher temperatures, concentrations, and pressures. In this manner, when life cycle costing is considered, tantalum or its alloys (Ta-2.5W or Ta-10W) can represent the most economical approach. Either tungsten-bearing alloy, for the most part, can be substituted for tantalum when improved mechanical properties such as strength and abrasion resistance are required. KBI Alloy 40 can reduce the raw material cost even further.

At lower temperatures, niobium or Nb-1Zr alloy may be considered with significant savings. One can still have the benefit of minimum product contamination and use of thin cross sections.

Cathodic Protection Applications

Niobium is becoming increasingly important in cathodic protection systems [*9–12*] such as for protecting North Sea oil rigs and oil well casings. Niobium, which is becoming the preferred substrate material, has an anodic breakdown voltage of 120 V in sodium chloride solutions and seawater representing an increase by a factor of twelve over that for titanium (10 V) [*12*]. Tantalum, which has a breakdown voltage in excess of 180 V, can also be used.

In these applications, niobium, titanium, or tantalum serve as substrates for the platinum anode. The very high cost of platinum ($475/troy ounce, December 1982) renders solid platinum anodes uneconomical. Metals that form electrically insulating oxide films, such as the reactive and refractory metals, serve as substrates for platinum while not taking part in the anodic reaction. The electrically insulating amorphous oxide films on them prevent current flow from the substrate into the electrolyte and at the same time provide a corrosion-resistant barrier.

Good electrical conductivity of the substrate is required to allow current to flow from the niobium to the platinum. Therefore good bonding of the platinum to niobium is required. This can be accomplished by electroplating or by metallurgical co-processing routes. Often copper cores are used to increase electrical conductivity.

The selection of titanium, niobium, or tantalum is generally dependent upon economics. One has a choice between many large titanium anodes operating at low voltage or a few small niobium or tantalum anodes operating at high voltage with the highest current density possible on the platinum. Platinized niobium is being used for the protection of North Sea oil rigs because of its ability to handle high currents with a reasonably low number of anodes.

Niobium anodes are also finding use in small diameter, deep well, open hole ground beds for the protection of production oil well casings [*10*]. Substantial savings have been reported in the installation cost of anode beds as well as anode assemblies, some savings representing two thirds of the conventional anode bed cost and four fifths of the anode assembly cost. It is anticipated that all deep well casings will eventually be protected by platinized niobium anodes.

It should be noted that the first instance of the susceptibility of niobium (and tantalum) to crevice/deposit corrosion was reported in the deep well applications. Anodic breakdown voltages of as low as 20 to 40 V were recorded. Experiments demonstrated [*11*] that the low voltage was caused by contamination of the surface by copper, iron, and niobium particles. Other metals would also cause this problem. This instance of crevice/deposit corrosion does not limit the wide-scale applicability of niobium and tantalum for corrosion resistance, both polarized and unpolarized. It does, however, show the importance of careful preparation techniques to ensure a clean surface which will avoid initiation of the susceptibility to corrosion. Prefilming in uncontaminated electrolyte, such as pure brine or sodium sulfate, would seem a satisfactory practical expedient to combat any tendency for deterioration in corrosion resistance.

High Temperature Applications

Tantalum, niobium, and their alloys possess a combination of properties that make them excellent materials for high temperature corrosion applications in inert atmospheres or vacuum. The metals have high melting points, good elevated temperature mechanical properties, inertness due to the impervious surface oxide film, and good fabricability. Above 250°C, tantalum, niobium, and their alloys have poor resistance to attack by atmospheric gases (air, oxygen, nitrogen, hydrogen, carbon monoxide, and carbon dioxide). Embrittlement of these metals and alloys results from interstitial compound formation.

The ability of tantalum and niobium to react with large volumes of gases make them ideal as getters in vacuum furnaces and gas purification systems. Other high temperature applications include susceptors, resistance heaters, trays, thermowells, thermocouple sheaths, structural parts, crucibles, heat shields, evaporating dishes, and containers for liquid metals and vapors. Crucibles, particularly of tantalum, are used for high temperature reactions, fusions, distillations, and melting of special glasses. Tantalum crucibles are also used extensively in electronics and metallizing for containing materials for evaporation for thin film deposition.

Liquid Metals Handling

The resistance to liquid metal corrosion is outstanding for tantalum and its alloys and niobium and its alloys (Table 5). In addition to its excellent resistance to corrosion by molten alkali metals, niobium is also highly resistant to attack by sodium vapor at high temperatures and pressures. The Nb-1Zr alloy has been used for millions of end caps in high pressure sodium vapor lamps [5].

Surgical Uses

Tantalum has long been used as a prosthetic material in surgery. In addition to its chemical inertness and ease of fabrication, tantalum is accepted by body tissue. Its surgical advantages include workability, minimal electrolytic action in body fluids, and nontoxicity; these properties allow connective tissue to anchor on the implant and continue normal growth unhampered.

Tantalum is used for repairing cranial damage, for sutures, and as a mesh for repairing large or recurrent hernias. Braid sutures are pliable and strong

TABLE 5—*Resistance of tantalum and niobium to corrosion by molten metals* [14].

Molten Metal	Good Corrosion Resistance of Tantalum up to (°C)	Good Corrosion Resistance of Niobium up to (°C)
Bismuth	900	560
Gallium	450	400
Lead	1000	850
Lithium	1000	1000
Mercury	600	600
Potassium	1000	1000
Sodium	1000	1000
Th-Mg eutectic	1000	850
Uranium	1450	1400
Zinc	450	450

and approach silk with respect to ease of handling and tying knots that do not slip. The wire mesh used to repair hernias is made of strands 0.076 mm (0.003 in.) in diameter, woven into a 50-mesh screen. This metallic gauze supplies the needed support to the weakened area immediately after surgery. Shortly thereafter, fibrous tissue attaches itself to the mesh to provide permanent strength to the abdominal wall. The chemical inertness of tantalum minimizes the damage of post-operative infection. At present, KBI alloy 40 and niobium are not used in surgery. Niobium is suitable for surgical implants [5]. KBI alloy 40 has not been tested.

Conclusions

1. Tantalum, niobium, and their alloys are cost effective compared to materials of lower initial cost, provided their outstanding corrosion properties are properly employed, resulting in trouble-free operation and increased productivity due to reduced downtime and maintenance.
2. Laboratory corrosion tests show near equivalence in corrosion resistance between tantalum and KBI alloy 40 in many corrosive environments. The significantly lower density of KBI alloy 40 dramatically reduces the weight of the product per square foot of alloy sheet when compared to tantalum.
3. Tantalum, niobium, and their alloys can be advantageously employed where conditions are highly corrosive, cost of loss of production is critical, or downtime costs cannot be tolerated.
4. When product contamination cannot be tolerated, the use of these materials is a logical choice such as in the processing of pharmaceuticals, plastics, explosives, insecticides, and dyestuffs.

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Tantalum and Niobium in Some Electronic Applications

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ABSTRACT: The evolution of tantalum and niobium capacitors is reviewed. Present tantalum capacitor technology and commercial activity are summarized. Superconducting materials are reviewed, with specific discussion of niobium alloys and intermetallics. The use of tantalum and niobium oxides is described in the production of tantalate and niobate piezocrystals.

KEY WORDS: tantalum, niobium, capacitors, superconductors, piezocrystals

Electrolytic Capacitors

A capacitor is a device that stores electrons much the same as a surge tank would store water and water pressure in a pipeline. The electrons are stored by using two conductors or electrodes, separated by an insulator. A voltage on one electrode controls the charge on the other electrode by a field effect through the insulator and without any appreciable electron movement between the electrodes. Any two conductors separated by an insulator will have a capacitive reactance. The quantity of electrons stored or involved is expressed in farads. In engineering practice, this value is expressed in microfarads and picofarads. The conventional schematic is shown in Fig. 1. The basic capacitance expression is

$$C = \frac{K(\text{area})(\text{dielectric constant})}{\text{spacing}} = \frac{KAD_K}{t}$$

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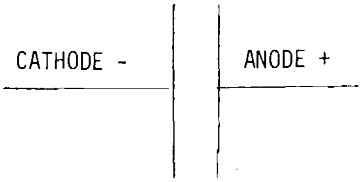


FIG. 1—*Schematic of capacitor dielectrics.*

where

C = capacitance expressed in fractional farads,
K = a constant,
D_K = the dielectric constant of the insulator,
A = area, and
t = insulator thickness or spacing between the electrodes.

This equation demonstrates the benefit of using very thin layers of insulators with high dielectric constants. Capacitors are produced that use insulators made of air, oil, plastics, mica, and ceramic sections. Electrolytic capacitors are made by growing an anodic insulating film on a suitable metal electrode. This procedure provides insulator thicknesses much less than can be produced manually. Thus electrolytic capacitors are used to provide relatively large capacitance values or relatively small physical size.

Many metals can be anodized in an electrolyte to produce an insulating oxide film. Two metals, however, tantalum and aluminum, can be anodized to relatively high voltage and therefore enjoy commercial importance and competition. Niobium can also be anodized to a useable high voltage, but the rate of crystallization of the amorphous oxide film is a distinct technical disadvantage that limits its operating temperature range. Other metals that can be anodized to relatively low voltages include silicon, titanium, zirconium, hafnium, and beryllium. None of these metals is used in commercial capacitor production.

Table 1 compares the dielectric constants and dielectric thicknesses for tantalum, aluminum, and niobium. Barium titanate is included because it is the

TABLE 1—*Capacitor dielectrics.*

	D_K	t, Å/V
Ta_2O_5	25	16
Nb_2O_5	41 [*1*]	25
Al_2O_3	9	14
$BaTiO_3$	5000	(300 V/0.025 mm)
Air	1	...

base material used to produce a monolithic ceramic capacitor, which is a clever design of several individual ceramic capacitors in parallel. As such, it is commercially competitive with tantalum and aluminum electrolytics.

In its simplest form, an electrolytic capacitor is made using a tantalum or aluminum sheet, usually in the form of thin foil. Firstly, the foil is etched to increase the surface area. This involves a special type of electrolytic etching that produces undercut irregularities in the surface of the metal foil. Surface area increases up to 15-fold are achieved in tantalum, and 20-fold with aluminum. Some of this surface area is lost when the amorphous oxide film is grown on the metal. However, the surface area increase is commercially significant.

After the etching operation, the foil is immersed in another electrolyte and the amorphous oxide insulating film is grown by passing a direct current holding the electrode at a positive voltage. This oxide film will grow to a thickness controlled by the voltage drop across the film. Sample thicknesses, in terms of angstroms per volt, are given in Table 1. In this basic form, the capacitor anode is rolled up, placed in a tubular container with a suitable paste or liquid electrolyte, and the ends of the container are sealed to retain the electrolyte and provide egress for a wire connector. In a real case, the interface of the electrolyte and the container wall is also a smaller capacitor in series, which could reduce the performance of the etched foil element. To avoid this, capacitors are made by rolling up two etched foil electrodes, one of which is anodized. In this configuration, the anodized electrode must always be kept at a positive voltage—a polarized capacitor. A nonpolar capacitor can be produced by anodizing both electrodes, with subsequent loss of total capacitance.

Billions of aluminum electrolytic capacitors are built each year. Aluminum has the advantage of relatively low cost, but has the disadvantage of using materials that are actively corrosive, which can lead to failures during extended shelf storage or periods of inactivity in actual circuits.

On the other hand, the tantalum systems used are chemically inert and have indefinite life during periods of inactivity, either on the shelf or in a circuit. This characteristic of tantalum capacitors is the main reason they are used in military, missile, computer, and communication electronics where long life and high reliability are required. This requirement can result from the actual demands on the circuitry, or the cost or complexity of replacement.

These anodic films are polar in the sense that they must remain at a positive voltage in order to remain insulating. If the voltage reverses, the film will pass current. As such, we have the elements of a rectifier. Indeed, tantalum rectifiers were used in railway signaling in the 1930s. This application involved remote operation with infrequent servicing. This rectifier use evolved into capacitor use after World War II when tantalum foil capacitors were made for missile systems and computers. Almost simultaneously, the sintered powder element of a rectifier was used as a capacitor. High purity tantalum powder was pressed to approximately 50% density and sintered around 2000°C to produce a pure surface in a mechanically sound body. The surface was anodized to give an amorphous tantalum oxide film that could be used in sulfuric acid. Many millions of these wet slug capacitors have been produced. They are less expensive than the foil type and offer the advantage of relatively small size. All electrolytic capacitors that use a liquid or paste electrolyte are tough and rugged because in their normal function they can heal any damage to the insulating film. This derives from the fact that the anode, during operation, is always under a positive voltage, and the electrolytes are able to form more amorphous oxide in the event of damage. As mentioned previously, tantalum is compatible with sulfuric acid, which has good conductivity over a wide temperature range. These advantages of temperature range and ruggedness make the wet slug capacitor very useful in military systems.

The use of liquid electrolytes requires a delicate end seal. Many systems and designs are used, but almost all show some degree of electrolyte loss or leakage. This changes the capacitance value of the unit which, in turn, changes circuit characteristics. Many attempts have been made to produce a wet electrolyte tantalum with a hermetic seal. Many proposed designs involved a double-can concept where the inner can, silver or tantalum, and compatible with sulfuric acid, was fitted in a hermetic steel can. These systems are used in quantity today. They are not truly hermetic because there is electrolyte movement from the inner to the outer can space, with subsequent change in capacitance value. Over the last several years, the military has pressed for the production of a true hermetic wet electrolyte tantalum capacitor. This design uses a tantalum can and a tantalum-glass header which is attached to the porous body anode element. The parts of this design are relatively expensive and the final closure is tedious, but the overall performance of the finished unit is excellent. The electrolyte is added before the final closing. The header and can wall are electron-beam welded. This operation must be done properly and rapidly before the electrolyte is exposed to excessive heating. These hermetic wet tantalums are expensive. Their use is almost exclusively military. The present market is estimated somewhere less than one million units per year, with potential use approximately five million units per year.

Tantalum capacitors are referred to as foil, wets, and solids. The most popular type is the solid; this uses a manganese dioxide (MnO_2) electrolyte instead of a liquid electrolyte. This system is then solid state with inherent reliability, and it obviates end seals and electrolyte loss. Also, the solid electrolyte is less affected by temperature changes than the liquid electrolyte. Between two and three billion solid units are produced each year in the Free World. Their simplicity of design and concept has led to broad use. The tantalum is in the form of a pressed and sintered powder body. The voids of this body are impregnated with a manganese nitrate solution which is decomposed at approximately 350°C to leave a thin MnO_2 coat on the amorphous tantalum oxide surface. A thick MnO_2 layer is produced by repeated pyrolysis, and an electrical contact is made to the MnO_2. Today, solid tantalums are made in hermetic metal cans, molded plastic, or dipped epoxy resin. In the industry, these parts are called herms, molded, and dips. Table 2 presents the approximate annual Free World production of these different types along with average selling prices. From these data, one can see the areas of competition. Aluminums are cheap but, in the past, they have been bulky and subject to the internal corrosion cited previously. Over recent years, considerable progress has been made in reducing the size of aluminum electrolytics and reducing the effect of internal corrosion. Aluminums are a good choice if the use provides adequate volume and limited temperature range in an active circuit. Tantalum is the best choice in applications where size and solid-state reliability are required. All solid tantalums have a broad operating temperature range and reduced capacitance change over this temperature range. Tantalum wets and foils are used in special applications resulting from environment, voltage, and reliability. Monolithic ceramics are bulky, but offer broad voltage and temperature ranges.

Among the materials involved, tantalum is the least abundant. Tantalum is mined in relatively small quantities in rather remote places. These conditions bring about relatively big changes in market availability and price. Over the last ten years, the market price of tantalum products has increased about sevenfold; this increase has had the obvious effect on the price of tantalum capacitors. The demand for and price of tantalum varies with overall commercial activity in the world because it is used also in cemented carbide cutting tools, high temperature alloys, and chemical processing equipment. The tantalum capacitor industry must defend its domain with energetic use of demonstrated, innovative skills in reducing the amount of tantalum used in a capacitor.

The basic capacitor equation given before shows that the product of capacitance and insulator thickness is relatively constant for an anodized film. This hyperbolic relationship permits the industry to relate the surface areas available for capacitance in terms of the product of capacitance (microfarads or C) times the voltage (V) used to grow the amorphous film, allowing that this voltage controls the film thickness. Today, conversation about capacitor-grade

TABLE 2—*Free World production and average selling prices of capacitors.*

	Millions of Units/Year	Relative Price, cents/unit
Al	9000[a]	15
Ta solids	2500	35
Ta wets	20	200
Ta foils	4	400
M/L $BaTiO_3$	4000	65

[a] Data from Electronic Industries Association, Washington, D.C., and private communications with producers (1982).

tantalum powder always involves the *CV* per gram available from powder. Early powders operated between 1000 and 3000 *CV* per gram. This product was increased slowly during the early 1970s. Further increases were expedited by increasing costs of tantalum materials so that today powders of 10 000 *CV* per gram are in common use. Beyond this, a fair segment of production is planned at 15 000 *CV* per gram and, indeed, capacitors with good performance have been produced using powders about 20 000 *CV* per gram. This requires powders with more surface area and modified capacitor production that preserves this area. In addition to the *CV* per gram term, the industry now uses other esoteric terms that involve the chemical, physical, and functional performance of the materials involved. Capacitor powder must be of optimum purity, have good feed and flow characteristics for pressing, have adequate strength at approximately 50% porosity, and have optimum internal surface area. These powders have bulk densities of 2 to 3 g/cm^3 and surface areas of approximately 0.26 m^2/g before sintering and 0.09 m^2/g after sintering.

Most commercial powders are produced by the sodium reduction of K_2TaF_7. Some special high voltage and high reliability powders are produced from electron-beam melted ingot. Workers in this field are now engaged in vigorous technical and commercial competition. The future is both challenging and promising.

Superconductivity

The electrical resistance of normal conductors increases with increasing temperature, whereas resistance of most semiconductors normally decreases with increasing temperature. In 1911, Onnes was studying the electrical resistance of mercury at very low temperatures. History records that this work exposed the phenomenon of superconductivity where the resistance to electron flow essentially disappears. Superconductivity remained a laboratory curiosity for a long time. Much work was done in measuring the critical temperature (T_c), where a specific conductor's resistance would go to zero. Critical temperatures of most elements and other materials are well defined in the literature [*2*]. From the beginning this phenomenon was fascinating in terms of its possible applications in machines where current (I^2) is important. However, early superconductors went normal when relatively small currents were passed. This value is called critical current J_c and is expressed usually as amperes per square millimeter. J_c varies with the ambient magnetic field (H).

The practical application of superconductivity accelerated in the early 1960s with the evolution of the BCS theory (Bardeen-Cooper-Schrieffer) of superconductivity and the development of some niobium-base alloys that showed useable current densities. The BCS theory in a simple form states that at 4.2 K conducting electrons couple to each other and move in a synchronous, ordered motion that avoids collisions (resistance).

The development of practical superconductors was aided in no small part by the work at Bell Telephone Laboratories, Westinghouse, and elsewhere. Today, applied superconductivity is a very active technology deeply involved in many major projects. The general areas of interest can be defined as:

- High energy physics.
- Fusion energy.
- Power generation.
- Energy storage.
- Magnetic levitation.
- Power transmission.
- Nuclear magnetic resonance (NMR).
- Magnetic separation.

Niobium and niobium alloys are used widely in these programs. This is probably because pure niobium has the highest T_c of the more common elements available. Table 3 lists some superconducting materials now in use in applied superconductivity projects. This listing compares critical temperature T_c, critical field H_c, and critical current density J_c. These are the values of temperature, magnetic field, and current that will cause a given conductor to lose its superconducting properties and go normal. Vanadium gallium is included in this table because of its current densities at high fields and its use in ship propulsion where space is critical. Nb_3Sn and Nb_3Ge are brittle intermetallics. Their preparation and use in practical conductors require the unique procedures described subsequently.

Niobium is a Type I or soft superconductor which has a low H_c. As such, niobium finds its biggest use in making radio frequency (RF) cavities used to accelerate particles in high energy particle research. The other materials are Type II or hard superconductors with high H_c. These materials fix or pin the flux, and the multifilament designs, described below, further reduce the normalizing effects of flux moves or jumps.

Niobium-titanium is the most common superconductor because it is relatively easy to produce and being relatively ductile can be fabricated into the intricate geometries required for practical superconductors. The niobium alloys used have titanium contents between 35 and 55 weight percent. The most commonly used alloy is 46 weight percent. Typical specifications would require oxygen below 1000 ppm, iron below 200 ppm, with commensurate values for other normal impurities. These alloys are produced by the consumable electrode arc casting of pure niobium and titanium. The cast ingots are fabricated into rods and other sections by combinations of forging, extrusion,

TABLE 3—*Critical values of some superconductors.*

	T_c, K	H_c, T	Relative J_c (10 T, 4 K)
Nb	9	4	low A/mm^2
Nb-Ti	10	10	200
Nb_3Sn	18	24	3000
Nb_3Ge	23	34	2000
V_3Ga	16	22	2000

swaging, and drawing. The alloy producer usually delivers rods or billets to the conductor producer in diameters between 3 and 76 mm (0.125 and 3 in.).

In a practical application, the design of the superconductor must allow for the possibility of the conductor going normal due to excessive temperature, magnetic field, or current. To avoid attendant problems, the superconductor is imbedded in a stabilizing conductor that has low resistance at cryogenic temperatures. Copper and aluminum are both used. Copper is more common.

Pure direct current could be handled in a superconductor with simple uncomplicated large cross-sectional area elements. However, practical superconducting machines involve pulsating currents and magnetic fields. In order to reduce the undesirable effects therefrom, the Nb-Ti alloy is in the form of small filaments imbedded in the stabilizing copper. This improves the cooling and reduces the effect of flux jumps or penetration. These multifilaments develop losses due to eddy currents from the pulsed currents. To reduce this loss, the conductor (and filaments) are twisted longitudinally, which reduces eddy current reinforcement. Typical niobium-titanium multifilament conductors use filament diameters in the 10 to 50 μm range. Figure 2 is a cross-sectional photo of a typical niobium-titanium conductor.

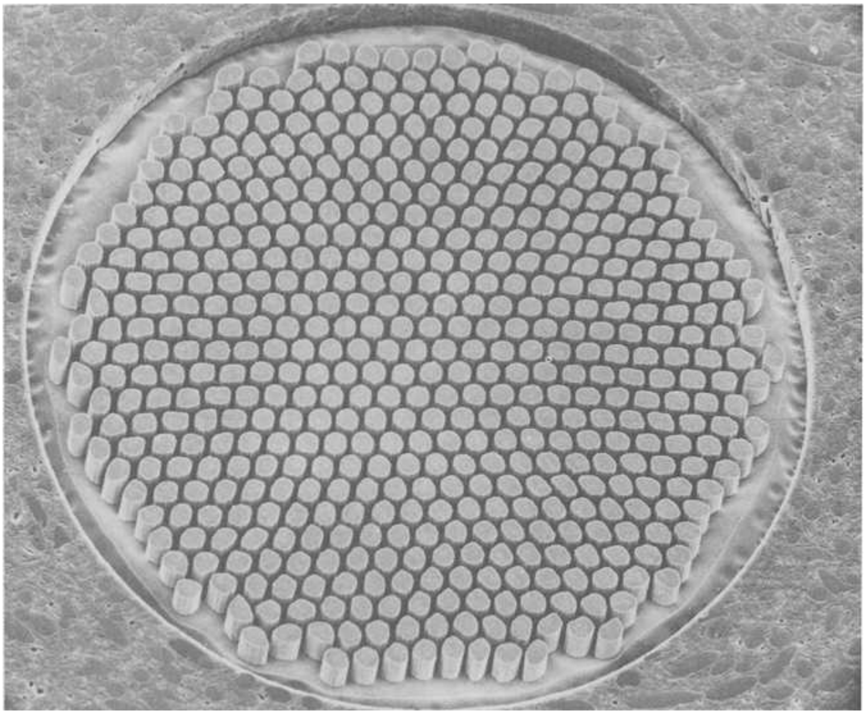


FIG. 2—*Multifilament niobium-titanium in copper stabilizer. 517 filaments, each 10 μm diameter.*

These conductors are produced by extrusion and drawing [*3*]. An extrusion billet is assembled using individual niobium-titanium rods placed inside thin wall copper tubing with a round inside diameter and a hexagonal outside surface. These elements are stacked in a section of heavy-wall copper tubing or pipe to produce an extrusion billet that will contain typically between twenty and several hundred individual niobium-titanium elements. Ends are fitted to this billet for extrusion. In some cases the resulting round extrusion is made into a hexagonal outside surface and a second extrusion billet is stacked to produce a conductor with several thousand individual niobium-titanium filaments. The conductor itself is produced by various combinations of extrusion, swaging, and drawing. The conductor, as finally produced, is in an as-worked condition with high internal stresses. Current capacity is optimized by a delicate heat treatment which varies according to the design and intended use. The design, production, and performance of many conductors is well reported in the literature.

Nb_3Sn and Nb_3Ge are interesting materials because of their higher T_c. The entire superconducting community anticipates the day when a T_c of approximately 30 K is available. This event would promote the use of liquid hydrogen at 21 K instead of the relatively expensive and less abundant helium, at 4.2 K. Originally, thin layers of Nb_3Sn were produced by depositing tin on niobium foil followed by a high temperature treatment. The thickness of the layer must be controlled in order to maintain some ductility in the conductor. Flat tapes for conductors have obvious drawbacks. A need for a round geometry lead to the development of the bronze process [*4*] wherein pure niobium is extruded in a tin bronze sheath. Multifilament conductors are produced by this procedure. In the final form a high temperature treatment will diffuse the tin from the bronze into the niobium surface to again produce thin layers of Nb_3Sn. These multifilament tin conductors are very popular today and are expected to enjoy broad use in the future. In this design a barrier layer of pure niobium or tantalum is used to prevent diffusion of tin into the stabilizing copper which would lower the conductivity of the stabilizer. These Nb_3Sn conductors are sensitive to physical elongation.

Nb_3Ge is produced by the vapor decomposition of the metal chlorides on a suitable substrate [*5*]. Practical superconductor production is difficult, but development is ongoing and results are encouraging.

V_3Ga is presently produced by inserting Va · 5 to 10 wt% Ga alloy rods in a gallium bronze and using a process similar to multifilament Nb_3Sn production [*6*]. Vanadium is a potential problem metal that may retard development and use. Its advantage is high J_c at high field.

Piezoelectricity

The essence of piezoelectricity was discovered in the last century when feeble voltages were observed during the physical compression of certain crystal forms. The reverse of this phenomenon is the basis for the production and use of numerous devices in electronics where voltages are impressed across crystals, and the crystal contracts in terms of physical motion. Other crystal parameters such as photon transmission can be varied by the impression of an external voltage. This phenomenon has an obvious application in modulating electromagnetic radiation from a laser or maser.

In devices, metal electrodes can be applied to a crystal surface, and an a-c signal, in terms of electron motion, can be transmitted through the crystal by physical movement to the other electrode where crystal movement is transformed back into electron motion [7]. The electrodes serve as transducers and in devices are called interdigital transducers (IDTs), usually in the form of a vacuum-deposited metal geometry. The transmission of the signal through the crystal involves a delay; hence their use in the production of delay line devices. The time of the delay can be controlled by the choice of material, the spacing, and the geometry of the transducers. These variables allow the design and production of a large number of electronic devices. To describe the functions of these devices is beyond the scope of this paper. However, such devices can be used to:

- Delay an a-c signal.
- Filter an a-c signal.
- Compress or expand (change frequency) a fixed a-c signal.
- Modulate electromagnetic radiation in a conductor.

Quartz (SiO_2) is the most commonly used material in piezoelectric devices. A thin section of a quartz crystal is used in an electric watch in the conversion of electric energy into precisely timed mechanical motion. Quartz crystals for this purpose are grown from strong alkali solutions of SiO_2 under high temperature and pressure. The cutting, lapping, mounting, and assembly of the crystal section in a device follows conventional and standard practices. Quartz is a very popular material in this application, but it has relatively high losses in converting the electron signal into mechanical motion and vice versa. This efficiency is broadly called the coupling coefficient or Q factor. Other raw materials are now coming into popular use that have more efficient coupling or higher Q factors. These include lithium niobate ($LiNbO_3$), lithium tantalate ($LiTaO_3$), and bismuth germanate ($Bi_{12}GeO_{20}$). Table 4 compares the advantages and disadvantages of these four materials and provides relative piezovalues for a more defined comparison.

The availability of these new materials has accelerated the development of many devices used in telecommunications—radar, color television, etc. One application in color TV sets is the replacement of a tuneable filter, used to split the audio and visual signals, with a nontuneable, fixed, solid-state, surface acoustic wave (SAW) filter. At present this popular device is produced with both lithium niobate and lithium tantalate.

Niobate and tantalate crystals are produced by fusing lithium carbonate with either niobium or tantalum pentoxide in a noble metal crucible. The

TABLE 4—*Piezocrystal comparison* [8].

	Advantages	Disadvantages	Relative Coupling	Relative Velocity
Quartz	temperature stable low cost	high loss low coupling	6	3200
$LiNbO_3$	low loss good coupling	temperature sensitive	260	3700
$LiTaO_3$	less temperature sensitive low loss good coupling	expensive raw material	40	3200
$Bi_{12}GeO_{20}$	lower velocity more delay	medium loss expensive raw material	60	1600

Czochralski method is used to produce a single crystal with designated crystalline orientation and properties. Typical Nb_2O_5 and Ta_2O_5 suitable for this work has Si $<$ 10 and Fe $<$ 3 ppm. The purity of the oxide is more important because it represents between 90 and 94% of the crystal weight. Impurities are important in this procedure because they can have a profound effect on the yield and the quality of produced crystal in terms of operating efficiency.

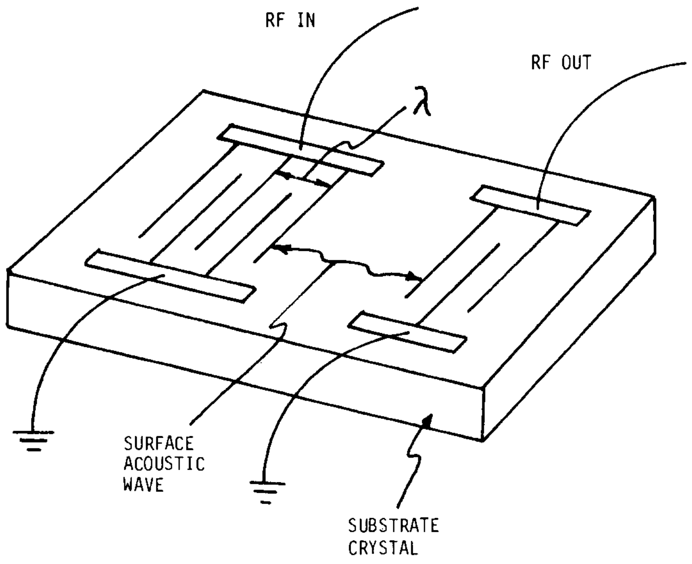
Crystals are ground round, sliced, lapped, polished, and sectioned according to the design of the device. The IDTs are deposited by conventional means of metal deposition. Figure 3 shows a typical device. Again, the design and dimensions of the transducers and the crystal substrate can be varied and controlled to handle specific frequencies and time delays. The distance between the input and output transducers sets the time delay. The spacing of the individual electrodes (parallel to the SAW) sets the frequency.

Lithium niobate would appear to be the preferred material in this application in terms of efficient performance and cost of raw materials. However, technical competition continues. Bismuth germanate is included in this comparison because it has a lower velocity of mechanical motion. This permits longer delay times in the same physical size.

Nb_2O_5 and Ta_2O_5 are also used to control the refractive index of special glasses and to temperature stabilize $BaTiO_3$ in ceramic capacitors. Tantalum and niobium oxalates are used to introduce these refractory oxides in special geometries.

Summary

The industrial history of tantalum and niobium has been fascinating. The future is promising, in both technical and commercial terms. Tantalum use will continue restrained because of its scarce availability and high density



IDT - SHAPE/SIZE CONTROLS FREQUENCY/POWER

SAW - LENGTH CONTROLS TIME DELAY

FIG. 3—*SAW schematic.*

(16.6 g/cm^3). Niobium use will flourish in many areas because of its desirable properties and availability.

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Tungsten: Its Manufacture, Properties, and Application

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ABSTRACT: A brief review is given of the manufacture of tungsten from ore to finish product. Some of the important properties are discussed, and a comparison is made of the properties of tungsten and those of other metals. The uses of tungsten are given as they relate to its properties.

KEY WORDS: tungsten, manufacture, properties, application

Tungsten has the highest melting point of any metal, a very low vapor pressure, and the highest tensile strength of any metal above 1650°C. Its name, in Swedish meaning *heavy stone*, is derived from its very high density. The symbol for tungsten, W, is from its German name, Wolfram. Metallic tungsten was first formed in 1783 by the carbon reduction of tungstic acid (H_2WO_4). It was not until late in the 19th century, however, that tungsten became of commercial importance as an additive to steels for the manufacture of high-speed tool steels. Early in the 20th century, metallic tungsten found use as a filament in the incandescent lamp and later for welding electrodes. In the 1920s, cemented tungsten carbides were first developed in Germany for use as wiredrawing dies for the manufacture of tungsten wire. Cemented carbides now account for 65% of the tungsten consumption.

Occurrence

The concentration of tungsten in the earth's crust is estimated between 1 and 1.3 parts per million, which places it 18th in the ranking of abundancy of metals. There are only four commercially important tungsten-bearing

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minerals. These are ferberite ($FeWO_4$), huebnerite ($MnWO_4$), wolframite ($Fe,MnWO_4$) (containing between 20 and 80% of each of the pure components), and scheelite ($CaWO_4$). All four are commonly found in association with igneous rocks. Figure 1 shows the location of the known world resources of tungsten. China has 53% of the known reserves; Canada is second at 10%. All but 2% of the remaining resources are accounted for in 17 other countries.

Extractive Metallurgy

Tungsten mines are generally small underground mines producing less than 2000 metric tons per day of ore. The deposits usually range from 0.3 to 1.5% WO_3. Some exceptional mines will go as high as 4%. Because of the low concentration, all mines have beneficiation facilities that will produce a concentrate containing from 60 to 75% WO_3. This is achieved by grinding and, in most cases, gravity separation by tabling. Flotation has also been used on scheelites ores. Since wolframite is weakly magnetic, magnetic separators are sometimes used.

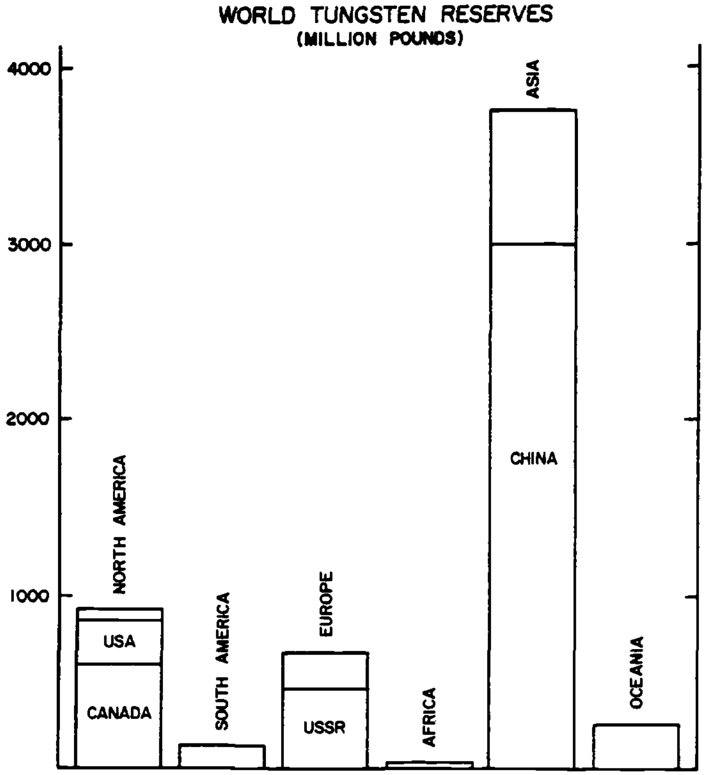

FIG. 1—*World tungsten reserves (million pounds)* [1].

The process by which the ore concentrate is converted into ammonium paratungstate (APT) is extremely critical. For all uses of tungsten except as an alloying additive, very high purity is required and that degree of purity must be achieved in the APT.

The first step in the process may be a pretreatment by leaching with HCl to remove phosphorus, arsenic, and sulfur, or roasting to eliminate sulphur, arsenic, and flotation residues. The next step is to digest the ore and extract the tungsten. There are various methods used to accomplish this but all involve one of the three reactions:

$$Na_2CO_3 + CaWO_4 \rightarrow Na_2WO_4 + CaCO_3$$

$$2NaOH + Fe,MnWO_4 \rightarrow Na_2WO_4 + Fe,Mn(OH)_2$$

$$2HCl + CaWO_4 \rightarrow H_2WO_4 + CaCl_2$$

For the first method the sodium carbonate and scheelite (or wolframite) are reacted in a rotary kiln at 800°C after which it is leached with hot water to remove the soluble sodium tungstate. In the second case sodium hydroxide is reacted with wolframite in a high-temperature autoclave to form sodium tungstate. Finally, scheelite can be reacted with hydrochloric acid to form insoluble tungstic acid.

The sodium tungstate from the first two reactions is removed by filtration. It must then be treated to reduce the silicon, phosphorus, arsenic, and molybdenum levels. This is done in two steps. Firstly, aluminum and magnesium sulfates are added to remove silicon, phosphorus, and arsenic. Then sodium hydrogen sulfide is used to remove molybdenum as a sulfide along with other heavy metals. Both treatments are done at controlled pH levels and the precipitates are removed by filtration.

Next the sodium tungstate must be converted to ammonium tungstate. This is usually done by a liquid ion exchange process. The sodium tungstate is contacted with an organic sulfate, and the tungstate and sulfate ions are exchanged to produce an organic tungstate. It is then reacted with aqueous ammonia to produce ammonium tungstate. Since the reactions involve the exchange of anions, most of the impurities, which are present as cations, are left behind.

The final step in the process is to evaporate the ammonium tungstate solution to form APT. This is done under constant agitation to a constant specific gravity. Further purification is achieved in this process, since most of the impurities still present remain in the mother liquor. The APT is filtered and washed repeatedly. Table 1 shows a typical change in impurity content that is achieved in going from ore concentrate to APT.

In the case of the third reaction, which formed tungstic acid, the process is somewhat simpler. The tungstic acid is digested in aqueous ammonia to produce ammonium tungstate. MgO is added to remove phosphorus and arsenic. Activated carbon is added to help remove colloidal metal hydroxides and sil-

TABLE 1—*Purification: concentrate to ammonium paratungstate (APT).*

Element	Ore Concentrate, ppm	APT, ppm
Al	5 000	<0.7
As	200	<5
Ba	200	<1
Ca	1 500	<0.4
Cr	50	<0.7
Cu	50	<0.1
Fe	150 000	<0.7
Mg	100	<0.3
Mn	40 00	<0.7
Mo	300	<6
Na	1 000	<5
K	1 000	<10
Ni	50	<0.7
P	100	<7
Si	20 000	<1

ica. After filtering, the ammonium tungstate is then evaporated to form APT as described earlier.

Reduction to Metal Powder

Reduction is normally done to an intermediate oxide and then to metal powder. The intermediate oxides encountered are yellow oxide (WO_3), blue oxide (W_4O_{11}) [actually a mixture of $W_{18}O_{49}$ and $W_{20}O_{58}$]), and brown oxide (WO_2). Either carbon or hydrogen can be used as a reducing agent. Carbon introduces many impurities, however, so for most applications hydrogen is used. Both rotary furnaces and tube furnaces with gas or electric heating are used. Rotary furnaces are usually used in the first step. If yellow oxide is desired, air is passed through the furnace at a temperature of 800 to 900°C. The APT is fed into one end and the tilt and rotation of the furnace move it through the furnace as it reacts. For blue oxide, either hydrogen, nitrogen, or a partial vacuum can be used. Reduction directly to a metal powder can be done in a rotary furnace but it is usually not done since it gives a fine and poorly controlled particle size. Reduction to metal powder is generally done in tube furnaces that have a diameter of 80 to 150 mm and are 7 to 9 m long with three independently controlled temperature zones. The oxide is loaded into Inconel boats which are stoked through the furnace. The hydrogen atmosphere flows countercurrent to stoking direction. After each pass through the furnace, the hydrogen is scrubbed and dried and virgin hydrogen added to replace that consumed. The particle size of the tungsten, normally in the range of 1 to 9 μm, is controlled by the furnace temperature, bed depth, and hydrogen flow rate. For large particle sizes, a high temperature, deep bed depth, and low flow rate are used. The conditions used promote particle growth by virture of high moisture conditions in the powder bed.

Consolidation

Because of its very high melting point, tungsten is normally processed by powder metallurgy (PM) techniques. Some rod is produced by arc or electron beam melting but only in very limited quantities. For rod and wire manufacturing, tungsten powder is mechanically pressed into ingots which range in size from 12 to 25 mm square by 600 to 900 mm long. No binder is added to the powder and pressures of about 200 MPa are required. As-pressed, the bars are extremely fragile; therefore they are first presintered at 1200°C in hydrogen to increase their strength so they can be handled. Sintering is done by self-resistance heating. The bar is clamped between two water-cooled contacts inside a water-jacketed vessel containing a hydrogen atmosphere. A current is passed through the ingot and it is heated up to temperatures in the range of 2800 to 3000°C using a controlled heating rate with one or two intermediate holds. This results in a sintered density of 17.2 to 18.2 g/cm^3. A secondary advantage of this method is that considerable purification is obtained by the volatilization of impurities during sintering.

Larger billets for forging or rolling are isostatically pressed. The powder is placed in a plastisol bag, sealed tightly, and then pressed in a isostatic press at pressures of 200 to 300 MPa. In this case, sintering is done in hydrogen atmosphere electric furnaces or induction furnaces at temperatures in the range of 1800 to 2200°C.

Small PM parts are made by adding a binder to the powder and mechanically pressing the parts. The parts are dewaxed and then sintered at 1800 to 2200°C. For some applications the sintering temperature can be lowered to 1500°C by adding small amounts of nickel or palladium to the powder. These produce activated sintering but have the disadvantage of causing severe embrittlement.

Metalworking

Tungsten is inherently a very brittle material at room temperature in the unworked condition. Contrary to the behavior of most metals, as it is worked it becomes increasingly ductile. For that reason, tungsten is cold worked in the metallurgical sense. To overcome the initial brittleness, however, the working temperature must be very high, in the range of 1400 to 1600°C. As working proceeds, the working temperature can be gradually reduced, and in fact it should be reduced to avoid recrystallization which would return it to a brittle state. Another factor that has to be taken into account is its low specific heat and good thermal conductivity which when combined with the relatively small ingot size results in its cooling very rapidly. Any working operation requires rapid transfer from furnace to working equipment and frequent reheating during the working operation.

Swaging is the oldest method of working tungsten rod and is the method developed by Coolidge in 1908 for the manufacture of ductile wire. Swaging temperatures start at 1500 to 1600°C and decrease to about 1200°C as the bar is worked. Reductions per pass start at 10% and increase to 40% as the bar size decreases. Total reductions of 60 to 80% are typical between anneals. Swaging is normally done to sizes in the range of 2.5 to 4 mm. For rod and wire production, rod rolling has replaced swaging in the large sizes. Two high, oval-square grooved rolls are used with 15 to 25% reduction per pass. Temperatures are similar to those used in swaging, and the bars are reheated after one or two passes. More recently, Kocks rolling has also been used as a primary rolling operation. A Kocks mill consists of up to 12 roll stands in sequence with each stand consisting of three rolls at 120 deg to each other. Each stand is oriented at 180 deg to the previous stand so that a hexagonal cross section is produced. This mill has the advantage of rolling at very high speeds, thus obtaining a large total reduction with only one preheat.

Wiredrawing starts with temperatures of 1000°C and reductions per pass of 40%. As the wire size decreases, the drawing temperature is gradually lowered and the reduction per pass decreased. At sizes in the range of 15 μm, temperatures of 500°C and reductions of 10% are used. Carbide dies are used at diameters over 0.25 mm and diamond dies below that size. The lubricant is a graphite suspension in water. A layer of tungsten oxide on the wire provides a base for the lubricant. Drawing speeds for tungsten are slow compared with other materials. They start at 6 m/min and increase to about 120 m/min. Because of its high strength, wire can be drawn to as small as 8 μm. Even smaller sizes can be produced by electro-etching the wire.

Plate rolling on two high mills is also done starting with temperatures of up to 1500°C. One of the problems with rolling tungsten is that, because of the strength of the material, it is not possible to take as large a reduction per pass as might be desired. This leads to large center-to-edge variations in the amount of work in the material, which in turn can lead to delamination or to nonuniform annealed structures. Large total reductions must be used to overcome those problems. The temperature should be gradually lowered to avoid in-process recrystallization. Once reductions of over 95% are achieved, rolling can be done as low as 300°C. Forging is done using either hammers or presses. Because of the relatively slow deformation that is obtained in a press it is difficult to maintain temperature control. For that reason hammers are preferred. Starting forging temperature range from 1350 to 1500°C. Reductions of 30% for each heating are used. After about 50% total reduction the temperature should be lowered to avoid recrystallization.

Tungsten is extruded at temperatures in the range of 1200 to 1350°C using a molten glass lubricant. Since the heat generated in the die can cause a significant temperature rise, the extrusion rate must be carefully controlled to avoid recrystallization in the extruded bar.

Properties

Tungsten appears in Group VIa of the periodic table. It has atomic number 74 and an atomic weight of 183.85. There are five stable isotopes having atomic numbers (and relative abundances) of 180 (0.14%), 182 (26.41%), 183 (14.40%), 184 (30.64%), and 186 (28.41%).

Table 2 gives some of the more important physical properties of tungsten. Wherever possible, the dependence on temperature has been given. The relations are quite good but if extreme accuracy is required, then the sources should be studied. The density given is calculated from the lattice parameter. The value most commonly used is 19.3 g/cm^3. For wire, 19.17 g/cm^3 is used.

In 1968 a value of 3660 K was selected as a secondary reference for the International Practical Temperature Scale (IPTS) [*2*]. However, since 1961 the four values that have been reported ranged from 3680 to 3695 K [*3*].

A better appreciation of the properties of tungsten that make it a useful material can be obtained by plotting the properties of various elements as a function of their location in the periodic table. Figure 2 shows the density of the elements in the central portion of the periodic table. Tungsten, since it is in the third long period, has a high density and because of it, is used in many applications where a high mass is required. Melting point, boiling point, and vapor pressure data are shown in Figs. 3 to 5 respectively. Tungsten has the highest melting point of all the metals and is used as a high temperature material. Figure 6 shows the specific heat as being very low. This and its high thermal conductivity (Fig. 7) result in its cooling very rapidly from high temperatures and is the reason that handling is so critical in metalworking operations. The high thermal conductivity also makes tungsten useful as a heat sink. Tungsten has a very low coefficient of thermal expansion (Fig. 8) and it is therefore compatible with glasses and ceramics in high temperature applications. It has a high modulus of elasticity (Fig. 9) and is used where rigidity is required. Tungsten has a low electrical resistivity (Fig. 10). Although tungsten is used in electrical applications, the low resistivity is of no particular advantage. The high mass absorption coefficient of tungsten (Fig. 11) makes it a very good material for radiation shielding. Tungsten, because of its high atomic number and high temperature properties, is also a very good source for high intensity X-radiation. Another property of importance is tungsten's ability to generate thermal electrons. Table 3 shows a tabulation of the thermal electron current density for various elements. The current density is a function of the work function and the operating temperature. In this case, T_E is the temperature for each of these elements at which the vapor pressure is 10^{-5} torr. Thus it is apparent that tungsten's low vapor pressure is responsible for its high electron emission. The work function of adsorbed films on tungsten

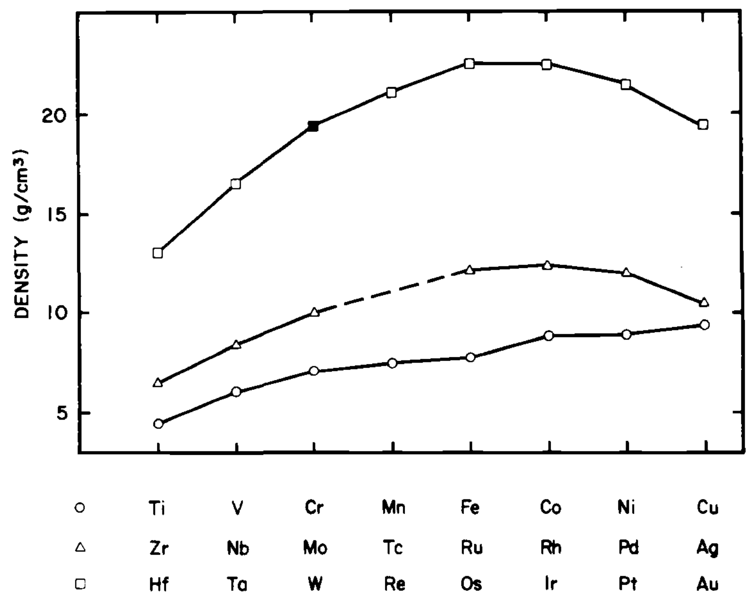

FIG. 2—*Density of elements in central portion of periodic table.*

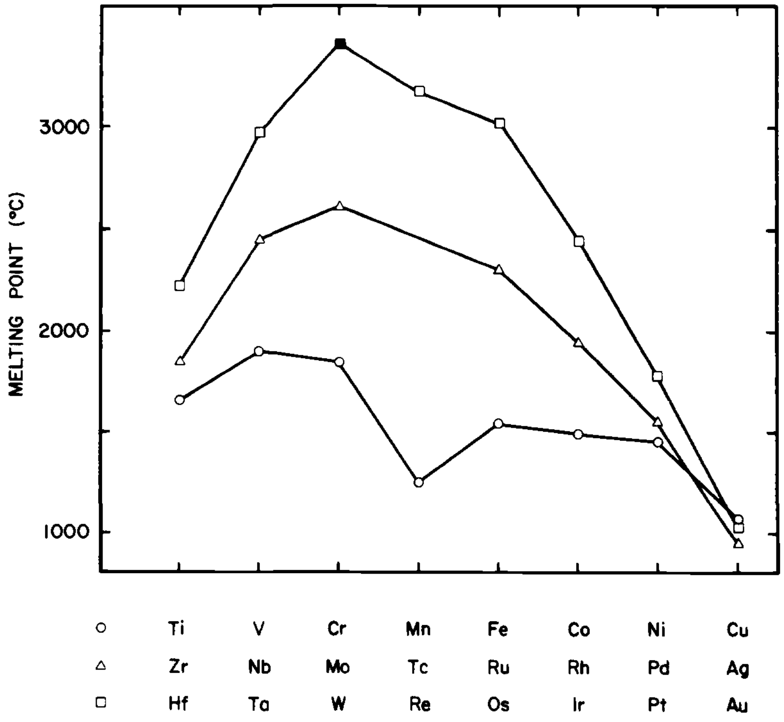

FIG. 3—*Melting point of elements in central portion of periodic table.*

TABLE 2—*Physical properties of tungsten.*

Property	Value	Limits
Structure	body centered cubic	
Lattice constant, nm	0.316 524	25°C
Shortest interatomic distance, nm	0.2741	25°C
Density (X-ray), kg/m^3	19 254	25°C
Melting point [2], K	3660	
Melting point [3], K	3695 ± 15	
Boiling point [4], K	5936	
Linear expansion [5], K^{-1}	$L/L_0 = 4.266 \times 10^{-6}(T - 293) + 8.479 \times 10^{-10}(T - 293)^2 - 1.974 \times 10^{-13}(T - 293)^3$	293 to 1395 K
	$= 0.00548 + 5.416 \times 10^{-6}(T - 1395) + 1.952 \times 10^{-10}(T - 1395)^2 + 4.422 \times 10^{-13}(T - 1395)^3$	
	$= 0.01226 + 7.451 \times 10^{-6}(T - 2495) + 1.654 \times 10^{-9}(T - 2495)^2 + 7.568 \times 10^{-14}(T - 2495)^3$	2495 to 3600 K
Specific heat [6], J/mol—K	$C_p = 24.94\left(1 - \frac{4805}{T^2}\right) + 1.674 \times 10^{-3}T + 4.25 \times 10^{-10}T^3$	273 to 3300 K
Enthalpy [4], J/mol	$H_T - H_{298} = 24.94\left(T + \frac{4805}{T}\right) + 8.372 \times 10^{-4}T^2 + 1.062 \times 10^{-10}T^4 - 7917.8$	
Entropy [4], J/mol	32.66	298 K
Heat of fusion [13, 7], kJ/mol	46.0	
Heat of sublimation [8], kJ/mol	859.8	298.13
Vapor pressure [8], Pa, K	$\log P = \frac{-45\,395}{T} + 12.8767$	2600 to 3100 K

<table>
<tr><td>Thermal conductivity [9], W/cm·K</td><td>T(K)</td><td>k</td><td>T(K)</td><td>k</td><td></td></tr>
<tr><td></td><td>1</td><td>0</td><td>500</td><td>1.46</td><td></td></tr>
<tr><td></td><td>10</td><td>97.1</td><td>1000</td><td>1.18</td><td></td></tr>
<tr><td></td><td>50</td><td>4.28</td><td>2000</td><td>1.00</td><td></td></tr>
<tr><td></td><td>100</td><td>2.08</td><td>3400</td><td>0.90</td><td></td></tr>
<tr><td>Electrical resistivity [10], nΩ·m</td><td colspan="4">$\rho = \dfrac{0.04535T^{1.2472} - 2.90 \times 10^{-9}T^{3}}{1 + \dfrac{3.442 \times 10^{5}}{T^{2.98}}} + \rho_0$</td><td>4 to
300 K</td></tr>
<tr><td>Total emissivity [11]</td><td colspan="4">$\epsilon_H = -2.685790 \times 10^{-2} + 1.819696 \times 10^{-4}T^{4} - 2.194616 \times 10^{-8}T^{2}$</td><td>1600 to
2800 K</td></tr>
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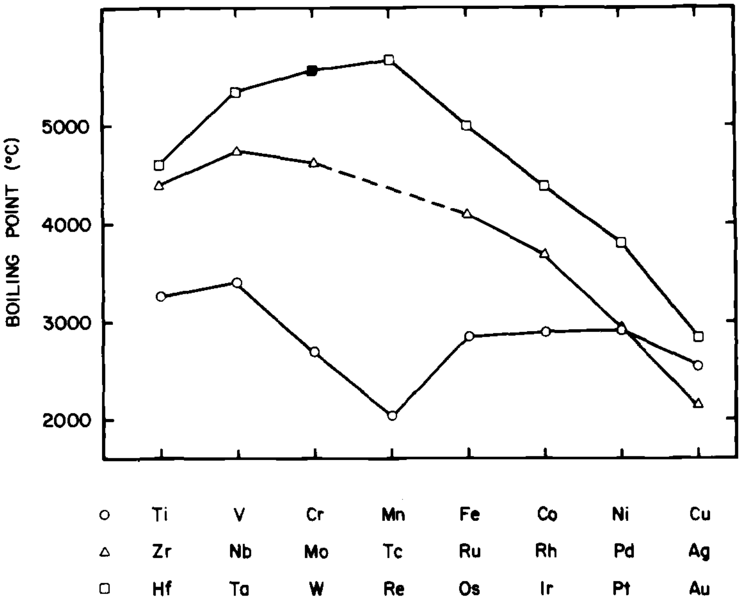


FIG. 4—*Boiling point of elements in central portion of periodic table.*

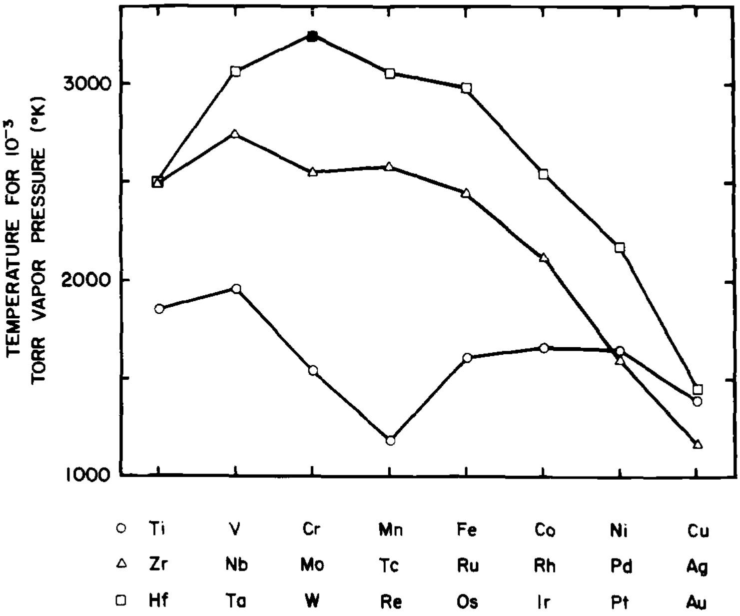


FIG. 5—*Vapor pressure data for elements in central portion of periodic table.*

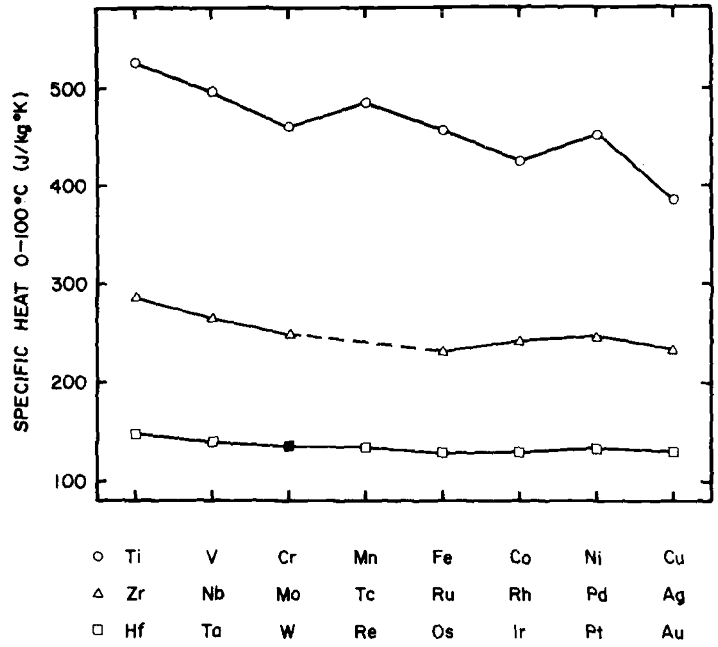


FIG. 6—*Specific heat of elements in central portion of periodic table.*

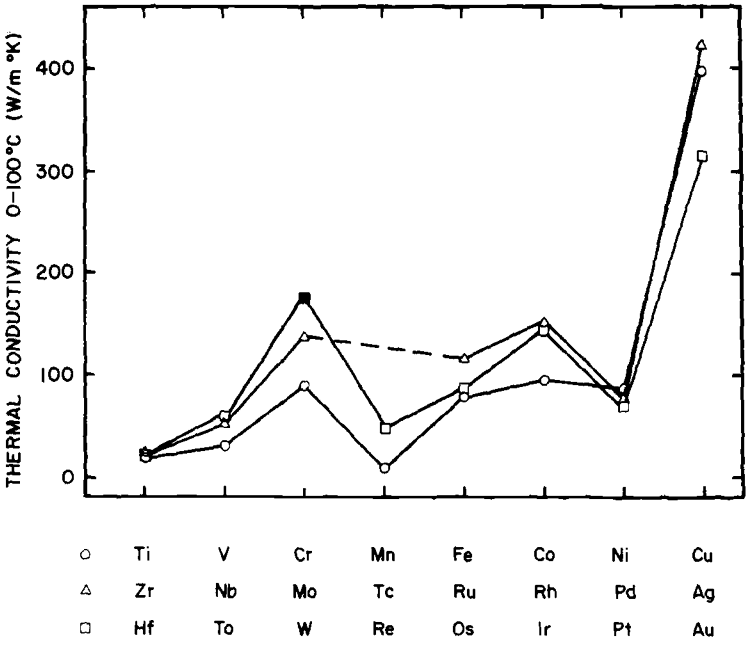


FIG. 7—*Thermal conductivity of elements in central portion of periodic table.*

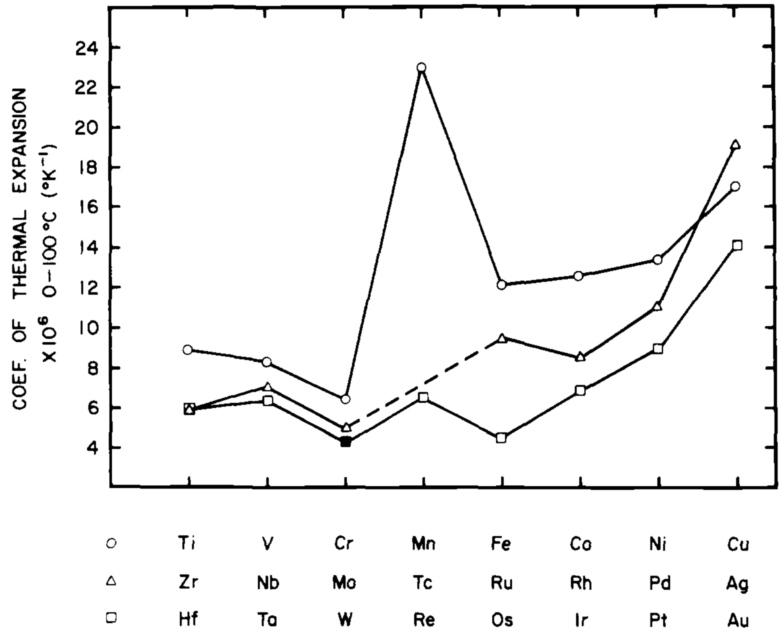


FIG. 8—*Coefficient of thermal expansion of elements in central portion of periodic table.*

is shown in Table 4. These low work functions give high electron emission at relatively low temperatures. Another important consideration in the use of tungsten is its chemical properties. A major factor in the use of tungsten at high temperatures is its lack of oxidation resistance. Figure 12 shows the oxidation rate as a function of temperature. Tungsten starts to oxidize at about 400°C. The oxide layer offers no protection against further oxidation and above 700°C the oxidation rate increases very rapidly. Above 900°C, WO_3 actually vaporizes, and the oxidation is catastrophic.

Table 5 shows the reaction of tungsten with acids and alkalies. It can be seen that tungsten is quite inert to most acids and alkalies. The only acids that attack tungsten are HF + HNO_3 cold or HCl + HNO_3 hot. NaOH or KOH with an oxidizing agent such as H_2O_2 is a common etchant of tungsten. Table 6 shows the stability of tungsten when in contact with various materials at elevated temperatures. Tungsten is attacked by certain gases at low temperatures but on the whole is quite resistant to most materials. It is compatible with most ceramics to high temperatures and has good resistance to molten metals.

The high temperature strength is another property that stands out. It is, however, more difficult to illustrate because it is dependent on many factors. Figure 13 compares stress-to-rupture data for some tungsten materials with data for molybdenum and niobium alloys.

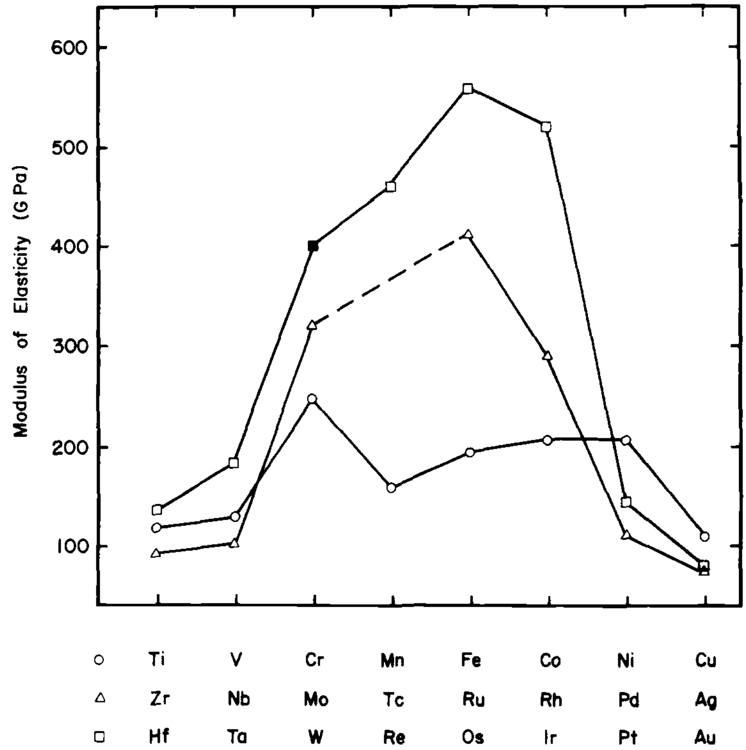


FIG. 9—*Modulus of elasticity of elements in central portion of periodic table.*

One characteristic of tungsten that must be allowed for is its brittleness at room temperature. Tungsten, like all body-centered-cubic (BCC) metals, undergoes a ductile-brittle transition. This is shown in Figs. 14 and 15. For recrystallized tungsten the transition temperature is in the neighborhood of 200 to 400°C, depending on the surface condition and impurity content. It can be seen that tungsten is very notch sensitive and is susceptible to oxygen and other interstitial impurities. As tungsten is worked its ductile to brittle transition temperature (DBTT) is lowered so that as a practical matter, if any ductility is required at room temperature, the tungsten must be in a highly wrought condition.

Applications

Tungsten is consumed in four forms: as tungsten carbide, as an alloy additive, as essentially pure tungsten, and as tungsten chemicals. Tungsten carbide is produced by reacting tungsten powder with carbon black at a temperature of 1500°C. The carbide is milled and between 3 and 25% cobalt is added

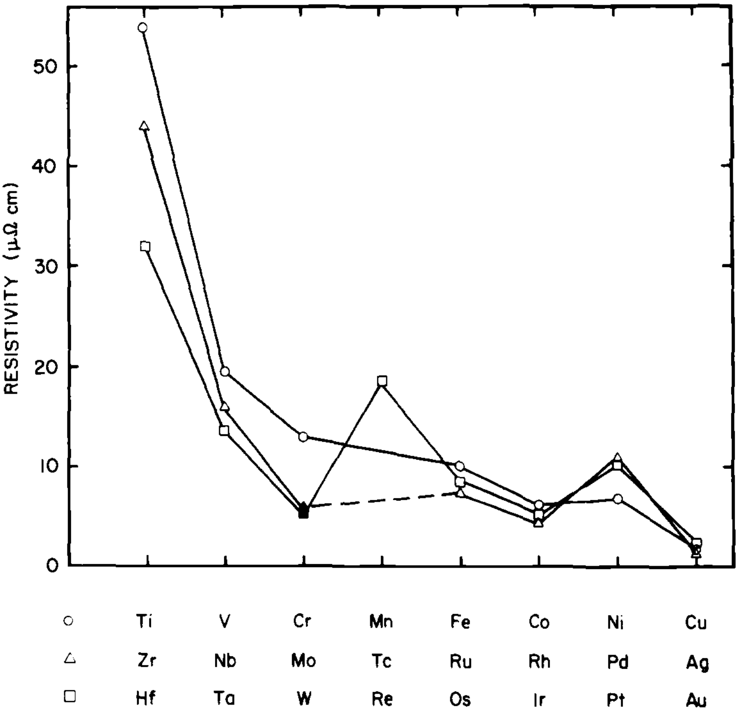


FIG. 10—*Electrical resistivity of elements in central portion of periodic table.*

to it. Tantalum and titanium carbides may also be added for improved hardness. A binder is also added and the mixture is pressed and sintered to form cemented carbides. These are used for cutting tools, mining and drilling tools, forming and drawing dies, bearings, and other wear-resistant applications. Tungsten carbide uses account for about 65% of the tungsten consumed today.

About 16% of tungsten usage is as an alloy additive to steels and superalloys. When added to steels it forms a tungsten carbide phase which refines the grain size and improves the high temperature strength. The fine grain size improves the toughness and provides a more durable cutting edge. For this type of application about 3% tungsten is used, usually with 1 to 4% chromium. For hot-work tool steels, up to 18% tungsten is used. This gives a material which, when quenched from a high temperature and tempered, will retain its hardness up to a red heat.

Metallic tungsten accounts for about 16% of the tungsten consumed. Before discussing these applications, it will help to first mention the more common alloys of tungsten. There are relatively few alloys of tungsten. There are two reasons for this. Firstly, any alloy will have a lower melting point or higher

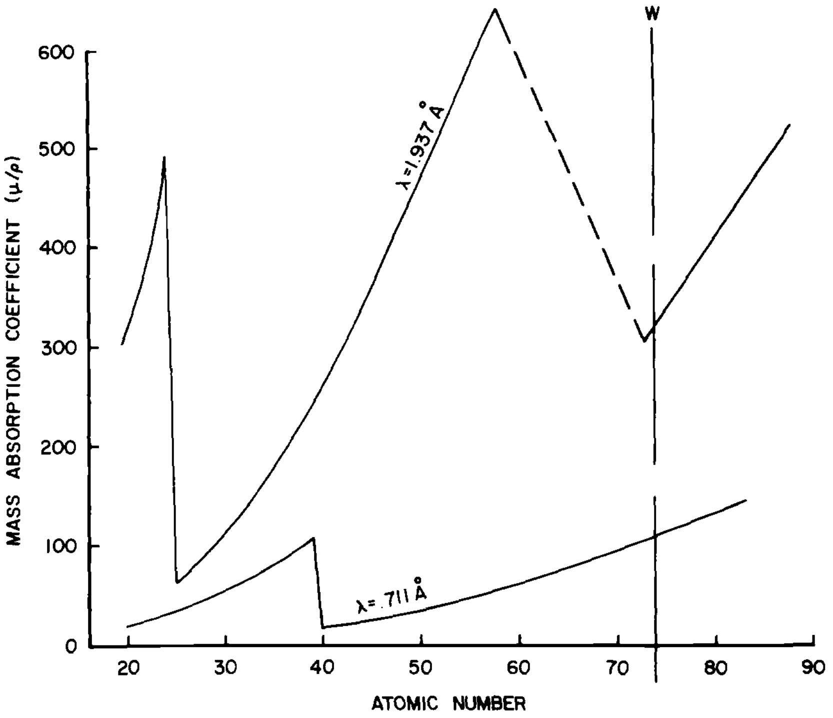


FIG. 11—*Mass absorption coefficient of elements in central portion of periodic table.*

TABLE 3—*Thermal electron current density.*

Element	θ_0, eV	T_e, K	J_s, A/cm^2
W	4.5	2840	5.6
Ta	4.1	2680	5.0
Nb	4.0	2390	0.7
Hf	3.65	2150	0.4
Re	5.1	2850	0.3
Os	4.7	2600	0.2
Mo	4.2	2210	0.05
Rh	4.8	1980	8×10^{-5}
Pt	5.3	1885	6×10^{-7}
Co	4.4	1450	4×10^{-8}
Ni	4.4	1440	3×10^{-8}
Fe	4.5	1385	3×10^{-9}

TABLE 4—*Work functions for adsorbed films.*

W-Cs	1.5 eV
W-Ba	1.6
W-Th	2.7
W-Ce	2.7
W-La	2.7

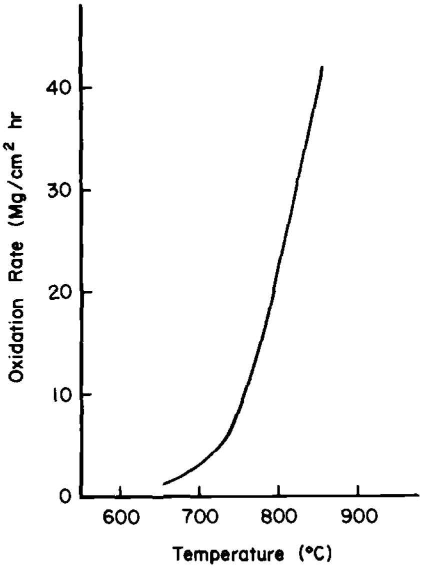


FIG. 12—*Oxidation rate of tungsten at 138 kPa (20 psi) O_2* [12].

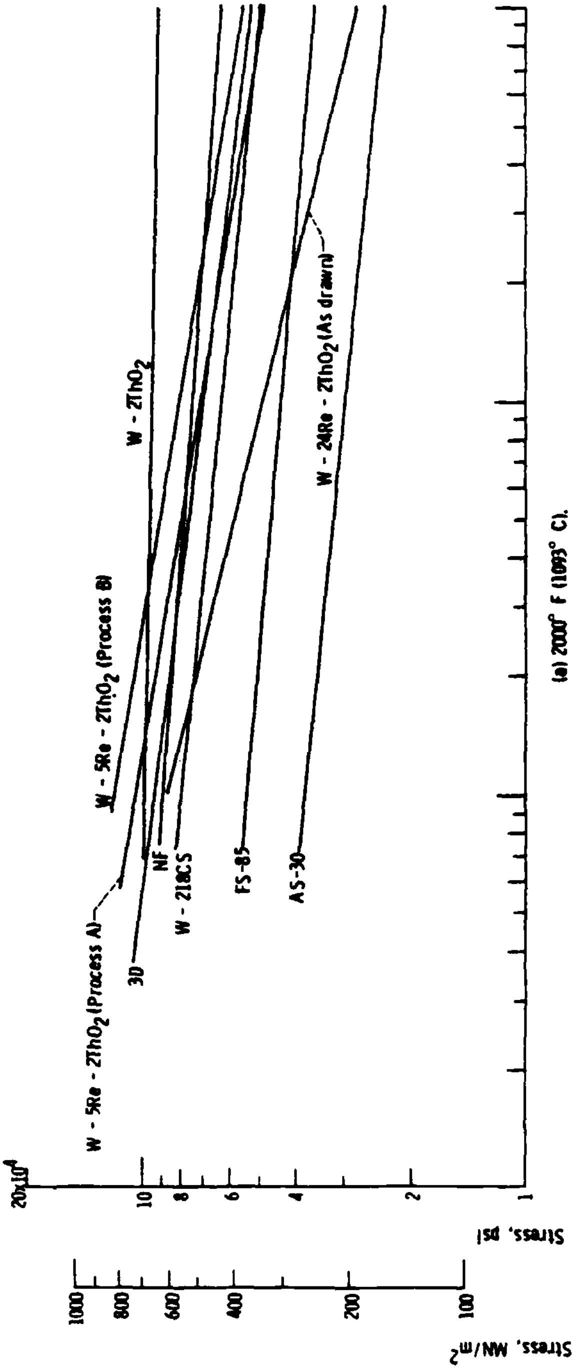
TABLE 5—*Reaction of tungsten with acids and alkalies.*

Temperature	None	Slight	Vigorous
Cold	HF HNO_3 H_2SO_4	HCl + HNO_3	HF + HNO_3
Hot	HF NH_4OH KOH NaOH	HCl HNO_3 H_2SO_4 H_3PO_4 H_2O_2 Alk + H_2O_2	HCl + HNO_3

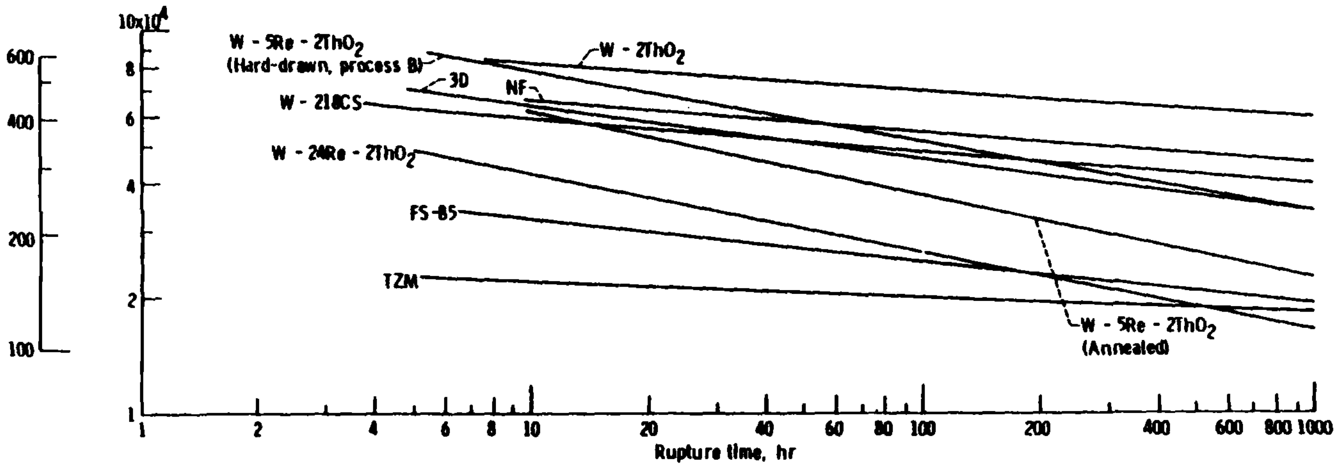
TABLE 6—*Stability of tungsten in contact with various materials.*

Temperature, °C	Gases	Alkalies	Furnace Materials	Molten Materials
20	F			
	Cl			
	O_2			
500	Br	NaOH		Mg Hg
	H_2O HCl	$NaNO_2$		Al
	I H_2S SO_2			Zn
	$N_2ONO_2C_xH_y$			Ga Na
1000	CO			Bi
	CO_2			
			graphite	
1500			MgO	
				Li
2000			Al_2O_3	
			BeO	
			ZrO_2	
			ThO_2	
	N_2			
2500				
No attack	H_2 inert gases			molten UO_2 K

vapor pressure which will detract from the main reason for using tungsten. Secondly, pure tungsten is difficult to work by itself and alloy additions make it even more difficult to work which limits their usefulness. In terms of quantity, the most common alloys are the so-called heavy alloys. These alloys consist of 90 to 98% tungsten with the balance commonly nickel and iron or nickel and copper. The alloys are made by liquid-phase sintering to give a structure consisting of almost pure tungsten particles in a matrix of the alloy elements. Pure tungsten is very difficult to machine. These alloys are used where the high density of tungsten is required but in a machineable form. The only solid solution alloys of tungsten that are commonly used are those with 3 to 25% rhenium. Rhenium is unique in that it imparts low temperature ductility to tungsten. Since the elements are adjacent on the periodic table, the alloys can be worked only with some difficulty. Rhenium also increases the recrystallization temperatures of tungsten and the electrical resistivity. The other common alloys of tungsten are those with 1 to 5% ThO_2. The ThO_2 is either added as thorium nitrate to a slurried blue oxide or directly to the metal powder. The structure consists of a fine dispersion of ThO_2 particles in the tungsten. Thorium, as mentioned earlier, reduces the work function of tungsten and therefore improves electron emission and arc stability. The ThO_2 particles will give increased strength and increase the recrystallization temperatures. ThO_2 also improves the machineability of tungsten.



(a) 2000° F (1093° C).



(b) 2200° F (1204° C).

FIG. 13—*Stress to cause rupture of wires at 1093 and 1204°C (2000 and 2200°F)* [13].

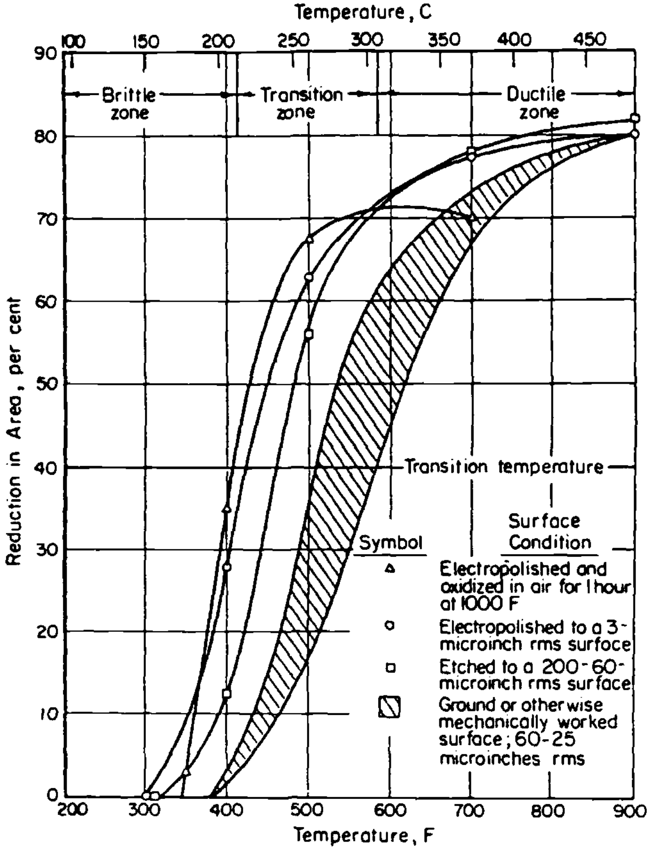


FIG. 14—*Effect of surface condition on low-temperature ductility of recrystallized (1 h at 3500°F) powder-metallurgy tungsten rod (0.170 in.)* [14].

The applications of tungsten can be roughly classified by property. Density accounts for the largest usage of tungsten in the form of the heavy alloys. It is used for kinetic energy penetrators, for counterweights in aircraft applications, for gyroscope rotors, for flywheel rims, and in governors. Tungsten heavy alloys are also used for radiation shielding. Tungsten's high atomic number and high temperature properties also result in the wide usage of pure tungsten for X-ray targets in high intensity applications.

The high melting point and high temperature strength account for many uses of tungsten. Probably the most familiar application is its use as a filament in incandescent lamps. Originally pure tungsten was used and at temperatures over 2000°C creep became a limiting factor in the life of the lamp. This was due to the fact that the wire would recrystallize at a temperature of 1600°C to an equiaxed structure with a grain size on the order of the wire diameter. Grain boundary sliding would then occur, distorting the filament and causing short

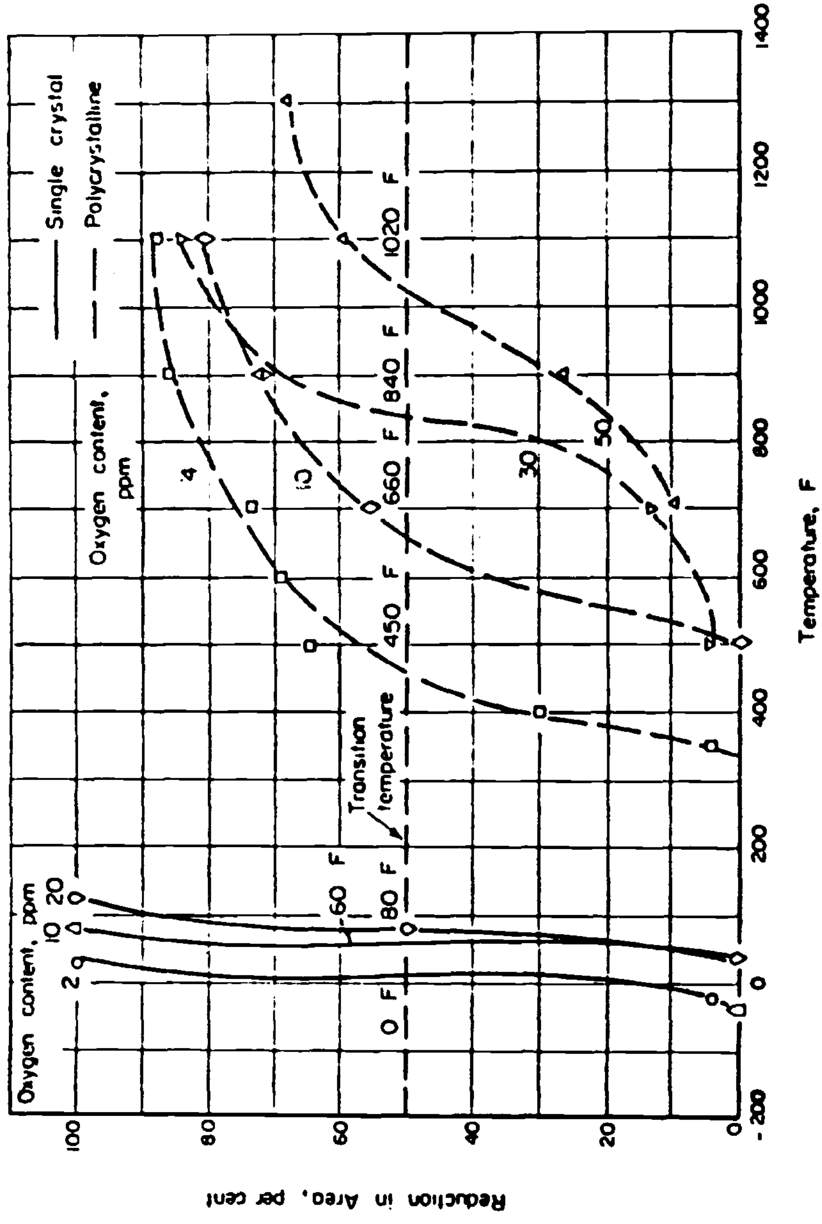


FIG. 15—*Effect of oxygen on ductility of powder-metallurgy tungsten rod (0.125 in.)* [14].

life. Through a combination of accident and invention it was found that much better high temperature strength resulted from the addition of "dopants" to the oxide during the reduction process. Today about 2000 ppm potassium and 1000 ppm aluminum and silicon are added to a slurried blue oxide. This is dried and reduced to metal powder. The dopants that are not mechanically entrained serve no purpose so the powder is washed in hydrofluoric acid to remove the excess dopants. At that point about 100 ppm potassium, 50 ppm aluminum, and 250 ppm silicon remain. During sintering most of the aluminum and silicon are volatilized so that the ingot contains 60 to 70 ppm potassium, 10 ppm aluminum and, 1 ppm silicon. As the ingot is rolled, swaged, and drawn into fine wire, the dopants are stretched out into long stringers. When the wire is heated, the potassium, having a high vapor pressure, will form long rows of tiny bubbles of about 50 Å diameter. These bubbles then act to greatly restrain grain boundary movement, especially in the direction perpendicular to the wire axis. As a result, full recrystallization is delayed until a temperature of about 2200°C, at which point the boundaries break away from the pining points and move rapidly down the wire to form a structure with a grain length many times the wire diameter and whose boundaries are at a small angle to the wire axis. This structure is very creep resistant and permits a reasonable lamp life at temperatures as high as 3200°C.

Tungsten wire is also used as heater wires in cathode ray tubes or other electronic devices. It is used as a heat source in vacuum metallizing. On a larger scale it is used for furnace-heating elements, either in rod form or as mesh element heaters. Tungsten is also used for heat shields, boats, crucibles, structural elements, and a variety of similar uses in high temperature applications. Included here are tungsten-tungsten rhenium thermocouples, which are in wide usage for high temperature control. An added factor in its use at high temperatures is its compatibility with other materials such as ceramics and glasses.

As mentioned earlier, because of its high melting point, tungsten is a very good electron emitter and finds usage in various electronic devices for that purpose. It is also commonly used in conjunction with ThO_2 and BaO in cathodes for emission at lower temperatures. A major use of tungsten is for welding electrodes. Tungsten-2% ThO_2 is commonly used because of its better arc stability and longer life. A similar application is for electrodes in arc lamps where a very intense light source is required.

Tungsten is widely used as a contact material in electrical circuits. In low current applications, such as automotive ignition systems, pure tungsten is used. In higher load systems an alloy of tungsten with copper or silver is used. Tungsten and tungsten-silver alloys are also used as rocket nozzles because of their high temperature properties and ability to withstand the corrosive effects of the burning fuel.

The low thermal expansion of tungsten makes it compatible with many glasses and ceramics in glass to metal seals and as power feed throughs. It is also used as a substrate and heat sink for silicon in high power rectifiers. Finally its high modulus is advantageous in high speed printers where it is used as the impacting member and in boring bars where high rigidity is required.

The final use of tungsten is in the form of tungsten chemicals and accounts for about 3% of tungsten usage. Those include organic dyes and pigments, phosphors in flourescent lights, cathode ray tubes and X-ray screens, and catalysts used in petroleum refining.

This has been a very brief review of a large topic. For more detailed treatments of the topic, the excellent reviews by Rieck [*15*], Smithells [*16*], and Yih and Wang [*17*] are highly recommended.

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Use of Refractory Metals in Chemical Process Industries

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ABSTRACT: The chemical process industry utilizes many different materials of construction to contain and to instrument the many varied and often aggressive chemical processes. Molybdenum, niobium, tantalum, and tungsten, known as the refractory metals, see limited use in the chemical process industry. A summary of the corrosion resistance, mechanical properties, fabricability, economic factors, and special properties of the refractory metals for chemical process applications is given. The various refractory metals are compared to more traditional materials used in the process industry.

KEY WORDS: molybdenum, niobium, tantalum, tungsten, refractory metals, corrosion resistance, properties, chemical process industry applications

The chemical process industry makes or refines various chemicals from raw materials which are then usually sold to others for a multitude of end uses. In considering materials of construction for the various process equipment in chemical plants, the design engineer should consider the economic factors, corrosion resistance, mechanical properties, and fabricability of the materials being evaluated. The refractory metals (molybdenum, niobium, tantalum, tungsten) have desirable properties as well as severe limitations that affect their selection. Not only are materials required to contain the process but suitable materials are needed for instrumentation to control the process.

Process Equipment Material Considerations

The primary consideration in the design of any chemical process plant is that a suitable economic return must be realized on the investment with due regard to safety and environmental considerations. The consideration and use

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of any material depends upon its being more cost effective during the equipment's service life than other metallic and nonmetallic materials. Part of any economic consideration is the requirement that the equipment must have a predictable reliability during its intended service life. Equipment reliability should be an important factor in materials selection and due consideration should be given to increasing equipment reliability even at additional purchase cost. Shortcuts taken in the design and fabrication of equipment solely to lower initial construction cost are usually false economies and should be avoided.

When a materials engineer speaks of corrosion-resistant materials he generally means a material with an acceptable corrosion rate consistent with the economics of the process. In some rare cases materials with very high corrosion rates (greater than 25 mm per year (1000 mpy)) are knowingly selected when they are the most cost-effective materials of construction even though they would not be considered corrosion resistant. However, the general practice is to select materials that have uniform corrosion rates less than 0.25 mm per year (10 mpy) and to add a corrosion allowance so that equipment has a useful service life of 10 years or more. Materials with corrosion rates much lower than 0.25 mm per year (10 mpy) are preferred when thin wall components such as heat exchanger tubing are required. In some cases the corrosion rate of the material must be negligible to prevent product contamination or to preserve the exact geometry of parts even though much more costly materials are necessary to achieve these goals. There are other forms of corrosion besides uniform or general corrosion, and the general practice is to avoid selecting a material prone to attack by these other corrosive mechanisms if the alternative materials are not prohibitively expensive. The mental process used to select materials resistant to abrasion, erosion, and other forms of wear is similar to that used to select corrosion-resistant materials.

The vast majority of chemical process equipment are constructed of materials with room-temperature tensile strengths less than 689 MPa (100 ksi); most materials have room-temperature tensile strengths of 275 MPa (40 ksi) to 517 MPa (75 ksi). High-strength materials with room-temperature tensile strength exceeding 689 MPa (100 ksi) are often used for fasteners, shafts, mandrels, and other relatively small components which usually do not involve welding and are not pressure containing. The usual design practice for pressurized components is to follow the ASME Boiler and Pressure Vessel Code, Section VIII, Division 1, or more rarely Section VIII, Division 2. Piping design practices generally follow the guidelines given in ANSI/ASME B31.3; this is based on the ASME Boiler and Pressure Vessel Code. Design for equipment other than pressure vessels and piping generally does not follow any national design code, but the allowable stresses used in design are usually similar to those given in the ASME Codes. Since many states require ASME Code design, use of materials, design, and fabricating practices outside the code are generally avoided. Nonmetallic coatings and linings are allowed in code design as long as they are not principal pressure parts. Nonmetallic pressure vessels are generally not used, though a few have been built and designed in accordance with ASME Section X (Fiberglass-Reinforced Plastic Pressure Vessels), but nonmetallic piping and nonmetallic internals in pressure vessels are commonly used.

The size requirements of mill products used in chemical process equipment vary from the very small to very large. For example, the majority of process plant piping is ½ to 4 in. NPS; smaller piping is rarely used but larger piping is fairly common. Not only does the correct size have to be available but fabrication techniques also must be suitable for process conditions. Some materials are more suitable for small equipment, while other materials lend themselves more readily to large equipment items. Ductility is a very important aspect of any material selection, since abuse during service or maintenance is fairly common; in fact, brittle materials such as glass are often avoided by operating personnel even though they are entirely suitable for the service.

The refractory metals have certain properties that are attractive, but other properties are severe deterrents to greater utilization in the process industry. A review of the attractive properties and limitations of each of the refractory metals follows.

Economic Considerations

The initial cost of refractory metals is several times greater than the corrosion-resistant nickel-based alloys. Adding to the price is the higher cost of fabrication, since welding must be done under inert gas or vacuum. Prices of the refractory metals have fluctuated considerably since the early 1970s, but in general molybdenum is the least expensive while tantalum is the most costly. However, the price differences tend to disappear when fabrication costs are considered, since tantalum and niobium are more easily fabricated into equipment by welding and explosive cladding. Molybdenum still holds a cost advantage over tantalum if welding is not involved.

While niobium is usually similar in price per pound to tantalum, the lower density of niobium translates to about half the price of tantalum on a volume basis. The lower cost per unit volume of niobium has been taken advantage of in the 60Ta-40Nb alloy, which in many environments has similar corrosion resistance to tantalum but is lower in cost.

The use of refractory metals has been limited by their much higher cost compared with other metallic or nonmetallic materials. The refractory metals are used only when their life cycle costs become a distinct advantage over other competing materials. The economic advantage of the refractory metals must usually be very significant compared with the more familiar corrosion-resistant materials for process industry designers and engineers to select them. This prejudice towards what is termed the "exotic metals" is less for tantalum than for the other refractory metals. A couple of instances of reverse prejudices are known where a refractory metal was selected over silver, which was similar in initial cost, but in those cases the theft of silver was of concern to operating personnel.

Corrosion Considerations

The corrosion resistance and physical properties of the refractory metals fall into two groups (molybdenum-tungsten and niobium-tantalum). As would be expected from their position in the periodic table, the lower atomic number elements (molybdenum and niobium) almost always have poorer corrosion resistance than their sister elements (tungsten and tantalum). All these metals suffer severe oxidation in air, with the attack becoming of engineering concern at about 300°C for tantalum and niobium and somewhat higher for molybdenum and tungsten. All these metals will corrode or react at high temperatures with nitrogen, water (steam), carbon monoxide, and carbon dioxide, with serious attack occurring at a lower temperature for tantalum and niobium than for molybdenum and tungsten. Molecular hydrogen will be absorbed by tantalum and niobium at 250°C and above, and severe embrittlement from atomic hydrogen generated by electrochemical means may occur at room temperature. Conversely, hydrogen at any temperature has no effect on molybdenum and tungsten.

At temperatures below 300°C the refractory metals, especially tantalum, have useful corrosion resistance to acids, salts, and organic compounds. All refractory metals are attacked by strong bases, though they usually have useful corrosion resistance in alkaline solutions at room temperature. Table 1 compares the usefulness of the refractory metals with titanium and zirconium in several environments.

The common alloys of these metals have similar corrosion resistance to that of the pure element. Two alloys (70Mo-30W and 60Ta-40Cb), however, have corrosion resistances falling between the two parent elements. These two alloys are considerably more corrosion resistant in some environments than the lower atomic number element, but are less costly than the higher atomic number element.

Molybdenum and tungsten are corrosion resistant to reducing mineral and organic acids over a wide range of concentration and temperature. Oxidizing acids and oxidizing agents ($FeCl_3$, oxygen, etc.) in reducing acids will attack both molybdenum and tungsten, with tungsten being the more corrosion resistant. Unlike tantalum and niobium, both molybdenum and tungsten are very corrosion resistant to hydrofluoric acid and to acid fluoride salt.

Molybdenum is almost always used instead of tungsten in chemical processes operating below 300°C, since it is more ductile and less costly than tungsten. Even though molybdenum is one of the few metals that can resist hydrochloric acid over most concentration and temperature ranges, it is rarely

TABLE 1—*Corrosion resistance of refractory and reactive metals in boiling solutions.*[a]

Solution	Mo	Nb	Ta	W	Ti	Zr
10% HCl	S	S	S	S	NR	S
10% HCl + 1% $FeCl_3$	NR	S	S	NR	L	NR
5% HF	S	NR	NR	S	NR	NR
65% HNO_3	NR	S	S	NR	S	L
10% oxalic acid	S	NR	S	S	NR	S
15% H_2SO_4 + air	NR	S	S	S	NR	S
40% H_2SO_4	S	L	S	S	NR	S
70% H_2SO_4	L	NR	S	L	NR	NR
10% NaOH	NR	NR	NR	NR	L	S

[a]S - Satisfactory for use; corrosion rates less than 2 mpy.
L - Corrosion rates exceed 2 mpy; possible hydrogen embrittlement or stress corrosion cracking, but alloy has been successfully used.
NR - Excessive corrosion; considered unsatisfactory for use.

used for this service since much less expensive metals like Hastelloy B-2 (70Ni-30Mo) and zirconium have similar corrosion resistance. Molybdenum has useful corrosion resistance in all strengths of sulfuric acid up to 75% at the boiling point but only at lower temperatures in higher concentrations due to the oxidizing nature of sulfuric acid under these more extreme conditions.

Molybdenum is generally used under the extreme temperature and concentrations conditions in reducing acids where Hastelloy B-2 or zirconium is not suitable and weld fabrication is not required. Tantalum is generally used when welding is required. The exception is in hydrofluoric or acid fluoride environments where zirconium, tantalum, and niobium suffer catastrophic corrosion. Under these hot acid fluoride conditions few materials other than certain fluorocarbons, molybdenum, tungsten, and certain precious metals have useful corrosion resistance. Usually molybdenum components used in process services are machined from solid mill stock. These relatively small items are used as valve seats and trim, pump seals, gaskets, and other components that must experience very low corrosion rates.

Occasionally molybdenum will be used for components in equipment that experiences abrasion or other forms of wear and require a material with high corrosion and wear resistance. Tungsten would perhaps be more resistant to the wear but the limited size of shapes available, brittleness, and higher cost favors molybdenum.

Molybdenum or tungsten coatings are not considered useful corrosion-resistant materials since the coatings are not considered pin hole free. Some limited success has been achieved using a molybdenum flame spare coating on a substrate which was corrosion resistant to the process but not abrasion resistant. These spray coatings have suffered spalling, often over a large area, and are of questionable merit. Flame spray coatings of either molybdenum or tungsten would not protect a substrate from corrosion attack since the coatings are porous.

Niobium and tantalum have good to excellent resistance to reducing acid environments, but are also able to withstand oxidizing acid environments. The corrosion resistance of niobium is similar to that of the much less costly zirconium except that zirconium is resistant to strong alkaline conditions but is attacked by oxidizing metallic chlorides. Niobium is less resistant than tantalum to almost all process streams with the notable exception of some complex fluoride plating baths where it is preferred over tantalum.

Platinized niobium anodes are used for cathodic protection process equipment and for electrochemical processes. Platinized niobium electrodes have a breakdown voltage higher than that of platinized titanium but less than that of platinized tantalum.

One possible use for niobium in the process industry is in strong acid chloride systems that sometimes have strong oxidizing agents present at fairly high concentrations. Titanium alloys can tolerate such a system only when the strong oxidizers are present in significant amounts, while the reverse is true for zirconium or Hastelloy B-2. Tantalum is the only other metal that is resistant to both reducing and oxidizing chloride systems, but many nonmetallic materials are also resistant.

The great majority of refractory metal applications in the process industry involve tantalum. Tantalum has useful corrosion resistance below 300°C to all process streams except strong alkaline solutions, fluorine, acid fluorides, fuming sulfuric acid, and free sulfur trioxide. Its corrosion resistance is comparable to that of glass, and the two materials are used interchangeably in many processes, tantalum being selected for those applications requiring the thermal and electrical conductivity of a metal and where good ductility is needed.

While the major use of tantalum is for applications where corrosion rates for other metals are very high, considerable tantalum is used where no corrosion at all can be tolerated, such as instruments, spinnerettes for synthetic fibers, or rupture disks.

A relatively new alloy (60Ta-40Nb) is occasionally used, primarily in those applications requiring negligible corrosion rates. While this alloy is not as corrosion resistant as tantalum to the more aggressive process conditions, its corrosion resistance in many cases is equal to that of tantalum and it is less expensive.

Physical Properties

Refractory metals are often selected for process industry application over competing nonmetallic materials because they have properties that are normally associated with more common metals. The combination of high thermal and electrical conductivity, tensile strength, modulus of elasticity, and formability of the refractory metals is not to be found in any nonmetallic material. Niobium, tantalum, and to a limited extent molybdenum also combine high strength with good to excellent toughness. Often overlooked but important in lining applications is the impermeability of refractory metals to process fluids and gases that usually penetrate plastics, elastomers, and most ceramics. The physical properties of the refractory metals at up to 300°C are similar to those of other metals used in the process industry (Table 2). Between 300 to 1100°C the tensile properties of the refractory metals remain at fairly high levels, while those of the more common metals fall sharply with an increase in temperature.

Perhaps the major use of refractory metals in the process industry is that of tantalum for heat transfer surfaces such as heat exchangers, heating coils, and bayonet heaters. The vessel or other containers that heat transfer equipment is used in may be constructed of glass or fiber-reinforced plastic, or lined with acid brick, glass, or an elastomer. While nonmetallic materials have the required corrosion resistance, they do not have the required combination of strength, creep resistance, ductility, or thermal conductivity associated with metals.

Another major use of tantalum is as linings for high-pressure service where the strength, ductility, and welding properties are important considerations. Usually the tantalum is explosively bonded to steel so that an impervious corrosion-resistant metallic lining metallurgically bonded to a high-strength substrate results.

The use of tantalum or some of its tungsten or niobium containing alloys for relatively small parts like spinnerettes is justified not only because of its immunity to corrosion and high strength but also because of its machinability.

One specialized use of molybdenum and possibly tungsten is for chemical process components requiring a high modulus of elasticity in tension combined with good thermal conductivity, ductility, and strength. Some applica-

TABLE 2—*Typical mechanical properties of plate at room temperature.*

Material	Tensile Strength, MPa	Yield Strength, MPa	Elongation in 50 mm, %	Modulus of Elasticity in Tension, 10^4 MPa
1020 C/S	450	240	25	21
Type 304 S/S	515	205	40	19
CP-Titanium	345	275	20	10
Hastelloy B-2	750	345	40	21
Molybdenum	690	515	30	32
Niobium	170	105	25	10
Tantalum	205	140	30	19
Tungsten	1860	...	0	41
Zirconium	380	205	15	10

tions that require these properties are mandrels and other components used in the extrusion of various plastics and resins.

Fabrication

For a material to have wide usage in the process industry it must be capable of being joined by welding or other bonding techniques so that the joint is sound, corrosion resistant, and ductile. Although molybdenum is capable of being welded with sound joints, the welds are very brittle and thus its use is limited. Tantalum, while weldable only under specialized conditions, has welds and heat-affected zones equivalent in corrosion resistance and ductility to the parent metal.

Because of its high cost tantalum is usually used in a very thin gage. Tantalum heat exchanger tubing is usually unlined and uncladded. This thin material must have the necessary strength to withstand the service stresses. For this reason tantalum equipment must be handled with more care than is the usual practice with more common metals. The design of this thin wall equipment must also take into account the use of a margin of safety less than is considered normal in industry practice.

At least some part of tantalum equipment requires a backing material for strength, which is almost always steel. The tantalum is used to loose-line the steel or is explosively clad. Where welding is required, special weld joint designs have been developed to get around the problem of tantalum's high melting point and the requirements for contamination-free welds. Another special consideration is the relatively small size of mill products available, and for large equipment this may require more joints than would be the practice for more common metals. An ideal design would have as few joints as possible, since more joints add to the cost and decrease reliability. Fortunately many of these problems have been overcome and some very large pieces of process equipment have been constructed out of tantalum.

Small items such as instruments will often be plated with tantalum by a fused salt process. Components so plated have given excellent service and represent one of the few cases where plating has been a successful technique in preventing process industry corrosion.

The welding of tantalum and niobium usually involves very thin material. The area to be welded must be absolutely clean of any foreign materials and must be welded under inert gas or in a vacuum to prevent weld contamination. While this does not present too much difficulty in a properly equipped shop for new equipment, it causes great difficulty in the field in repairing equipment. Due to these welding difficulties, the probability of severe corrosion of the substrate material, and the possibility of hydrogen embrittlement of tantalum and niobium due to corrosion, it is of the utmost importance that all joints be sound and leak-free. Often weep holes are drilled in the steel-backing material to monitor leakage at joints.

Conclusions

Refractory metals continue to be used in the process industries even though newer metallic and nonmetallic materials have appeared on the scene. This consistent use is partly due to more aggressive conditions being encountered in the newer processes and partly due to the unsatisfactory performance of competing materials. As traditional sources of feedstock may no longer be economically feasible and as the demands for lower operating and maintenance costs increase, the process industries will have to develop and operate processes that are very reliable and cost effective.

The equipment needed for these newer processes will have to be as reliable if not more reliable than that used in the past. Since refractory metals are relatively quite costly compared with other materials, it is important that their life cycle cost effectiveness and reliability be compared with other materials and not their initial cost. Sacrificing reliability to increase sales will in the long run decrease the acceptance of the refractory metals in the process industries.

Refractory metals equipment has in most cases given very good to excellent service in the process industry. When it has failed to give cost-effective and reliable service it usually has been that the manufacturer and purchaser did not have a complete understanding of each other's needs and capabilities. It is hoped that this presentation of a user's view of the process industries requirements will promote the needed dialogue between producers and consumers.

Summary

The ASTM Symposium on Refractory Metals and Their Industrial Applications was conceived in order to provide a guide and a handbook on practical usage of these materials in today's complicated technology of industrial production. Seven papers were presented, six papers from producers and one from a user of refractory metals.

Mullendore and *Burman* give a brief review of the manufacture of tungsten and molybdenum respectively from ore to finish product. The important properties of each metal are given and a comparison of these properties with other materials is made. The uses of tungsten and molybdenum are given as they relate to their properties.

Webster covers the manufacture, properties, and uses of niobium. *Hunkeler* considers the application of tantalum in the chemical process industry. Additional information on the corrosion resistance of tantalum and niobium is provided by *Burns et al. Belz* discusses the use of tantalum and niobium for capacitors, super-conducting materials, piezoelectricity, and other electronic applications. A user's view on the applications of refractory metals in the chemical process industry is given by *Smallwood.*

The refractory metals have high melting points, relatively high tensile properties at elevated temperatures, and experience catastrophic oxidation in air at elevated temperatures. Molybdenum and tungsten have high elastic moduli, relatively poor ductility and, except for a limited number of environments, are not particularly outstanding in terms of corrosion resistance. Niobium and tantalum are ductile materials with oxide films that are responsible for their excellent corrosion resistance and electronic properties.

The refractory metals, despite relatively high cost and fabrication difficulties, have many engineering uses. Engineering applications of refractory metals are so varied that they will be found as filaments in the smallest light bulb and as linings of very large distillation columns. As more engineers and designers become familiar with the refractory metals the different applications are certain to increase.

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