NIOBIUM AND NIOBIUM ALLOYS IN CORROSIVE APPLICATIONS

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Abstract

Niobium and niobium alloys have been used in a number of industries and applications for many years. These applications include alloying in steels and reactive metals, cathodic protection anodes, superconductivity, rocket nozzles, rivets for aircraft, sodium vapor lamps, jewelry, oxygen lances for pressure oxidation of ores, as well as chemical processing applications. During the past 10–15 years, niobium has been considered and applied in more and more chemical processing applications because it exhibits excellent corrosion resistance in many environments. Important chemical processing applications for niobium alloys include hydrochloric acid, nitric acid, sulfuric acid, chromic acid, organic acids, salts and liquid metals. This paper will describe the corrosion resistance of niobium in a variety of environments. It will also show those applications that niobium and its alloys are currently being used in, and describe those applications being considered for the future.

Introduction

General Uses

Niobium and its alloys find a wide range of industrial application. The widest application is as a microalloying element (carbide former) in steels, and for additions to nickel-base superalloys like some of the Inconels and Rene 95, where it strengthens by solid solution formation, carbide precipitation, and coherent phase formation.

Niobium is used as the principal component in applications where reasonable strength is required in high temperature applications, without the density penalty of elements like tungsten or tantalum. Alloys of niobium for these applications can be divided into low strength like Nb-1Zr, medium strength like C-103 and C-129Y, and high strength like Cb-752, WC-3009, and FS-85. In these applications, creep strength and coatings imparting resistance to high temperature oxidation are primary concerns.

Niobium finds further application in superconducting applications (1, 2). The primary superconducting alloy, Nb-47Ti, is fabricated into multifilamentry wires, encased in copper, for applications like magnetic resonance imaging magnets, and high energy physics, where it is used in the magnets for detectors and beam handling equipment. Future applications envision use of niobium-based wires/cables for magnetic confinement of fusion reactions, and utilizing high purity (RRR) niobium for superconducting cavities for high energy physics apparatus.

Corrosion Resistant Applications

Niobium and niobium alloys have excellent resistance to a wide variety of corrosive environments. These environments include mineral acids, most organic acids, liquid metals, most salts and liquid metals. Recently niobium has been considered for applications in steel pickling where hydrochloric acid is used. Niobium is also resistant to some fluoride-contaminated solutions, which is unique among the reactive metals.

One of the more common uses for niobium has been in overhead condensers and heat recovery sections (3) of nitric acid facilities. Niobium has also been considered for use in the pharmaceutical industry (4), where high corrosion resistance is critical.

Niobium has been used for over 20 years as cathodic protection devices for oil drilling rigs, ship hulls, bridges, and underground storage tanks (5, 6). These cathodic protection devices, such as platinum clad niobium anodes, use an impressed current to force the corroding structure to become a cathode. These anodes provide a cost effective method to protect structures from corrosion attack caused by galvanic action. Niobium has also been specified for anodes in a water purity system. This electro-chemical based system effectively combined seven different proven water treatment processes in a self-contained unit (7).

Niobium has also been used in the evaporators in the chrome plating industry to resist the hot, concentrated chromic acid media (8). The niobium was shown to resist the chromic acid environment, even those that could possibly contain small amounts of free fluorides. Potential applications in other environments include aqueous bromine, chromium plating solutions, and hydrogen peroxide.

Niobium has been used during the past few years as rupture disks (9) for chemical applications with good success. The applications of niobium in this application have decreased the cost of the rupture disks significantly over the other material of choice, tantalum.

Figure 1: A 46 cm diameter niobium rupture disk installed in a vapor line of an acetic acid drying column.

Niobium also has excellent compatibility with liquid metals like sodium, potassium, lithium, and uranium. Niobium is currently used in sodium vapor lamps because of its corrosion resistance to metallic sodium, either in vapor or molten form (10). The Nb-1Zr piece holds the metallic sodium, which is heated to 875–925C (11).

Table 1 compares niobium's corrosion resistance to zirconium, tantalum, and titanium in various media. Individuals are cautioned to test coupons in their own media prior to commissioning fabrication of large scale vessels or structures. Specific conditions may be sufficiently different from published data that trials are warranted.

Two general references that readers should be aware of include the ASM Metals Handbook volume on Corrosion (12) and Wah Chang's Niobium Brochure (13). Both of these deal extensively with the corrosion performance of niobium and niobium alloys in various media.

Niobium Alloys

There are several niobium alloys that find use in corrosion resistant applications. These include Nb-1Zr and Nb-55Ti. Nb-1Zr finds use wherever pure niobium is too structurally weak. As mentioned, one of the primary examples of its use is in containing hot sodium liquid or vapor in sodium vapor lamps. Nb-55Ti finds applications in high pressure, highly oxygenated, autoclaves used to leach gold and nickel. The alloy is particularly resistant to ignition under these conditions.

Nb-55Ti has also been used in a wet oxidation process for oxidizing organic materials in an aqueous waste stream to improve biodegradability. The LOPROX® (14) process requires material

Table I Qualitative Comparison of Nb with Zr, Ta, and Ti (15)

Media	Niobium	Zirconium	Tantalum	Titanium
HCl	Fair	Excellent	Excellent	Poor
H_2SO_4	Fair	Very Good	Excellent	Poor
Oxidizing without Cl^-	Excellent	Excellent	Excellent	Excellent
Oxidizing with Cl^-	Excellent	Poor	Excellent	Excellent
HNO_3	Excellent	Excellent	Excellent	Good
H_2O_2	Good	Excellent	Very Good	Fair
Acid with F^-	Good	Poor	Poor	Poor
Acetic Acid	Excellent	Excellent	Excellent	Excellent
NaOH	Embrittled	Very Good	Embrittled	Embrittled

that can survive 200C and 20 bar pressures while injecting pure oxygen into an acidified waste stream. Pure titanium has sufficient corrosion resistance, but it is self-ignitable under the stated conditions. The addition of niobium reduces the propensity for ignition, and improves the corrosion resistance. Nb-55Ti has been used in the oxygen injectors, and recently in a Nb-55Ti clad pressure vessel.

In other applications, principally nuclear fuel related, niobium is used as an alloying element with zirconium to confer strength and corrosion resistance in steam and/or heated water environments. Zr-1Nb is used in the Russian VVER reactors for the fuel cladding. It has been given the designation, Alloy E-610, by the Russians. A variant of this alloy, M5, is being proposed for high burnup fuel in reactors that have high coolant exit temperatures. The salient feature of M5 is outstanding corrosion resistance in high temperature, high pressure water with trace amounts of lithium hydroxide. Another zirconium-niobium alloy used in nuclear applications is Zr-2.5Nb. The Canadian CANDU reactors use Zr-2.5Nb as horizontally oriented pressure tubes which must resist sagging and provide corrosion resistance to heavy water. The pressure tubes contain the fuel assemblies and provide a channel for flowing coolant (heavy water.)

The other class of important niobium alloys for corrosion resistant applications are with tantalum**.** In this case niobium serves principally as a diluent to the tantalum to reduce the cost. Niobium has a density of 8.57 g/cm^3, compared with tantalum's density of 16.65 g/cm^3, which means that more volume is available per unit weight. Since these metals are typically sold on a weight basis, the cost of pure tantalum can be reduced by the addition of less expensive niobium. Robin and Rosa (16) have performed extensive testing of niobium and Nb-Ta alloys in hot hydrochloric and phosphoric acid solutions.

Lupton, et al., have reported (17) on the performance of Nb-Ta alloys in boiling 70% H_2SO_4. The tantalum-rich alloys showed a decrease in corrosion rate with increasing exposure time, as was found for pure tantalum, whereas Nb-50Ta and Nb-40Ta showed a constant or increasing corrosion rate. They further report that the corrosion rate of tantalum-rich alloys like Ta-40Nb are very much lower than would be expected for a simple mixture of niobium and tantalum in which corrosion rate was proportional to niobium activity. They propose that Ta-40Nb could be considered for service in 70% H_2SO_4 at 165C.

Oxide Layer Formation

Niobium, like many other reactive metals, owes its corrosion resistance to the presence of a readily formed, adherent, passive oxide film. The oxide film can be composed of NbO, NbO_2, Nb_2O_5 or a mixture of the three. This oxide film will exist in the lower valence state under reducing conditions. Niobium's oxide coating is therefore conditional, depending on the media it is exposed to. The presence of oxidizing impurities in the media will improve the corrosion resistance of niobium.

Films of amorphous niobium oxides are only a few nanometers thick. They form according to (18):

$$Nb + H_2O \rightarrow NbO + 2H^+ + 2e^- \quad (1)$$
$$NbO + H_2O \rightarrow NbO_2 + 2H^+ + 2e^- \quad (2)$$
$$2NbO_2 + H_2O \rightarrow Nb_2O_5 + 2H^+ + 2e^- \quad (3)$$

Niobium reacts readily with water to form a niobium oxide. If the oxide forms a thin compact film, as is the case in pure water and many dilute aqueous solutions, the corrosion resistance is excellent. In the presence of complexing agents like fluorine ion in H_2SO_4 and HCl, the corrosion behavior of niobium is dominated by the dissolution of the oxide layer.

The oxide layer also serves to preclude hydrogen pickup. Monatomic hydrogen is easily absorbed by the bare metal, and if the oxide layer fails in aqueous solutions, niobium will suffer from embrittlement due to hydride precipitation.

Niobium Properties

Niobium is a soft, ductile metal which can be cold worked over 90 percent before annealing becomes necessary. The density of 8.57 g/cm^3 is moderate compared to the majority of high melting point metals, being only half that of tantalum at 16.65 g/cm^3. Pure niobium can be strengthened with additions of Zr, Ti and Hf.

Table II Niobium Physical Properties

Property	Value
Atomic Weight	92.9064
Density	8.57 g/cc
Melting Point	2750K, 2468C, 4490F
Boiling Point	5017K, 4927C, 8571F
Coefficient of Thermal Expansion (20¡ C)	7.1 x 10^{-6}/K
Electrical Resistivity (20¡ C)	15 microhm-cm
Specific Heat	2300 J/g¥K
Thermal Conductivity	52 W/m¥K
Crystal Structure	Body centered cubic

Table III Niobium Mechanical Properties

Annealed	Ultimate Tensile Strength	195 MPa (28 ksi)
	Yield Strength	105 MPa (15 ksi)
	% Elongation	30%+
	% Reduction in Area	90%+
Cold Worked	Ultimate Tensile Strength	585 M Pa (85 ksi)
	% Elongation	5%
Hardness	Annealed	60 HV
	Cold Worked	150 HV
Poisson's Ratio		0.38
Strain Hardening Exponent		0.24
Elastic Modulus	Tension	103 GPa (14.9x 10^6psi)
	Shear	37.5 GPa (5.4 x 10^6psi)
DBTT		<147K
Recrystallization Temperature		1073–1373K

Niobium Fabrication Properties

Niobium can be fabricated similarly to tantalum. Typical equipment includes heat exchangers, reactor vessels, thermowells, rupture disks and lined pipe. Due to niobium's higher cost, it is typically supplied as a lining for equipment. Using a Nb-1Zr alloy will increase the yield strength by about 50% and have similar corrosion resistance in many solutions.

Niobium may be machined using standard techniques. However, due to the tendency of the material to gall, special attention needs to be given to tool angles and lubrication. Niobium also has a tendency to stick to tooling during metal forming operations. To avoid this, specific lubricant and die material combinations are required in high pressure forming operations (13).

Turning

Machining on a lathe is best performed with high speed steel tools. For cooling and lubricating, air, soluble oil, Rapid-Tap™ or other suitable products may be used. The metal turns very much like lead or soft copper. It must be sheared with the chip allowed to slide off the tool's surface. If any buildup of material occurs, the pressure will break the cutting edge, ruining the tool.

Carbide tooling should be used only for fast, light cuts to work efficiently (0.25 to 0.40 mm deep). Tooling recommendations are given in Table 4. The data applies to both high speed steel and carbide tools unless otherwise noted (13).

Drilling

Standard high speed drills, ground to normal angles, may be used. However, the peripheral lands wear badly so that care must be exercised to ensure the drill has not worn under size.

Screw Cutting

Niobium may be screw-cut using a standard die-cutting head, provided that an ample amount of lubricant is used. The use of sufficient lubricant prevents galling on the die resulting in the tearing of the thread. Roll threading is the preferred method for producing threaded fasteners.

Table IV Tooling Recommendations

Approach Angle	15° - 20°
Side Rake	30° - 35°
Clearance:	
Side	5°
End	5°
Plan Relief Angle	15° - 20°
Nose radius	0.50–0.75 mm
Cutting Speed (meters/minute):	
High Speed Steel	5- 25
Carbide	75 - 90
Feed:	
Roughing	0.25 +/- 0.05 mm
Finishing	0.125 mm max.
Depth of cut	1–3 mm

Spinning

With some minor modifications, normal techniques of metal spinning may be applied successfully to niobium.

It is generally better to work the metal in stages; for example, when spinning a right-angled cup from flat sheet, several formers should be used to perform the operation in steps of approximately 10 degrees. Wooden formers may be used for the rough spinning, but a brass or bronze former is essential for finishing. This is because niobium is soft and readily accepts the contour of the former. For small work, aluminum, bronze or narite tools should be used with a radius of approximately 3/8 inch. Note that if sharp angles are required, the tool must be shaped accordingly.

Yellow soap or tallow is suitable for lubricating the material. The peripheral speed of the work piece should be approximately 150 meters per minute. Niobium is prone to “thinning” during this process. This is avoided by working the tool in successive, long, sweeping strokes with light pressure instead of a few heavy strokes.

Welding

Niobium is a highly reactive metal. It reacts with common interstitial elements, oxygen, hydrogen, nitrogen and carbon. At the melting point and above, niobium will react with all the known fluxes. This restricts the choice of welding methods.

Niobium can be welded to several metals, one of which is tantalum. This can be readily accomplished by resistance welding, gas tungsten arc, plasma welding and electron beam welding.

It is critical to ensure that the metal is clean prior to welding. An acid pickle wash is recommended. For ambient temperature pickling, a typical solution is 25%–35% HF, 25%–33% $HN0_3$ with the balance H_20. Coupons should be used before immersing the part to check the etchant rate. Removal of approximately 2.5 µm is generally acceptable. Care should be exercised to prevent surface contamination with copper welding chills, aluminum, etc. as these form low melting point eutectics which can severely embrittle the finished joint. Surfaces to be heated above 300C should be protected from oxidation by an inert gas such as argon or helium to prevent embrittlement.

Gas Tungsten Arc Welding

Niobium can be welded satisfactorily by applying standard gas tungsten arc (GTAW) procedures. It is essential to completely cover the area of the molten pool and the heated zone with inert gas to avoid contamination of the weld metal. This protection must be given to both the back of the weld and the face. The back of the weld may be protected with a stream of argon from a manifold positioned just below the weld bead. A trailing shield will provide further protection to the hot metal after the main shield has passed.

When niobium is exposed to air at elevated temperatures, it acquires a relatively thick and adherent oxide film that is extremely difficult to remove. Contamination free welds can be produced using inert shielding only if the proper procedures are employed.

Cleaning Niobium

To properly clean niobium, the following steps are recommended:

* Degrease.
* Immerse in commercial alkaline cleanser for 5 - 10 minutes.
* Rinse with water.
* Immerse in 35 - 40% $HN0_3$ for 2 - 5 minutes at room temperature.
* Rinse with tap water, followed by a rinse with distilled water.
* Force air dry.

Mineral Acid Corrosion Resistance

Sulfuric Acid Solutions

Niobium generally has good corrosion resistance to sulfuric acid at the low concentrations of sulfuric acid at room temperature, but may embrittle in the higher concentrations. Table 5 shows the corrosion resistance in various concentrations and temperatures of sulfuric acid. At elevated temperatures, niobium will corrode rapidly if the sulfuric acid concentration is above 40%.
Fe^{+3} and Cu^{+2} ions can improve the corrosion resistance in sulfuric acid.

Hydrochloric Acid Solutions

Niobium and niobium alloys have been shown resistant in hydrochloric acid environments in the lower concentrations (<13%) above boiling, and at the higher concentrations and lower temperatures. Table 6 shows the corrosion data of niobium in HCl environments. The addition of ferric ion increases niobium's corrosion resistance greatly especially at the higher temperatures. Table 7 shows the effect of ferric ion addition to HCl. Niobium is not expected to need aeration for its corrosion resistance. Recent preliminary testing has shown that niobium may embrittle at the higher concentrations of hydrochloric acids. Future work is planned to study this further. Niobium is being considered for use in HCl steel pickling applications to replace polyethylene tubing, where an abundance of iron is present (19).

Table V Corrosion Resistance of Niobium in Sulfuric Acid Solutions

Sulfuric Acid	Impurity	Concentration, ppm	Temperature, Celsius	Corrosion Rate, mm/yr (mpy)
5 - 40	…	…	RT	nil
25	…	…	100	0.125 (5.0)
98	…	…	RT	Embrittle
10	…	…	Boiling	0.125 (5.0)
25	Cl^-	200	Boiling	0.25 (10)
	F^-	5		
40	…	…	Boiling	0.5 (20)
40	$FeCl_3$	2%	Boiling	0.25 (10)
60	…	…	Boiling	1.25 (50)
60	$FeCl_3$	1%	Boiling	0.5 (20)
20	HCl	7%	Boiling	0.5 (20)
	F^-	50		
20	HCl	7%	Boiling	0.5 (20)
	F^-	100		
20	HCl	7%	Boiling	0.25 (10)
50	HNO_3	20%	50-80	nil
50	HNO_3	20%	Boiling	0.25 (10)
60	…	…	90	0.05 (2.0)
65	…	…	153	2.5 (100)
70	$CuCl_2$	200	158	>5.0 (200)
70	$CuCl_2$	1,000	153	2.5 (100)
70	$CuCl_2$	10,000	154	2.5 (100)
70	…	…	167	5.0 (200)
70	Cr^{+3}	15%	100	nil
70	Cr^{+3}	15%	125	0.125 (5.0)
70	Cr^{+3}	15%	Boiling	3.75 (150)
72	CrO_3	3%	100	0.025 (1.0)
72	CrO_3	3%	125	0.125 (5.0)
72	CrO_3	3%	Boiling	3.75 (150)

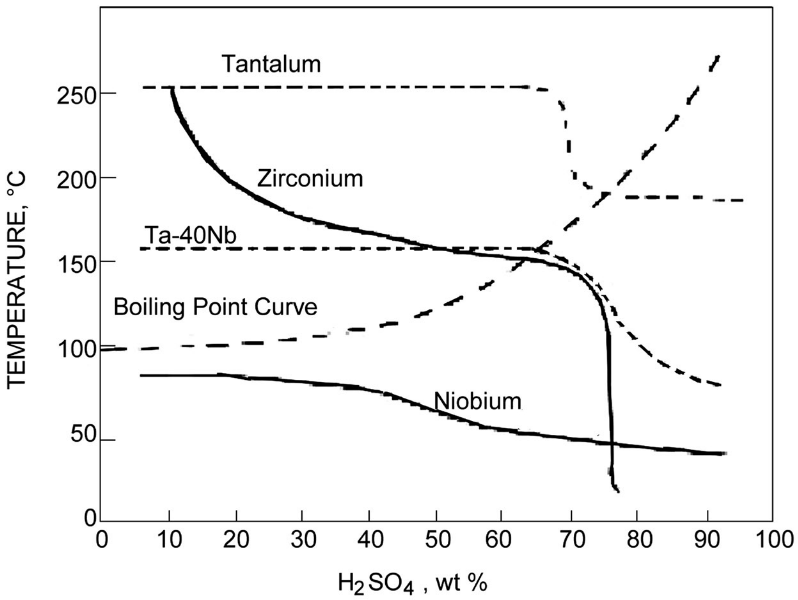


Figure 2: Temperatures and concentrations of sulfuric acid producing 0.13 mm/yr (5 mpy) corrosion rate, for niobium and other reactive/refractory metals used in corrosion service.

Table VI Corrosion Resistance of Niobium Alloys in Hydrochloric Acid Solutions

HCl (%)	Temperature, Celsius	Corrosion Rate, mm/yr (mpy)
1	Boiling	nil
11	70	0.0025 (0.1)
15 (aerated)	RT-Boiling	nil
15 (aerated)	100	0.025 (1.0)
30 (aerated)	35	0.025 (1.0)
30 (aerated)	60	0.05 (2.0)
30 (aerated)	100	0.125 (5.0)
35	22	0.0025 (0.1)
37	RT	0.025 (1.0)
37	22	0.015 (0.6)
37	60	0.075 (3.0)
37	94	0.21 (8.4)

† Niobium may embrittle at these higher concentrations.

Table VII Corrosion Resistance of Niobium Alloys in ron-contaminated Hydrochloric Acid Media

HCl (%)	Impurity	Conc. ppm	Temperature, Celsius	Corrosion Rate, mm/yr (mpy)	
				Nb	Nb-1Zr
15	Ferric	500	60	0.003(0.1)	0.003(0.1)
15	Ferric	1000	60	0.003(0.1)	0.003(0.1)
15	Ferric	1500	60	0.005(0.2)	0.003(0.1)
15	Ferric	500	100	0.01(0.2)	0.01(0.2)
15	Ferric	1000	100	0.02(0.6)	0.02(0.6)
15	Ferric	1500	100	0.01(0.2)	0.01(0.2)
15	Ferric	0.15	93	0.003(0.1)	0.005(0.2)
10	$FeCl_3$	0.1%	Boiling	0.03 (1.0)	
10	$FeCl_3$	0.6%	Boiling	0.13 (5.0)	
15	$FeCl_2$ $FeCl_3$	35% 2%	Boiling	0.05 (2.0)	
15	Ferric	500	177	12.3(491)	10.2(408)
15	Ferric	1000	177	0.42(17)	0.33(13)
15	Ferric	1500	177	11.5(463)	7.7(308)
18	Ferric chloride	1%	150	0.7 (v) / 0.14 (l)	
18	Ferric chloride	1%	150	0.78 (v)/ 2.5 (l)	
18	Ferric chloride	2%	150	0.14 (v) / 0.68 (l)	
18	Ferric chloride	2%	150	2.3 (v) / 2.9 (l)	
18	Ferric chloride	1.5%	150	0.33 (v) / 1.0 (l)	
20	Ferric	1000	60	0.057(2.3)	0.07(2.7)
20	Ferric	1500	60	0.03(1.2)	0.03(1.2)
20	Ferric	500	100	0.06(2.2)	0.02(1.1)
20	Ferric	1000	100	0.06(2.2)	0.09(3.6)
20	Ferric	1500	100	0.07(2.6)	0.062(2.5)
20	Ferric	15%	93	0.005(0.2)	0.008(0.3)
20	Ferric	2%	93	0.05(2.1)	0.05(2.1)
25	Ferric	500	60	0.008(0.3)	0.005(0.2)
25	Ferric	1000	60	0.005(0.2)	0.005(0.2)
25	Ferric	1500	60	0.005(0.2)	0.005(0.2)
25	Ferric	500	100	0.3(12)	0.31(12.4)
25	Ferric	1000	100	0.21(8.5)	0.23(9)
25	Ferric	1500	100	0.32(13)	0.3(12)
37	Cl_2		60	0.5 (20)	

v) vapor phase, (l) liquid phase

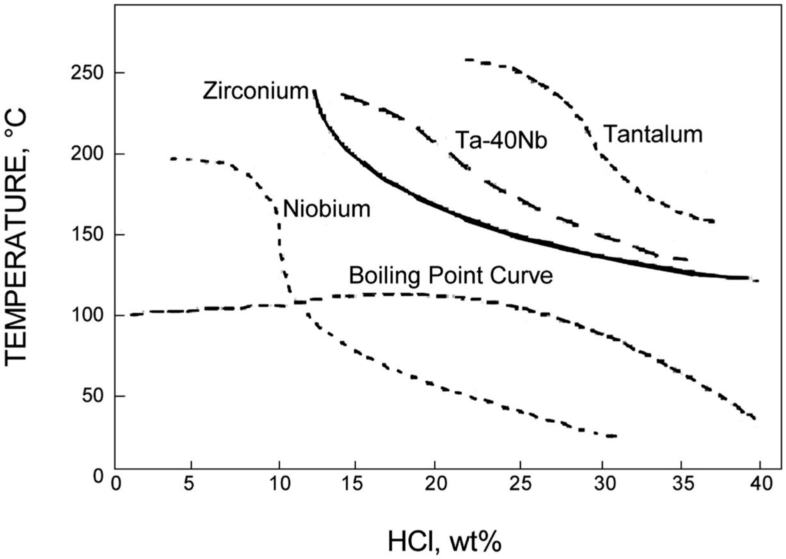


Figure 3: Temperatures and concentrations of hydrochloric acid producing 0.13 mm/yr (5 mpy) corrosion rate, for niobium, tantalum and zirconium.

Nitric Acid

Niobium is very resistant to corrosion in nitric acid environments. It is resistant through the full range of concentrations, and to temperatures above boiling in nitric acid. Unlike other reactive metals, niobium is not susceptible to stress corrosion cracking at the higher concentrations of nitric acid.

Niobium, like many reactive metals, is susceptible to high corrosion rates in hydrofluoric acid. Niobium is, however, less sensitive than other reactive metals in acidic environments with small amounts of fluoride ion. Table 8 shows the corrosion resistance of niobium in nitric acid, as well as the influence of small amounts of fluoride ion on the corrosion resistance of niobium in nitric acid.

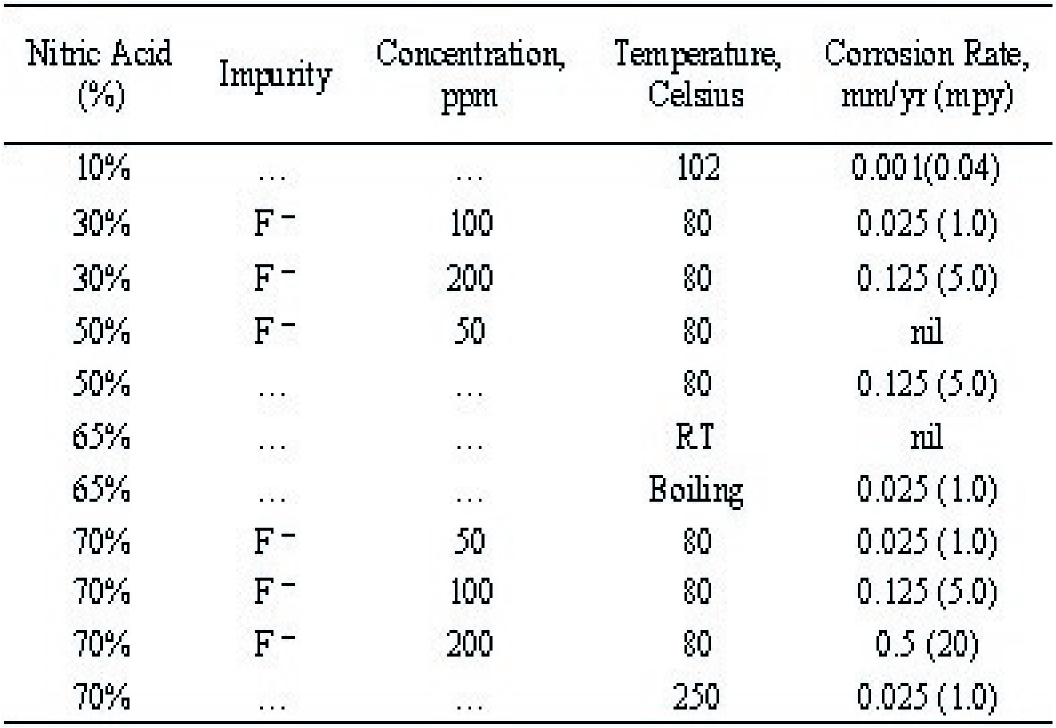
Phosphoric Acid

Niobium displays excellent resistance to corrosion in phosphoric acid solutions. Robin and Rosa studied the corrosion behavior of niobium and niobium-tantalum alloys in hot phosphoric acid solutions (16). Their data show that large additions of tantalum are required to significantly improve the corrosion resistance of niobium. Table 9 presents selected corrosion data for pure niobium in phosphoric acid solutions.

Organic Acids

Niobium shows high resistance to many different types of organic acids. Table 10 shows examples of those acids where niobium has been tested and shown to have good corrosion resistance. These acids include acetic acid, citric acid, formaldehyde, formic acid, lactic acid, tartaric acid, and trichloroacetic acid.

Table VIII Corrosion Resistance of Niobium in Nitric Acid



Nitric Acid (%)	Impurity	Concentration, ppm	Temperature, Celsius	Corrosion Rate, mm/yr (mpy)
10%	...	...	102	0.001(0.04)
30%	F⁻	100	80	0.025 (1.0)
30%	F⁻	200	80	0.125 (5.0)
50%	F⁻	50	80	nil
50%	...	...	80	0.125 (5.0)
65%	...	...	RT	nil
65%	...	...	Boiling	0.025 (1.0)
70%	F⁻	50	80	0.025 (1.0)
70%	F⁻	100	80	0.125 (5.0)
70%	F⁻	200	80	0.5 (20)
70%	...	...	250	0.025 (1.0)

Table IX Corrosion Resistance of Niobium in Phosphoric Acid Solutions

Phosphoric Acid, (%)	Impurity	Conc. ppm	Temperature, Celsius	Corrosion Rate, mm/yr (mpy)
50			30	nil
50			90	0.125 (5.0)
60			Boiling	0.5 (20)
85			30	nil
85			RT	0.0025 (0.1)
85			88	0.05 (2.0)
85			100	0.125 (5.0)
85			155	3.75 (150)
85			Boiling	3.75 (150)
85	HNO_3	4%	88	0.025 (1.0)
30	F⁻	5	Boiling	0.25 (10)
40	F⁻	5	Boiling	0.25 (10)
50	F⁻	5	Boiling	0.5 (20)
68	HNO_3	3.5%	45	0.125 (5.0)
	and Acetic Acid	5%		

Table X Corrosion Properties of Niobium in Organic Acids

Media	Concentration, (Wt%)	Temperature, Celsius	Corrosion Rate, mm/yr (mpy)
Citric Acid	10	Boiling	0.025 (1.0)
Formaldehyde	6	Boiling	nil
Formaldehyde	37	Boiling	0.0025 (0.1)
Formic Acid	10	Boiling	nil
Formic Acid	50	Boiling	0.025 (1.0)
Lactic Acid	10–85	Boiling	0.025 (1.0)
Tartaric Acid	20	RT–Boiling	nil
Trichloroacetic acid	50	Boiling	nil
Acetic Acid	5–99.7	Boiling	nil

Miscellaneous Environments

Bromine

Niobium is resistant to a number of media including bromine, chromium plating solutions and hydrogen peroxide. Aqueous bromine is a highly corrosive media to many materials. Niobium has been shown to have excellent corrosion resistance in liquid and gaseous bromine. Niobium has been considered previously for use in the processing, storage and transportation of liquid and gaseous bromine. Table 11 provides corrosion rates for niobium in bromine, chromium plating solutions, seawater, and hydrogen peroxide.

Alkaline Solutions

Niobium is resistant to most alkalis at room temperature. It is, however, seriously attacked by hot alkalis, and will be embrittled in concentrated alkalis even at room temperature. Similar to tantalum, niobium will embrittle in salts, such as sodium, potassium carbonates and phosphates that hydrolyze to form alkaline solutions. The relatively poor corrosion resistance to alkalis is likely due to the formation of hexaniobate salts, $M_8Nb_6O_{19}.18H_2O$, (where M = Na, K) which are soluble in alkaline aqueous solutions (20, 21). Table 12 shows that most all combinations of alkaline solutions lead to embrittlement. Embrittlement is typically by absorption of hydrogen species.

Corrosion in 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 solution at room temperature, and it is resistant to attack in seawater. Niobium exhibits resistance similar to tantalum in salt solutions. Table 13 provides the corrosion resistance of niobium in many of the common salt solutions, as well as some more complex

Table XI Corrosion Resistance of Niobium in Miscellaneous Media

Media	Concentrations, (Wt%)	Temperature, Celsius	Corrosion Rate, mm/yr (mpy)
Bromine	liquid	20	nil
Bromine	vapor	20	0.025 (1.0)
Chrome Plating	25% CrO_3	92	0.125 (5.0)
Solution	12% H_2SO_4		
Seawater	natural	Boiling	nil
Chrome Plating	25% CrO_3	Boiling	0.125 (5.0)
Solution	2% Na_2SiF_6		
Hydrogen Peroxide	30	RT	0.025 (1.0)
Hydrogen Peroxide		Boiling	0.5 (20)

Table XII Corrosion Resistance of Niobium in Alkaline Media

Media	Concentrations, (Wt%)	Temperature, Celsius	Corrosion Rate, mm/yr (mpy)	
			Nb	Nb-1Zr
NaOH	1-40	RT	0.125 (5.0)	
NaOH	1-10	98	Embrittle	
NaOH	10	98		Embrittle
KOH	5-40	RT	Embrittle	
KOH	1-5	98	Embrittle	

media.

Liquid Metals

Niobium has excellent resistance to many types of liquid metals, even at very high temperatures. The presence of excessive amounts of gas impurities, however, may reduce niobium’s resistance to these liquid metals. Table 14 shows the corrosion resistance of Zr in liquid metals. Small amounts of zirconium (Nb-1Zr) scavenge oxides which tend to form on the grain boundaries. This precludes grain boundary attack by some liquid metals.

Table XIII Corrosion Resistance of Niobium in Salt Solutions

Solutions	Concentrations, (Wt %)	Temperature, Celsius	Corrosion Rate, mm/yr (mpy)
$AlCl_3$	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
$CaCl_2$	0.2% with 0.1% $MgCl_2$	80	0.25 (10)
$CaCl_2$	2% with 1% $MgCl_2$	80	0.125(5.0)
$CaCl_2$	6.6% with 3.3% $MgCl_2$ + 200 ppm NaF + 9800 ppm CaF_2	80	0.025 (1.0)
$CaCl_2$	6.6% with 3.3% $MgCl_2$	80	0.025 (1.0)
$Cu(NO_3)_2$	40	Boiling	nil
$CuSO_4$	40	104	0.025 (1.0)
$FeCl_3$	10	RT - Boiling	nil
Fe^{+3}	12% with 6%HCl	66	nil
$HgCl_2$	Saturated	Boiling	0.0025 (0.1)
H_2SiF_6	10	90	5.0 (200)
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	Saturated and pH = 1	Boiling	0.025 (1.0)
NaCl	5% with 0.5% Acetic Acid	100	nil
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_4Cl	40	Boiling	0.025 (1.0)
NH_2SO_3H	10	Boiling	0.025 (1.0)
$NiCl_2$	30	Boiling	nil
$Ni(NO_3)_2$	40	104	0.025 (1.0)
$ZnCl_2$	40 - 70	Boiling	nil
$ZrCl_4$	70	Boiling	nil
$ZrCl_4$	88	Boiling	nil

Table XIV Corrosion Resistance of Niobium in Liquid Metals

Molten Metal	Temp, Celsius
Bismuth	< 510
Gallium	< 400
Lead	< 850
Lithium	< 100
Mercury	< 600
Sodium	< 1000
Potassium	< 1000
Sodium-potassium (NaK)	< 1000
Thorium-magnesium eutectic	< 850
Uranium	< 1400
Zinc	< 450

Gaseous Environments

Niobium has a large solubility for oxygen, nitrogen and hydrogen. The gas atoms exist in interstitial locations. As hydrogen is dissolved, the level will eventually exceed the terminal solid solubility (TSS) limit, and niobium hydrides will precipitate. Hydrides are brittle and create internal stress risers that fail under low applied loads. Oxygen and nitrogen (in solution) are potent hardeners and will significantly decrease the ductility of the matrix. Additionally, oxygen forms surface oxides that are non-protective; e.g., they spall, owing to the fact that the oxides have a larger molecular volume than the base metal.

The oxides of niobium have a relatively high vapor pressure (compared with the metal) and under conditions of low oxygen pressures and high temperatures the loss of metal via evaporation of the oxides can be substantial. Oxygen uptake can be divided into three regions (20) as a function of time: 1) a linear region where oxygen dissolves without oxide formation; 2) a parabolic region associated with the formation of a protective NbO_2 layer and NbO growing into the metal; and, 3) another linear region where the formation of porous Nb_2O_5 on top of the NbO_2 occurs. At temperatures greater than 1600C, evaporation of the NbO dominates.

The hydrides of niobium exist over a range of compositions (20). Homogeneous solid solutions (α-phase) form up to $NbH_{0.1}$. Beyond this hydrogen concentration a second, β-phase appeared. The $\alpha + \beta$ phases co-exist between $NbH_{0.1}$ and $NbH_{0.9}$. Beyond this composition, the system again becomes homogeneous up to the monohydride, NbH. The α-phase is bcc, while the β-phase is orthorhombic. At temperatures above 150C, the miscibility gap disappears. A dihyrdide exists as an unstable compound, and at low pressures decomposes by loss of hydrogen into the monohydride.

Future Work

1) Niobium is being studied further to determine the effect of fluoride ion in chemical media on

the corrosion resistance.

2) Niobium and niobium alloys are being tested in contaminated HCl solutions to determine their resistance to acid pickling applications.

3) Niobium is being evaluated for some pharmaceutical applications where tantalum is currently being applied.

Summary

1) Niobium is a highly corrosion resistant metal in mineral acids under oxidizing conditions.

2) Niobium is a good candidate for use in applications where low concentrations of fluoride ions are present.

3) Niobium has excellent corrosion resistance in liquid metals.

4) Niobium is readily fabricable, and with its relatively low density, compares very favorably, economically, with tantalum in appropriate applications.

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