NIOBIUM IN CORROSIVE ENVIRONMENTS

David Lupton, Fritz Aldinger and Klaus Schulze*

W. C. Heraeus GmbH
Heraeusstrasse 12-14
6450 Hanau
West Germany

*Max-Planck-Institut fuer Metallforschung
Institut fuer Werkstoffwissenschaften
7000 Stuttgart 80
West Germany

Summary

The broadly defined corrosion behavior of niobium and niobium alloys in a variety of environments is reviewed. The environments discussed are:

vacua and inert gas atmospheres containing impurities;

aqueous environments - water, steam, alkalis, acids;

liquid metals and metal vapors;

molten salts.

In each case, the basic corrosion mechanisms are outlined and data on corrosion rates are presented. The advantages and disadvantages of niobium are, wherever possibe, highlighted and discussed.

Although niobium and a number of its alloys possess corrosion properties which make them interesting for a large range of uses, few major applications have yet been realized. The current and potential applications of niobium and its alloys are reviewed and contrasts are made with the competing materials.

Introduction

The current and potential applications for niobium involve the exposure of this metal and its alloys to a wide variety of corrosive environments. Therefore, before discussing the corrosion behavior, we shall attempt to define what we understand by "corrosion". The original meaning of the word, derived from the Latin cor rodere, indicates a gradual destruction by gnawing. Thus, processes such as rusting, oxidation, the attack of metals by acids and the destruction of gas-turbine alloys by reaction with hot salts are all adequately described by the term. Other processes which do not necessarily involve the removal of material have also been labelled as corrosion, for example, the carburization of high temperature alloys. Many interactions between niobium and the service environment fall into this second category. We shall therefore adopt the broad definition given in the DIN standard 50900 (1975):

"Corrosion is a reaction of a metallic material with its surroundings, which causes a measurable change in the material and can lead to corrosion damage (i.e., impairment of the function of a metallic structural component or a complete system by corrosion). In most cases this is a reaction of the electrochemical type. However, it can also relate to chemical or physical metallurgical processes."

In this way, we intend to distinguish between, for example, the intentional nitriding of alloys to increase surface hardness and the undesirable uptake of nitrogen from the service environment which causes embrittlement of the structural component.

The chemistry and corrosion behavior of niobium have been reviewed in a number of publications, e.g. (1-6).

Niobium chemistry

Niobium, atomic number 41, is in Group Va of the periodic table. It is characterized by the high valency of 5 in its most stable oxidation state. This location in the periodic system, remote from the electron configurations of the inert gases, results in complex chemical behavior. For example, niobium does not function as the electro-negative constituent of salt-like compounds and, whereas niobium itself has typical metallic properties, the pentoxide is acidic, although basic properties are exhibited in lower valence states. In any discussion of the corrosion behavior of niobium, similarities and contrasts with its neighbor in Group Va, tantalum, atomic number 73, become apparent. Chemically, niobium and tantalum are very similar. However, the pentavalent state of tantalum is more strongly favored relative to the lower valencies than is the case for niobium. The atomic and ionic radii of tantalum and niobium are almost identical, which leads not only to full solid solubility of the metals but also to the formation of many mixed compounds. The niobium atom has only about half the mass of the tantalum atom and thus is "softer", i.e., niobium ions polarize more strongly with the result that they generally behave as if they have a smaller radius than tantalum ions.

Gases in niobium

Another important characteristic of niobium is its ability to dissolve large quantities of the gases hydrogen, nitrogen and oxygen. These elements can be retained at high concentrations in interstitial solution at room temperature, where they have a profound effect on the mechanical properties. At high temperatures, niobium can also dissolve substantial amounts of carbon, whereas, at room temperature, carbon is precipitated as Nb_2C and only small quantities (< 50 ppm, dependent on the cooling rate) are retained in solution.

Niobium alloys

The very considerable effort which has been applied to the development of niobium-base alloys has been aimed primarily at the achievement of materials with high strength and adequate oxidation resistance for use at temperatures above 1000 C. These applications are the subject of the paper by H. Inouye at this conference and so will not be discussed further here.

Only the Nb-1 percent Zr alloy has achieved considerable commercial importance in more general applications, in particular because of its greatly improved high temperature strength relative to unalloyed niobium and its excellent resistance to corrosion by the alkali metals. Alloys of niobium with tantalum have been found to offer interesting corrosion properties in mineral acids and will, therefore, be considered in more detail below.

Corrosive environments

The main corrosive environments in which niobium and its alloys are used or could be considered for use are:

- vacua and inert gas atmospheres containing traces of reactive gases such as O_2, N_2, H_2O, CO, hydrocarbons at partial pressures below about 1 pbar;

- aqueous environments and concentrated mineral acids;

- liquid metals, in particular sodium and lithium, and metal vapors, in particular sodium;

- molten salts.

The behavior of niobium and its alloys in each of these classes of environment is discussed below.

Behavior in Gaseous Environments

Interactions of niobium at high temperatures with the reactive elements hydrogen, nitrogen, oxygen and carbon of the surrounding gas atmosphere in vacua or inert gases are responsible for many undesired changes in physical and mechanical properties (6-13). The major impurities in inert gases and in the residual gases in vacuum systems are hydrogen, nitrogen, oxygen, water, carbon monoxide, carbondioxide and hydrocarbons. At low partial pressures (< 1 μbar) of these gases or of the corresponding mixtures and at elevated temperatures, the interactions are mainly processes of absorption and desorption of gas or carbon.

The elements hydrogen, nitrogen, oxygen and carbon are dissolved at interstitial sites in the niobium metal. The solubility of the interstitials is relatively large at high temperatures and decreases with falling temperature, so that, even in the course of extended high-temperature application of niobium, precipitates of compounds are only formed after slow cooling below the temperature of the corresponding solubility limit. Compounds, such as hydrides, nitrides, oxides or carbides, can be formed at the surface or in bulk regions near the surface, depending on the partial pressures, annealing temperatures and time, i.e., depending on the relative rates of transport in the gas phase, at the niobium/gas interface and in the condensed phase (diffusion). However, this compound formation does not normally occur under the actual exposure conditions of the niobium.

The maximum amount of gas that can enter a niobium specimen is determined by the number of gas molecules striking the surface per unit time. In general, the gas concentration in the metal increases less rapidly, since surface reactions and diffusion into the bulk retard the absorption rate. When niobium is annealed in an inert gas atmosphere, one has to keep in mind that even in a high-purity gas the partial pressures of impurities are relatively high when compared with the conditions in technical high-vacuum equipment.

Besides the kinetics and mechanisms of gas uptake and degassing, the solubility of the non-metals as a function of partial pressure and temperature and the terminal solubility as a function of temperature are of interest for the "corrosion behavior". Depending on the inital composition of the niobium specimen, degassing (nitrogen, hydrogen) or deoxidation may occur during annealing in carbon-containing atmospheres, as well as decarburization in oxygen-containing atmospheres.

The reaction mechanisms for the gas uptake and degassing of niobium are quite different: For hydrogen and nitrogen, equilibria between the gas phase consisting of diatomic gas molecules and the dissolved hydrogen or nitrogen atoms in niobium are established according to the reactions:

$$H_2\ (g) \rightleftarrows 2\ H\ (\text{in Nb}) \tag{1}$$

$$N_2\ (g) \rightleftarrows 2\ N\ (\text{in Nb}). \tag{2}$$

The rate of H_2 and N_2 uptake and the corresponding equilibrium concentrations can be calculated easily from kinetic and thermodynamic data given in (8).

Regarding the gaseous species containing oxygen and carbon, it can be stated that the gas uptake reactions are the same, but the degassing reactions are totally different. For oxygen dissolved in niobium, the degassing reaction takes place via the evaporation of the volatile oxides NbO and NbO_2, according to the reactions

$$O\ (\text{in Nb}) \rightarrow NbO\ (g) \tag{3}$$

$$2O\ (\text{in Nb}) \rightarrow NbO_2\ (g) \tag{4}$$

At low oxygen pressures and high temperatures, the rates of formation of volatile oxides can become equal to the rate of oxygen obsorption. The oxygen content in the metal specimen can then aproach a time-independent value. These steady states can be described by interrelations between temperature, gas pressure and oxygen concentration. A detrimental effect of the oxide evaporation is the marked increase of irreversible niobium losses at temperatures above **1600 C.** These losses exceed the rate of metal evaporation by several orders of magnitude. Therefore, this reaction must be considered as the most important corrosion reaction.

If gas molecules of unlike atoms (water, carbonmonoxide, hydrocarbon) decompose on the niobium surface, oxygen and/or carbon are dissolved in the metal. In atmospheres containing water vapor, oxygen is dissolved in niobium and, at temperatures above **1600 C**, steady states are established. In a CO-containing atmosphere, quasi-thermodynamic equilibria are established between uptake and release of carbon and oxygen:

$$CO\ (g) \rightleftarrows C\ (\text{in Nb}) + O\ (\text{in Nb}) \qquad (5)$$

Besides this, above **1600 C** some of the oxygen forms volatile NbO in a by-pass reaction.

Hydrocarbons dissociate at hot niobium surfaces with the dissolution of carbon in the specimen and the formation of molecular hydrogen according to the reaction

$$C_mH_n\ (g) \rightarrow mC\ (\text{in Nb}) + \frac{n}{2} H_2 \qquad (6)$$

Due to the low partial pressures and high temperatures, only small amounts of hydrogen from water or hydrocarbons are dissolved in niobium.

If several reactive gases are present simultaneously in the gas phase or dissolved in niobium, complicated niobium/gas reactions may be expected. From all the possible reactions, the decarburization in oxygen and the removal of oxygen in acetylene with the formation of carbonmonoxide have been established. A decarburization of niobium in pure hydrogen is not possible.

Niobium-hydrogen, niobium-nitrogen

For hydrogen and nitrogen, thermodynamic equilibria between the gas phase and the interstitially dissolved hydrogen and nitrogen atoms are established. Thus, the interstitial content will change in the direction of the equilibrium concentration dictated by the temperature and partial pressures (8).

The solubility of hydrogen in a-Nb, c_H, obeys the relation

$$\log c_H = 1/2 \log p_{H_2} - 2.91 + \frac{2070}{T}, \quad (150 < T < 1500°C), \qquad (7)$$

with p_{H_2} in mbar, T in K and c_H in at.%.

The rate of hydrogen absorption depends on the surface state. In technical vacuum systems, niobium only absorbs hydrogen at a perceptible rate at annealing temperatures above 300 - 500 C, because the oxide-like sorption layers, which serve as barriers, are then dissolved in the bulk (10). After degassing niobium in ultra-high vacuum at high temperatures (> 2000°C), the absorption rate for low hydrogen pressures (< 1 mbar) and low temperatures (< 300°C) is independent of the temperature, i.e., the transport in the gas phase is limiting the reaction rate. Each molecule striking the surface dissociates and the hydrogen atoms diffuse into the bulk until the equilibrium concentration is reached.

The nitrogen solubility in a-Nb, c_N, follows the relation

$$\log c_N = 1/2 \log p_{N_2} - 3.16 + \frac{9300}{T} , \quad (1500 < T < 2200°C) \tag{8}$$

with p_{N_2} in mbar, T in K and c_N in at - %.

For low partial pressures ($< 10^{-2}$ mbar) and high temperatures (> 1500°C), the initial rate of nitrogen uptake is given by

$$v_N = 2.96 \quad 10^3 \quad p_{N_2} \quad \exp(-668800/RT) \text{ in mg cm}^{-2} \text{ min}^{-1} \tag{9}$$

with p_{N_2} in mbar and R in J mol^{-1} K^{-1} (11).

The degassing reaction under high-vacuum conditions for 1600 < T < 2000 C obeys a second order law

$$v_N = 1.26 \quad 10^{11} \quad c_N^2 \quad \exp(-518320/RT) \text{ in mg cm}^{-2} \text{ min}^{-1} \tag{10}$$

with c_N in at - percent (12). It has been found that recombination of nitrogen atoms at the surface is the rate determining step for the degassing reaction (12). For experimental conditions which can be easily realized (final nitrogen partial pressures $<10^{-10}$ mbar, T > 2000 C), annealing times of several days may be required for large samples to reach the thermodynamic equilibrium concentrations (13).

Niobium-oxygen, niobium-water vapor

Absorption. The absorption of oxygen from oxygen and water at pressures $> 10^{-2}$ mbar and temperatures < 1000 C which results in the formation of oxides is described in detail in (8). The oxygen uptake at $p<10^{-2}$ mbar and 1000 < T < 1500 C can be divided into three regions as a function of time (14, 15):

- linear region I (solution of oxygen without oxide formation),
- parabolic region II (protective NbO_2 layer, NbO growing into the metal),
- linear region III (formation of porous a-Nb_2O_5 on NbO_2-layer).

For temperatures > 1600 C, evaporation of oxides is observed. The rate of oxygen uptake from O_2 in region I at $1100 < T < 2000$ C and $2.5 \; 10^{6} < p_{O_2} < 6.5 \; 10^{-4}$ mbar is given by

$$v_O = 8.7 \; 10^{2} \; p_{O_2} / (1 + 1.31 \; 10^{-2} \exp(59350/RT)) \qquad (11)$$

with v_O in mg cm^{-2} min^{-1}, R in J mol^{-1} K^{-1} and T in K (16).

The rate of oxygen uptake from H_2O vapor at $1100 < T < 1700$ C and $6.5 \; 10^{-5} < p_{H_2O} < 6.5 \; 10^{-3}$ mbar for small oxygen concentrations is given by

$$v_O = 9.5 \; 10^{2} \; p_{H_2O} \; \exp(-26460/RT) \qquad (12)$$

with v_O in mg cm^{-2} min^{-1} (17). At higher pressures of oxygen and water vapor the rate of oxygen uptake decreases, because the surface coverage increases. For temperatures > 1800 C the evaporation of the volatile oxides NbO and NbO_2 leads to a decrease of the oxygen concentration. Figure 1 and 2 show the increase of oxygen concentration in niobium for given oxygen and water pressures until the steady state conditions are reached (18, 19). For comparison, the maximum rates of oxygen uptake according to the above equations are shown. It can be seen that, even for the thin wires used in these experiments, the time to reach the steady state is of the order of hours.

Steady state. These conditions are observed when niobium is annealed above 1800 C and at low gas pressures. The steady state p-T-c relations follow the equation

$$c_O = p_{O_2} \; 9.1 \; 10^{-8} \; \exp(-502000/RT) \qquad (13)$$

for oxygen (18) and

$$c_O = p_{H_2O} \; 1.47 \; 10^{-7} \; \exp(-480000/RT) \qquad (14)$$

for water vapor (20) with c_O in at - percent. The energy values are comparable with the activation energy for the degassing reaction of oxygen containing niobium. This indicates that at high temperatures and low pressures the transport of oxygen or water molecules to the metal surface is limiting the oxygen uptake (8).

Figure 3 shows a log c_O vs. log p_{O_2} and a lop c_O vs. log p_{H_2O} plot for three temperatures. Comparing the p-T-c relations in the O_2 and water vapor systems, it is convenient to relate the steady state concentration of oxygen with the rate of impingement of oxygen, i.e., an equal number of oxygen atoms contained in oxygen or water molecules shall strike the surface. In Figure 3 the isotherms are drawn for these normalized pressures of oxygen and water vapor. A reasonably good correspondence is observed. The isotherms show a slope of 1, i.e., at constant temperature c_O is proportional to p_{O_2} or p_{H_2O},

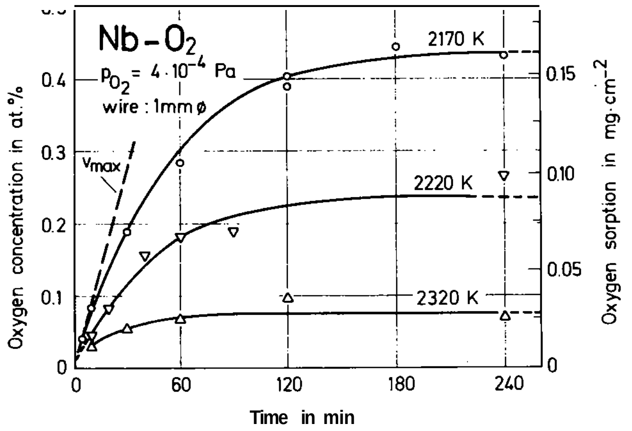

Figure 1 - Increase of O concentration with time for niobium in O_2 atmosphere.

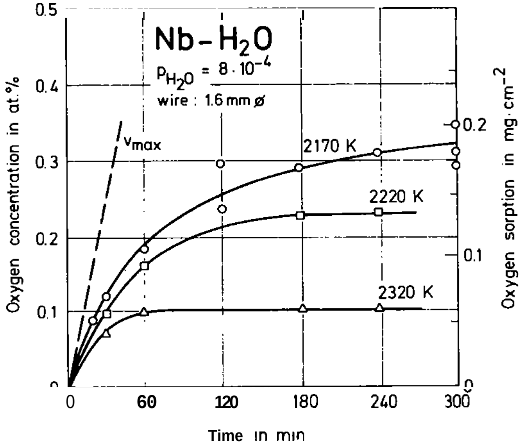

Figure 2 - Increase of O concentration with time for niobium in H_2O atmosphere.

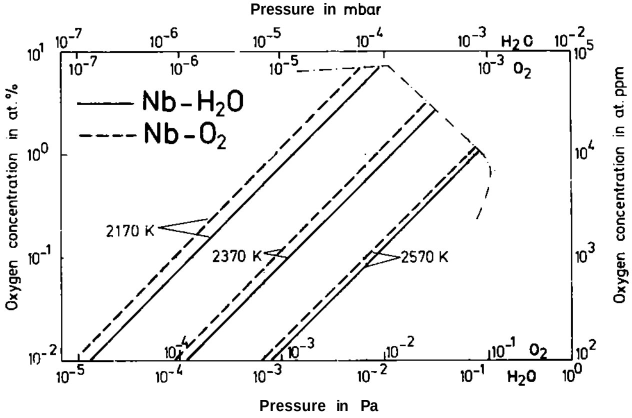

Figure 3 - Steady states for niobium in O_2 and H_2O atmospheres.

which indicates that the evaporation of NbO is predominant. The existence of the steady states is restricted to the region of the a-solid solution limited by the solvus and solidus lines. Furthermore, at low temperatures, the steady state conditions can no longer by realized because oxide evaporation becomes very slow resulting in a continuous oxygen sorption or oxidation. At very high temperatures in the low pressure region, the pure metal evaporation can exceed the oxide evaporation. In the steady state, the amount of oxygen involved in the overall reaction (liberated as NbO) is given by (21):

$$v_{O} = 2.22\ 10^{6}\ p_{O_2}\ \exp(-163600/RT)\ \text{in mg cm}^{-2}\ \text{min}^{-1}\ \text{for } O_2 \qquad (15)$$

$$v_{O} = 5.8\ 10^{5}\ p_{H_2O}\ \exp(-159440/RT)\ \text{for } H_2O \text{ vapor} \qquad (16)$$

From these data, the metal losses occurring during extended high-temperature application can be calculated for niobium components in vacuo containing O_2 and H_2O.

So far, the steady state conditions for annealing niobium in inert gases containing O_2 and/or H_2O are not known. From the de-oxidation of niobium via oxide evaporation in argon, it is known (22, 23) that the evaporation rate of the oxides depends on the argon pressure (< 1000 mbar) and is given by the relation

$$v = \alpha\ v_{O} \qquad (17)$$

with $\alpha = (1 + 0.395\ p_{Ar}^{0.9})^{-1}$ and p_{Ar} in mbar. In vacuo, the oxygen degassing rate of oxygen-containing Nb samples with 1 at - percent O v_{O} is given by the relation

$$v_{O} = 2.32\ 10^{11}\ c_{O}\ \exp(-530900/RT) \qquad (18)$$

with v_{O} in mg cm^{-2} min^{-1} and c_{O} in at .%.

It can be expected that the sorption rate of oxygen from inert gases containing O_2 or H_2O are not influenced by the argon pressure. As the degassing rate is slowed down with increasing pressure of inert gas, the amount of oxygen involved in the overall reaction should also decrease. This process must lead to increased oxygen concentrations in niobium in the steady state, for given partial pressures, compared with the p-T-c relation valid for vacuum conditions.

Niobium-hydrocarbons, niobium-carbonmonoxide

When niobium is exposed to hydrocarbons at high temperatures and low pressures, the hydrocarbon molecules decompose and the C atoms formed are dissolved in the metal until the solid solubility limit is reached corresponding to the temperature. The maximum concentration of carbon in a-Nb in equilibrium with β-Nb_2C is given by the equation

$$\log c_{C} = 3.65 - 7600/T \qquad (19)$$

for $1500 < T < 2200$ C with c_C in at - percent (8). As the carbon solubility decreases rapidly with falling temperature and the maximum concentration of carbon in niobium is very small at room temperature, nearly the entire carbon content precipitates as Nb_2C.

In the case of unsaturated hydrocarbons (e.g., C_2H_2, C_2H_4), the rate of carbon absorption depends on the transport of gas molecules to the surface or, in the case of saturated hydrocarbons (e.g., CH_4, C_2H_6), on the separation of the first H-atom from the hydrocarbon molecule. At constant hydrocarbon partial pressure, the reaction rate of niobium with methane is several orders of magnitude smaller (reaction coefficient $10^{-4} - 10^{-3}$) than with acetylene (reaction coefficient 0.5 - 0.9). Within the range of a-solid solution of carbon and $1500 < T < 2300$ C, the following equations for the carbon uptake are reported (24):

for Nb - CH_4 ($10^{-3} - 10^{-1}$ mbar):

$$v_C = 2.58 \quad p_{CH_4} \quad \exp(-59260/RT), \tag{20}$$

and for Nb-C_2H_2 ($10^{-6} - 10^{-4}$ mbar):

$$v_C = 630 \quad p_{C_2H_2} \tag{21}$$

with v_C in mg cm^{-2} min^{-1}, T in K and p in mbar.

In technical baked vacuum equipment, the residual partial pressures of oxygen and water vapor are normally higher than those of hydrocarbons, i.e., the rate of impingement of oxygen-containing gaseous species on the niobium surface is higher than the corresponding rate for carbon-containing molecules. In this case carbonmonoxide is formed at the surface according to the overall reaction $2C + O_2 \rightarrow 2CO$. The kinetics of decarburization of niobium by annealing in an O_2 stream have been investigated at temperatures between 1600 and 2300 C and O_2 pressures between $5 \cdot 10^{-6}$ and $5 \cdot 10^{-5}$ mbar *(24)*. During the decarburization of niobium, two reaction stages were found to occur. In the first stage, the chemisorbed oxygen atoms react with chemisorbed carbon atoms at the surface to form carbonmonoxide and, for relatively low oxygen pressures, no oxygen is dissolved in the metal. The rate of the decrease in carbon content in mg cm^{-2} min^{-1} is given by the expression

$$v_C = 6.2 \cdot 10^{2} \, p_{O_2} / (1 + 8.8 \cdot 10^{-3} \exp(73900/RT)) \tag{22}$$

with p_{O_2} in mbar, R in J mol^{-1} K^{-1}. After longer reaction periods, oxygen is present at the surface in excess and dissolves in part in the metal. The diffusion of carbon atoms to the surface is then the rate-determining step. Annealing of niobium in carbonmonoxide atmospheres below 10^{-3} mbar and at temperatures above 1600 C leads to dissolution of carbon and oxygen atoms according to the reaction

$$CO(g) \rightleftarrows C\ (\text{in Nb}) + O\ (\text{in Nb}). \tag{23}$$

The relationship

$$\log p_{CO} = \log c_C + \log c_O + 6.3 - 14700/T \qquad (24)$$

with p_{CO} in mbar and c_C, c_O in at - percent describes the temperature and pressure dependence of the equilibrium **(8)**. For tantalum, it was found that at $T > 2000$ C this reversible reaction is disturbed by the irreversible evaporation of the oxides leading to an increase of the carbon concentration (25). Similar reactions must be expected for niobium.

Behavior in Aqueous Environments

Figure *4* shows the potential - pH diagram constructed by van Muylder and Pourbaix (26, 27) for the system niobium - water at 25 C. The diagram is based on the reactions:

$$NbO + 2H^+ + 2 \cdot e = Nb + H_2O, \qquad E_o = -0.733 - 0.0591 \text{ pH} \qquad (25)$$

$$NbO_2 + 2H^+ + 2 \cdot e = NbO + H_2O, \qquad E_o = -0.625 - 0.0591 \text{ pH} \qquad (26)$$

$$Nb_2O_5 + 2H^+ + 2 \cdot e = 2\ NbO_2 + H_2O, \qquad E_o = -0.289 - 0.0591 \text{ pH} \qquad (27)$$

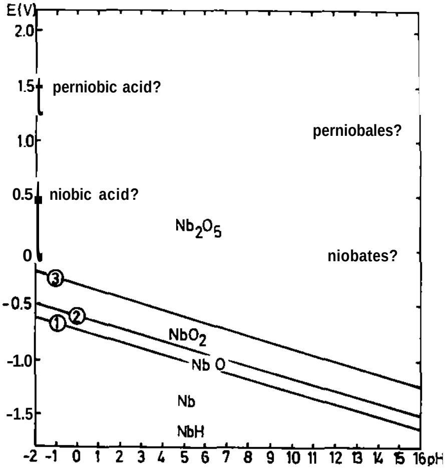

Figure *4* - Potential - pH diagram for the system niobium - water at 25 C (26, 27).

In essence, the diagram demonstrates that niobium - in common with tantalum - is far from noble. It reacts readily with water to form a niobium oxide, i.e., there is a direct transition from immunity to passivity without an intermediate region where corrosion occurs. The corrosion resistance of niobium, therefore, depends on the behavior of the oxide. If the oxide forms a thin compact film, as is the case in pure water and many dilute aqueous solutions at room temperature, the corrosion resistance is excellent. However, niobium-forms complex ions in a wide variety of solutions (e.g., in the presence of F ions, in concentrated H_2SO_4 and HCl or in caustic alkali solutions, as discussed in more detail below). In the presence of complexing agents, the corrosion behavior of niobium is dominated by the dissolution of the oxide layer.

Water and high pressure steam

Corrosion of niobium in water in the absence of complexants only becomes significant at temperatures above 150 C. With increasing temperature, there is a gradual change from typical "aqueous corrosion" behavior, i.e. dissolution, to oxidation similar to that discussed in the previous section on niobium-gas reactions.

Because of its reasonably favorable nuclear properties, niobium was at one time a candidate material for fuel element cladding in pressurized water reactors. Considerable effort was, therefore, devoted to studying the corrosion behavior of niobium in hot water (300 -'400°C) and high pressure steam, and to improving the corrosion resistance by alloying (28–31).

It was shown that the main corrosion process, when niobium is exposed to hot water and steam, is oxidation similar to that observed in air, i.e., the formation of a porous Nb_2O_5 scale overlying a thin dark adherent film. The scale was found to spall after a period of essentially parabolic weight gain. The time to the onset of spalling depended on the environment, temperature and purity of the niobium (e.g., 7 days for "commercial" purity and 100 days for "high purity" niobium in water at 360°C). The higher weight losses observed on the less pure material were associated with oxide penetrations which caused flaking of partially oxidized metallic particles.

The corrosion behavior was shown to be improved by single alloying additions of vanadium, titanium, zirconium and double additions of titanium and chromium; the best alloys were more corrosion resistant than the reference material Zircaloy 2. From the point of view of corrosion resistance and thermal neutron capture cross section, the niobium - vanadium and niobium - zirconium alloys were selected as the most promising, although their cross section is still 5 - 10 times greater than that of Zircaloy 2. The addition of vanadium influenced the type of oxide formed (29). At levels below 1.2 at – percent V, only Nb_2O_5 formed in steam. Addition of 8.9 at - percent vanadium suppressed the formation of Nb_2O_5, and only NbO_2 was observed. At intermediate levels, a duplex oxide scale formed. The weight gains were best fitted by a cubic rate law at all test temperatures between 360 and 482 C. The corrosion rate constant decreased with increasing vanadium content. Comparative tests at 360 C indicated no difference between the corrosion behavior in water and steam.

Heusler investigated the kinetics of corrosion of niobium at temperatures up to 250 C in dilute aqueous solutions with pH between 6 and 10 (32). From a determination of current-potential curves in buffered phosphate solutions, he showed that the corrosion current increased with temperature and with pH. The activation energy of the temperature dependence was found to be 12.5 kcal/mole (52.2 kJ/mole) which corresponds to an increase in corrosion rate by about a factor of 1.4 for each 10 C increase in temperature over the range 100–200 C. For a given temperature, the corrosion current at pH = 10 was 3 - 5 times greater than at pH = 6 - 7.

Alkalis

Niobium is attacked by alkalis in aqueous solution *(33–38)*. Corrosion rates reported for tests in NaOH and KOH are shown in Table I. The corrosion rates at room temperature are significant. Furthermore, particularly in the more concentrated solutions, embrittlement due to hydrogen absorption was observed *(35)*.

Table I. Corrosion Rates of Niobium in NaOH and KOH

Medium	Concentration %	Temp. (°C)	Corr. rate (mm/a)	Remarks	Ref.
NaOH	1	RT	0.021		35
	5	RT	0.028		33
	5	RT	0.013		35
	10	RT	0.018		34
	10	RT	0.012		35
	20	RT	0.013		35
	20	RT	0.102		38
	40	RT	0.033		34
	40	RT	0.012		35
NaOH	1	98	0.734	Ni container	35
	5	100	0.480		33
	5	98	1.17	Ni container	35
	10	98	2.00	Ni container	35
KOH	1	RT	0.009		35
	5	RT	0.021		35
	10	RT	0.029		35
	10	RT	0.024	Full immersion	36
	10	RT	0.008	Cyclic immersion	36
	10	RT	0.055	Cyclic immersion	37
	20	RT	0.023		35
	40	RT	0.094		34
	40	RT	0.036		35
KOH	1	98	0.610	Ni container	35
	5	98	2.57	Ni container	35
	10	75	0.030		36
	10	b.pt.	0.064		36
	10	b.pt.	0.004		37

At elevated temperatures, attack becomes rapid. (The literature values contain major discrepancies. The corrosion rates for niobium in 10 percent solutions reported in references *36* and *37* are lower than those in references *34* and *35* by factors of between *10* and *500*. The values in references *36* and *37* appear unrealistically low, possibly as a result of conducting the tests in a glass vessel which would be chemically unstable in hot alkalis). Embrittlement becomes an even more serious problem at elevated temperatures than at room temperature *(35)*.

The behavior of niobium in solutions of alkali phosphates, carbonates and sulphides was found to be similar to that in the hydroxides *(35)*.

The lack of resistance of niobium to attack by alkalis has been attributed to the formation of the hydrated hexaniobate salts ($Na_8Nb_6O_{19}$ .18 H_2O, $K_8Nb_6O_{19}$ .16 H_2O) which are soluble in alkaline aqueous solutions (3,35). The corrosion resistance of tantalum in alkaline solutions is considerably better than that of niobium (35-38) (although not according to reference 34). As might, therefore, be expected, alloying with tantalum increases the resistance of niobium to corrosion by KOH solutions (37, 38). Despite this improvement, however, niobium and its alloys must be regarded as unsuitable for use in alkaline environments.

Acids

In plant handling mineral acids at high temperatures, tantalum has achieved an important role because, for example in H_2SO_4, it possesses corrosion resistance paralleled or excelled only by gold, platinum and materials such as glass and 14 percent silicon-iron which, because of their lack of ductility, are limited in their applicability (39). In view of the chemical similarities between tantalum and niobium, it is tempting to believe that niobium might also be highly resistant to corrosion in acids. This is, however, only to a limited extent true.

Sulphuric acid. Niobium, in common with tantalum (40), is rapidly attacked by H_2SO_4 containing free SO_3. This results from the formation of stable complexes which are soluble in the acid (3).

At room temperature, niobium is resistant to H_2SO_4 at all concentrations up to about 95 percent (33, 34, 37). Hampel (40) reported, however, that niobium was attacked slowly by 98 percent H_2SO_4 at 20 C (0.002 mm/a) and that this led to partial embrittlement of the metal after one year.

The rate of corrosion of niobium increases with temperature. In boiling 10 percent H_2SO_4 (102°C), rates of between 0.006 and 0.075 mm/a have been reported (36, 37, 41). The corrosion rate continues to increase rapidly with increasing exposure temperature and acid concentration reaching about 1 mm/a in boiling 50 percent H_2SO_4 (122°C) (41). Figure 5 shows the corrosion data of Bishop (41) for niobium and, for the purpose of comparison, tantalum. Corrosion rates were determined both in boiling H_2SO_4 of various concentrations *(see* boiling point curve) and a series of pressure tests of 65 h duration at 190 and 250 C. A comparison of the curves indicates that, in dilute H_2SO_4, the acid concentration has a greater influence than exposure temperature on corrosion rate. Over about 50 percent concentration, however, temperature becomes the dominant influence (temperature range 120 - 190°C). This is analogous to the behavior of tantalum, although the corrosion rates are very different. Up to an acid concentration of 60 percent, the corrosion rate of tantalum at 250 C is low. It then jumps to about 0.3 mm/a in 70 percent H_2SO_4 and remains essentially unchanged with increasing concentration up to 96 percent, In this range of acid concentration, the corrosion rate of tantalum increases by about a factor of 3 for each 20 C increase in temperature (Figure 5 and reference 42). The temperature dependence of corrosion of niobium in 50-70 percent H_2SO_4 is seen from Figure 5 to be similar.

In a series of corrosion tests in boiling 70 percent and 75 percent H_2SO_4 (boiling points 165 and 185°C), the corrosion behavior of niobium, tantalum,

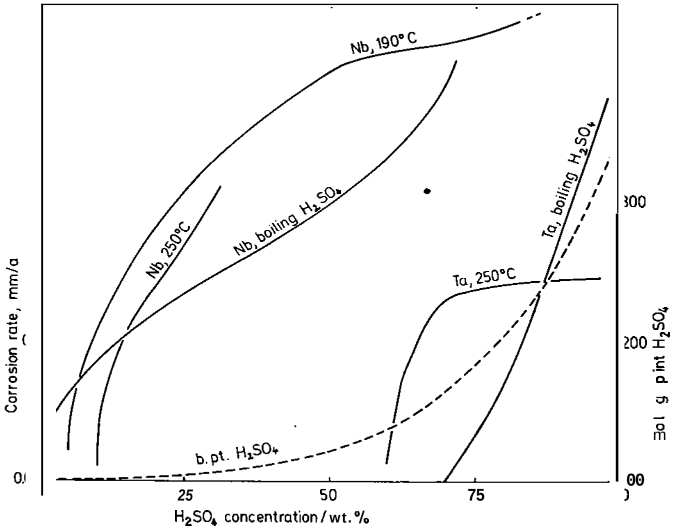

Figure 5 - Corrosion rates of niobium and tantalum in H_2SO_4 (41).

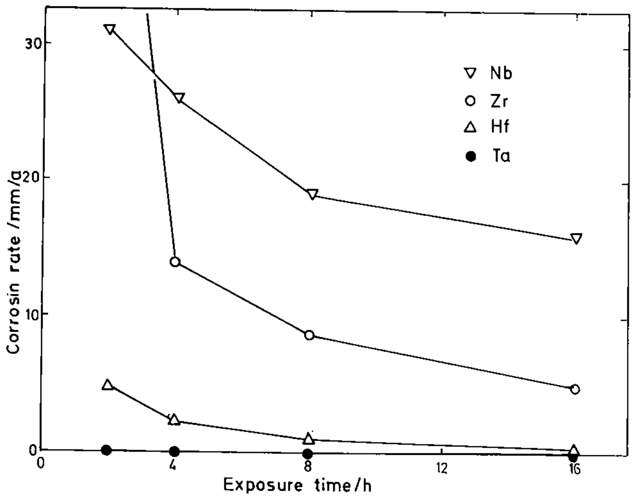

Figure 6 – Corrosion rates of niobium, zirconium, hafnium and tantalum in boiling 75 % H_2SO_4 (185°C) *(42, 43).*

zirconium and hafnium was compared (42, 43). The corrosion rates observed in short term exposures in the 75 percent acid are shown in Figure 6. This demonstrates not only the superior performance of tantalum relative, in particular, to niobium and zirconium, but also indicates that, under these test conditions, niobium has little ability to increase its passivity (i.e., reduce its corrosion rate) with increasing exposure time. After exposure, the tantalum revealed no trace of corrosive attack (corrosion rate $<$ 0.005 mm/a) whereas both zirconium and hafnium had developed rough, grey surface scales, presumably passive layers of oxide. In contrast, the niobium specimens were clean and brilliantly reflective. The corroded surfaces are shown in the SEM micrographs of Figure 7. The niobium specimens distinctly show a preferential attack on certain cyrystallographic planes.

The corrosion rates of niobium in H_2SO_4 are too high to permit its consideration as a competitor to cheaper materials. The problems with corrosion are exacerbated by the embrittlement due to hydrogen absorption, which can accompany even fairly low corrosion rates. However, as might be expected from the above comparison of the two elements, the corrosion resistance of niobium in H_2SO_4 can be markedly improved by alloying with tantalum. Niobium and tantalum form a single-phase solid solution throughout the whole alloying system. Largely as a result of the very similar atomic radii, the alloys show no solid solution strengthening, and the mechanical properties of the alloys lie between those of the two elements (44). Alloys of niobium and tantalum have been the subject of a number of corrosion investigations (6, 37, 42, 43, 45). The corrosion rates observed in boiling H_2SO_4 of various concentrations are presented in Figure 8. These results show, for example, that a corrosion rate below 0.05 mm/a, which corresponds approximately to the corrosion rate of tantalum in concentrated H_2SO_4 at 210 C (Figure 5 and reference 42), can be achieved by the alloy composition 60 percent Ta-40 percent Nb in boiling 70 percent H_2SO_4 (165°C). Alloying additions of elements from Groups IVa, Va and VIa of the periodic table did not improve the corrosion resistance of Ta-Nb alloys and, in same cases, tended to cause grain boundary attack and pitting (43). However, additions of noble metals (0.1 - 0.5 at - % Pt or 1 at - % Pd) reduced the corrosion rates of Nb-40 at - percent Ta and Nb-80 at - percent Ta alloys in 80 and 98 percent H_2SO_4 at 200 C, and prevented embrittlement (45).

Alloys of niobium with 8 percent Ti, 6.9 percent Ti + 0.81 percent Zr or 50 percent V have been reported to be more rapidly attacked in hot H_2SO_4 than unalloyed niobium (5). The same authors, however, observed no influence of an addition of 0.75 percent Zr on the corrosion rate of niobium, whereas other work has shown a detrimental effect of larger Zr additions on the corrosion behavior of Ta-Nb alloys (43). It has also been reported that, although an alloying addition of 8 percent titanium had little effect on corrosion rate in sulphuric or hydrochloric acid, it prevented hydrogen embrittlement of the metal (5).

Hydrochloric acid. The corrosion behavior of niobium and its alloys in HCl is qualitatively similar to that in H_2SO_4. Niobium complex ions can also be formed in concentrated HCl (3).

Figure 9 shows corrosion results obtained by Bishop (41) in various concentrations of HCl up to 20 percent at the normal boiling point (100-110°C) and at 190 C in all concentrations up to 37 percent (i.e., concentrated HCl). Corrosion rates for tantalum are also given. It is clear that both concentration and temperature have a considerable influence on the

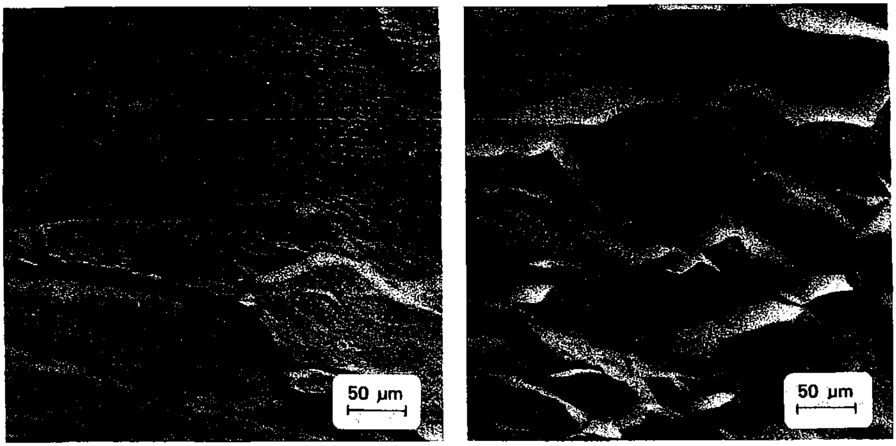

Figure 7a – Niobium, *37* h in 70% H_2SO_4.

Figure 7b – Niobium, *30* h in 75% H_2SO_4.

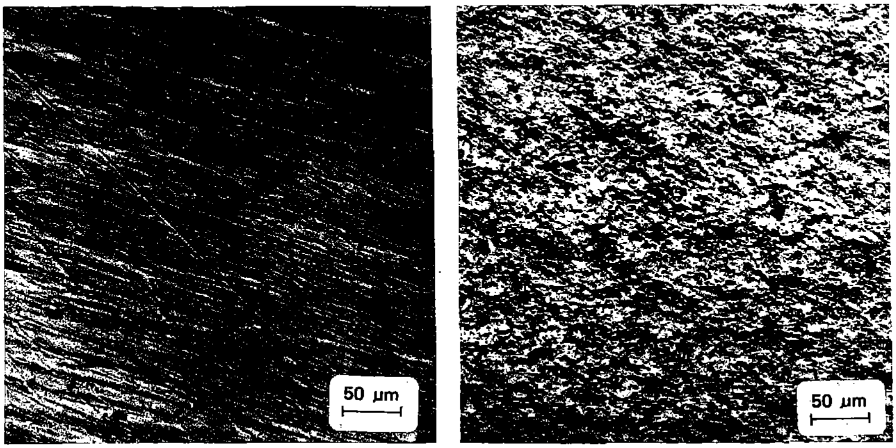

Figure 7c – Tantalum, *30* h in 75% H_2SO_4

Figure 7d – Zirconium, *30* h in 75% H_2SO_4

Figure 7 – Scanning electron micrographs of specimen surfaces after exposure in boiling *70%* and 75% H_2SO_4 *(42, 43)*.

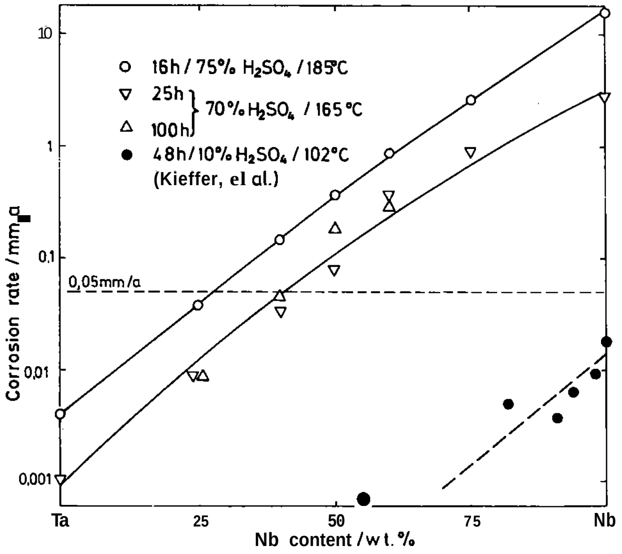

Figure 8 – Corrosion rates of Nb–Ta **alloys** in boiling H_2SO_4 (37, *42, 43*).

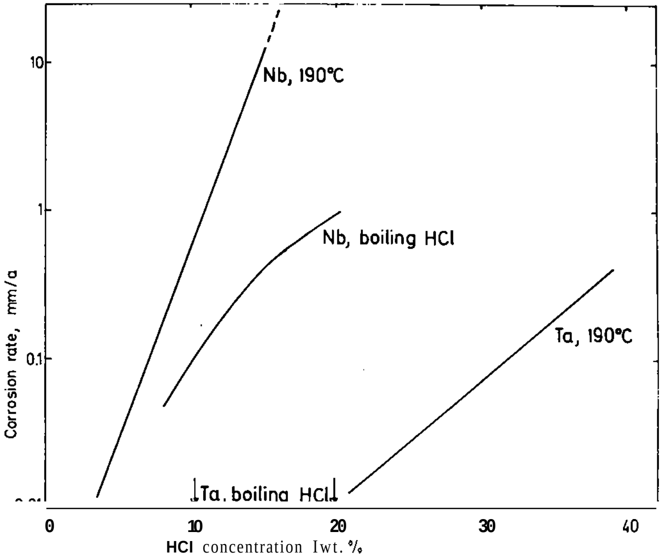

Figure 9 – Corrosion rates of niobium and tantalum in HCl (41).

corrosion rate. In common with the behavior in H_2SO_4, the effect of temperature is greater at higher acid concentrations. In HCl, as in H_2SO_4, the corrosion rate of niobium is about 1000 times greater than that of tantalum under equivalent conditions.

Apart from the work of Bishop (41), very little data relating to the corrosion of niobium in HCl is to be found in the literature. Furthermore, results from one or two series of tests, apparently conducted around 1950 (46, 47), have frequently been quoted without reference to the original source. The reported corrosion rates deviate significantly from those given by Bishop, and the reference to "concentrated HCl" at 110 C must be regarded with suspicion, because 37 percent HCl boils at a much lower temperature. Some rates reported are:

conc. HCl, RT : 0.003 mm/a (46, 47)
conc. HCl, RT : 0.08 mm/a (38)
conc. HCl, 110°C : 0.1 mm/a (47)
conc. HCl, 110°C : 0.025 mm/a (46)
20% HCl, bpt. : 0.3 mm/a (37)
10% HCl, bpt. : 0.007 mm/a (36, 37)

Alloying niobium with tantalum has been shown to increase very substantially the resistance to corrosion by HCl in a manner analogous to that described above for H_2SO_4 corrosion (37, 38, 45; 48, 49). Once again, hydrogen embrittlement has been reported, and it has been shown that additions of platinum and palladium can reduce the susceptibility to embrittlement (45).

Krehl (48) exposed Nb-Ta alloys in boiling 20 percent HCl after the specimen had been heat treated at 2600 K under ultra-high vacuum conditions in order to enrich the surface in tantalum by selective evaporation of the niobium. He observed severe intergranular corrosion in niobium-rich alloys. He also found that the corrosion attack resulted from a dissolution of the niobium: the tantalum was not dissolved by the acid.

Nitric acid. In contrast to its behavior in H_2SO_4 and HCl, where niobium is very much less corrosion resistant than tantalum, it has been reported to be resistant to attack by HNO_3. For example, Bishop (41) observed no corrosion (i.e., < 0.02 mm/a) of niobium in HNO_3 up to 0 percent concentration at temperatures up to 250 C. Results of exposure tests on Nb-Ta alloys in HNO_3 (concentation up to 75%) at temperatures up to 250 C have also been reported which show a slight weight gain of between 2 and 7 mg m^{-2} h^{-1} (49). This weight gain presumably results from the formation of a passive oxide film on the niobium.

Hydrofluoric acid. Niobium is rapidly attacked even at room temperature by HF and solutions containing fluoride ions. Somewhat surprisingly, this is the only medium in which niobium is slightly more resistant than tantalum (36, 37). Argent (38) reported that an addition of 1 percent HF to HNO_3 led to a corrosion rate of 0.3 mm/a at room temperature. However, it appears that little attempt has yet been made to define limiting fluoride concentrations in corrosive environments for either niobium or tantalum. Hampel (40) quotes some results from tests on tantalum which suffice to show the complexity of the influence of fluoride ions. He reports that levels of 2-3 ppm F in acid solutions may lead to corrosion and embrittlement of tantalum. However, in CrO_3 and CrO_3/H_2SO_4 chromium plating baths containing 0.3-0.5 percent F^-, a corrosion rate of between 0.0005 and 0.005 mm/a was observed at a temperature of 55-60 C.

In the German patent 1 123 836 (50) it has been shown that the corrosion resistance of niobium, tantalum and their alloys in HF can be greatly increased by alloying additions of tungsten and molybdenum. Thus, for example, the room temperature corrosion rate of niobium is quoted as 0.34 mm/a in 10 percent HF and 0.61 mm/a in 30 percent HF, whereas an addition of 20.5 percent molybdenum reduces the rate to 0.0001 mm/a in 20 percent HF. This rate is, in fact, much lower than has been reported for pure molybdenum and tungsten in 3 percent HF (36). The disadvantage of niobium-molybdenum and niobium-tungsten alloys in comparison with pure niobium lies in their poorer fabricability and the effect of the alloying additions in increasing the ductile-brittle transition temperature. It has been reported that niobium alloys containing more than about 10 percent tungsten or molybdenum are brittle at room temperature, at least in the recrystallized condition (51).

Phosphoric acid. Niobium is moderately resistant to attack by H_3PO_4. For example, a corrosion rate of 0.08 mm/a has been reported for exposure in 85 percent H_3PO_4 at 100 C (33). In U.S. Patent 3 186 837 (52), a corrosion rate of 31 mm/a is given for niobium in 85 percent H_3PO_4 at 205 C. In this patent, it is shown that the corrosion rate can be reduced to 6.4 mm/a by the addition of 33 percent tantalum and to 3.8 mm/a by the addition of 40 percent tantalum. The rate is reduced even further by the addition of 11 percent titanium, 11 percent nickel and 5 percent molybdenum with 33 percent tantalum (0.51 mm/a), although these additions result in a slight loss in corrosion resistance in H_2SO_4 compared with the simple binary Nb-33 percent Ta composition. The dependence of corrosion rate on alloy microstructure is described in particular in the patent. Resistance to H_3PO_4 corrosion was found to depend on the nickel content. Below about 2 percent nickel, the alloy is single phase, and corrosion is very rapid. Above 2 percent nickel, a second phase precipitates in the alloy matrix and leads to greatly enhanced corrosion resistance. However, the presence of the two-phase structure causes increased corrosion in H_2SO_4.

Tantalum is much more resistant to H_3PO_4 than niobium (e.g., 0.005 mm/a in 85 percent H_3PO_4 at 190 C (33)). Thus, it is to be expected that Nb-Ta alloys would have interesting corrosion properties for H_3PO_4 applications, as indicated by the results in the patent discussed above. However, no further corrosion data concerning the behavior of Nb-Ta alloys in H_3PO_4 could be found.

Other acid media. At temperatures up to 60 C, niobium shows good resistance to attack by aqua regia (0.025 mm/a at 60 C (46, 47)). Once again, however, it falls short of the corrosion properties of tantalum which shows no measurable attack under these conditions.

Niobium is attacked slowly by a number of organic acids in boiling aqueous solution (Table II). It has been reported that corrosion by organic acids can cause embrittlement of niobium even at room temperature (53).

Table II. Corrosion of Niobium in Organic Acids

(Boiling point exposure tests)

Acid	Concentration (%)	Corrosion rate (mm/a)	Ref.
Oxalic	10	0.023	34
		0.015	47
Acetic	5	nil	34
	10	0.001	36
	85	nil	34
	99.7	nil	34
Formic	10	nil	34
Citric	10	0.018	34
Lactic	10	0.010	34
	a5	0.003	34
Trichloroacetic	50	nil	34

Summary of corrosion behavior of niobium in aqueous media

The review of corrosion behavior presented above might give the impression that niobium has little to offer as a corrosion resistant material for use in aqueous environments. This would, however, be an unreasonably pessimistic picture, derived largely from the inevitable cpmparison of niobium with its truly outstanding neighbor tantalum.

Firstly, in hot water and steam, niobium can be alloyed with vanadium or zirconium to reach a level of corrosion resistance similar to that of Zircaloy 2.

Secondly, although niobium itself is unattractive for use in HCl or H_2SO_4, its alloys with tantalum offer considerable promise for applications in which the excellent properties of tantalum are not required in full.

Thirdly, the use of niobium and niobium-tantalum alloys could be seriously considered for handling H_3PO_4, and the use of niobium itself in aqua regia and a number of organic acids might be of interest.

Finally, the most promising field for the application of niobium is undoubtedly in handling hot concentrated HNO_3. There is no suggestion in the literature that niobium is subject to any significant corrosion in this medium.

Reactions with Metals

The resistance of niobium to corrosion by liquid metals has been the subject of a number of reviews (4, 5, 6, 54).

Niobium is resistant to:

bismuth	up to	550 C
gallium	up to	400 C
lead	up to	850 C
mercury	up to	600 C
thorium-magnesium eutectic	up to	850 C
uranium	up to	1400 C
zinc	up to	450 C

At higher temperatures than those indicated above, niobium is attacked by bismuth, gallium, uranium and zinc. Alloys of uranium with bismuth, iron, manganese, nickel or chromium corrode niobium at temperatures over 800–1000 C.

Niobium is of particular interest because of its excellent compatibility with the alkali metals lithium, sodium and potassium. This results primarily from the very low solubility of niobium in the molten alkali metals. **When** corrosion does occur, it is usually associated with impurities - in particular oxygen contamination - in the niobium or the molten metal. The reactions between various refractory metals, their oxides and the alkali metals containing oxygen, nitrogen and carbon have been discussed by Barker (55).

It is important to distinguish between lithium, which forms an oxide with considerably greater stability than Nb_2O_5, and sodium and potassium, which form oxides that have similar or lower stability than Nb_2O_5. Thus, niobium is rapidly attacked by lithium at temperatures of about 800 C if the oxygen. content exceeds 400 ppm, because the lithium tends to react with the dissolved oxygen in the niobium (56 - 59). Penetration of the niobium occurs by the formation of a ternary oxide on grain boundaries and preferred crystallographic planes. The presence of oxygen in molten lithium has no effect on niobium, whereas nitrogen and carbon can be transferred to the niobium. It has been demonstrated that a small addition of zirconium followed by heat treatment at 1300 C to precipitate ZrO_2 can prevent the lithium corrosion of oxygen-contaminated niobium (56). The oxygen: zirconium atomic ratio must be less than 2 : 1 to ensure effective removal of the oxygen from solution. The well established Nb-1 percent Zr alloy has proved particularly good in this respect.

The situation is completely different when we consider sodium and potassium. Although both alkali metals can reduce Nb_2O_5 to the ternary oxides Na_3NbO_4 and K_3NbO_4, they do not react with oxygen present at low activities in solution in the niobium. However, traces of oxygen in the alkali metal react with niobium to form a solid solution and a surface layer of the ternary oxide (55). It is also probable that nitrogen, hydrogen and carbon could be transferred from sodium or potassium to niobium.

In designing complex systems with alkali metal cooling, e.g., the liquid metal cooled fast breeder reactor, it is well known that the coolant provides a highly efficient means for transporting impurities from regions of high activity to regions of low activity. Thus, for example, carbon can be transported from low-alloy steel pipework to high-chromium austenitic steel components. In view of the high stability of niobium carbide, this will be a particularly acute problem in any system containing niobium components. Difficulties can only be avoided by careful design which takes into account the thermodynamics of carbide formation in the various materials in the system.

In addition to its excellent resistance to molten alkali metals, niobium is also highly resistant to attack by sodium vapor at high temperatures and pressures. The Nb-1 percent Zr alloy is in use as the end caps in many millions of high pressure sodium vapor lamps where it has proved its ability to withstand this severe environment over long periods of time. The arc tubes are either single crystal sapphire or polycrystalline aluminum oxide. Electrical contact is provided by a refractory metal feed-through or an end cap which is hermetically sealed to the aluminum oxide tube.

Behavior in Molten Salts

Fused salts have found wide technological application in high temperature electrochemical processes, as heat transfer media and as catalytic agents in high temperature organic synthesis. Besides this, molten salts can be formed during the combustion of petrochemical products which contain traces of salts and metals.

Although the chemistry of niobium salts is very well known (3), and niobium has been produced by electrochemical reduction from its halogen compounds and its oxide in molten salts (60-62), nothing appears to have been published about the corrosion behavior of niobium in molten salts, such as alkali halides, nitrates and carbonates. We undertook literature searches in several computerized data banks but found no reference to the molten salt corrosion of niobium.

From the results of niobium electrolyses in alkali fluorides and alkali chlorides and from the chemical properties of molten salts (63), the conclusion can be drawn that niobium is only slightly attacked by alkali halide melts which are free from excess halogens (HF, HCl, F_2, Cl_2), oxygen (O_2, H_2O, oxy-salts) and physically dissolved gases (H_2, N_2). If ions of more noble metals than niobium are present in molten alkali halides, niobium will be dissolved in cementation processes. In salt melts with oxygen-containing anions (nitrates, carbonates), strong interactions may be expected with the formation of oxides and oxy-nitrides.

Current and Potential Applications of Niobium in Corrosive Environments

Only a small fraction, perhaps 2–3 percent, of the total world production of niobium is used as niobium metal or niobium-base alloys. Considering the many favorable properties of this metal - good fabricability, reasonable strength, good nuclear characteristics - it is clear that the main hindrance to wider usage has been its high price in comparison to competitive materials. If the market price of niobium can be stabilized at a moderate level, the current range of applications under the corrosive conditions discussed in this paper could certainly be extended.

Vacuum applications

Niobium is found in a number of high temperature vacuum applications where its high melting point (246 C) and its getter properties can be used to advantage. However, it has not yet achieved the significance of tantalum, molybdenum or tungsten in this field. There appears to be considerable potential for wider use of niobium or the Nb-1 percent Zr alloy in, for example, heat shields and radiation heating elements.

Aqueous environments

Niobium metal shows considerable promise as a corrosion resistant material in plant handling hot concentrated nitric acid and a number of organic acids. Tantalum and zirconium are currently used under appropriate conditions in these media. At present, niobium offers a substantial cost advantage relative to tantalum together with the advantage of a lower density (i.e., more material per kilogram). The relative merits of zirconium and niobium in these media require closer examination.

A particularly promising material for use in hot mineral acids is the *60* percent Ta - *40* percent Nb alloy. In this material, the niobium serves principally to dilute the tantalum, thereby reducing its cost and its density. The alloy can be considered for use in a number of applications where tantalum is currently employed, for example, in heat exchangers and corrosion resistant cladding for sulphuric acid plant with temperatures up to about 165 C.

Although niobium-base alloys have good corrosion resistance in hot water and steam, it appears unlikely that they can now be considered a serious alternative to austenitic steels and the Zircaloy alloys in nuclear reactors with water as the coolant.

Niobium is also used as the basis for platinum clad anodes for current-impressed cathodic protection systems *(64).* Titanium is widely used in this application, but niobium offers the considerable advantage of a much higher anodic breakdown potential than titanium in the presence of chloride ions, for example, in sea water.

Liquid metals, metal vapor

The very good compatibility of niobium and Nb-1 percent Zr with a number of liquid metals indicates considerable potential for a number of applications. As liquid metals are excellent heat-transfer media, they can be used in very compact thermal systems, such as the fast breeder reactor, reactors for space vehicles and fusion reactors. So far, niobium has only been used in one application of this type, the Dounreay experimental fast breeder reactor, where nobium served as the outer canning for the fuel elements. Since then, reactor designers have learnt to live with the poorer nuclear properties of austenitic steels, although niobium still remains a serious candidate for reactors with increased operating temperatures or for increasing reactor efficiency.

Tantalum, molybdenum and tungsten are commonly used for boats for metal evaporation. It seems reasonable to assume that niobium could also be used in many instances.

The excellent performance of niobium in sodium vapor has already been mentioned. The well established application in high pressure sodium lamps is likely to increase. Another potential application is in heat pipes for use at temperatures over 1000 C.

Miscellaneous

Niobium, in common with titanium, zirconium and tantalum, shows very good compatibility with the human body. Thus, niobium and many of its alloys (e.g., Nb-50% Zr) are suitable for surgical implants (65). In this field, however, it has to compete with the cheaper titanium and Ti-6 percent Al-4 percent V and with tantalum, all of which are well established surgical materials.

Two other potential applications in which the corrosion resistance of niobium plays an indirect role are coinage and jewelry. Niobium has already been used for the production of commemorative medallions and it appears an interesting material for high quality Coinage. It has also been proposed for jewelry application because it can readily be anodized to yield brilliantly colored surface oxide layers.

References

1. H. V. K. Udupa and V. K. Venkatesan, pp. 53-123 in "Encyclopedia of Electrochemistry of the Elements", Vol. 11, ed. A. J. Bard, Marcel Dekker, New York, 1974.

2. I. M. Kolthoff and P. J. Elving, "Niobium and Tantalum" in "Treatise on Analytical Chemistry", Part II, Vol. 6, Interscience, New York, 1964.

3. F. Fairbrother, "The Chemistry of Niobium and Tantalum" in "Topics in Inorganic Chemistry and General Chemistry", ed. P. L. Robinson, Monograph 10, Elsevier, Amsterdam, 1967.

4. J. Bentley, pp. 5:24-5:33 in "Corrosion", ed. L. L. Shreir, Vol. 1, Newnes-Butterworths, London and Boston, 1976.

5. M. Stern and C. R. Bishop, pp. 304-346 in "Columbium and Tantalum", ed. F. T. Sisco and E. Epremian, Wiley, New York, 1963.

6. G. L. Miller, "Tantalum and Niobium", Butterworths, London, 1959.

7. D. J. Fast, "Interaction of Metals and Gases"; Vol. 1, "Thermodynamics and Phase Relations", Academic Press, New York, 1965; Vol. 2, "Kinetics and Mechanisms", McMillan, London, 1971.

8. E. Fromm and E. Gebhardt (ed.), "Gase and Kohlenstoff in Metallen", Springer-Verlag, Berlin-Heidelberg-New York, 1976.

9. E. Fromm and G. Hörz, International Metal Reviews, Nos. 5 and 6 (1980) p. 269.

10. E. Fromm in Proc. Second Int. Symposium on "Hydrogen in Metals", Minakami, Japan (1979).

11. G. Hörz and E. Steinheil, Z. Metallkde. 62 (1971) p. 849.

12. G. Hörz and E. Gebhardt, Z. Metallkde. 57 (1966) p. 737.

13. W. Grünwald, F. Haessner and K. Schulze, J. of the Less-Common Metals 48 (1976) p. 325.

14. P. Kofstad, High Temperature Oxidation of Metals, Wiley, New York (1966).

15. P. Kofstad and S. Espevik, J. Electrochem. Soc. 112 (1965) p. 153.

16. G. Hörz and K. Lindenmaier, Z. Metallkde. 64 (1973) p. 348.

17. H. Jehn and G. Hörz, Z. Metallkde. 67 (1976) p. 417.

18. K. Schulze and H. Jehn, Z. Metallkde. 68 (1977) p. 654.

19. K. Schulze and H. Jehn, in J. P. Langeron and L. Maurice (ed.) Proc. 8th Int. Vacuum Congress, Vol. II (1980) pp. 554-557.

20. J. Jupille and J. M. Michel, J. Less-Common Metals 79 (1975) p. 17.

21. E. Fromm and H. Jehn, Z. Metallkde. 58 (1967) pp. 61 and 120.

22. 9. Fromm and H. Jehn, Z. Metallkde. 67 (1976) p. 75.

23. E. Fromm and H. Jehn, High Temperature - High Pressures 10 (1978) p. 231.

24. G. Hörz, Metall 27 (1973) p. 680.

25. E. Fromm and G. Spath, Z. Metallkde. 67 (1976) p. 410, and E. Fromm, ibid, p. 413.

26. J. van Muylder and M. Pourbaix, Techn. Report No. 53, Centre Belge d'Etude de la Corrosion, Brussels, 1959.

27. M. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solution", Pergamon, London, 1966.

28. W. D. Klopp, W. E. Berry and D. J. Maykuth, pp. 685-718 in "Columbium Metallurgy" ed. D. L. Douglass and F. W. Kunz, Interscience, New York, 1961.

29. H. A. Fisch, D. L. Douglass and B. E. Dearing, ibid, pp. 597–613.

30. D. J. Maykuth, W. D. Klopp, R. I. Jaffee, W. E. Berry and F. W. Fink, BMI-1437, May 1960.

31. P. E. Blackburn and E. A. Gulbransen, WADC Tech. Rep. 57–344, Pt 11, Dec. 1958.

32. K. E. Heusler, Z. Metallkde. 61 (1970) p. 828.

33. M. G. Fontana, Metal Industry, (8th Aug. 1952) p. 112.

34. D. L. MacLeary, Corrosion - NACE, 18 (1962) p. 67t.

35. I. I. Tingley and R. R. Rogers, Corrosion - NACE, 21 (1965) p. 132.

36. R. Kieffer, H. Rach, F. Binder and F. Kurka, Werkstoffe u. Korrosion, 19 (1968) p. 312.

37. R. Kieffer, H. Bach and I. Stempkowski, Werkstoffe u. Korrosion, 18 (1967) p. 782.

38. B. B. Argent, J. Inst. Metals, 85 (1957) p. 547.

39. D. W. McDowell, Chem. Engineering, 81 (No. 24) (1976) p. 118.

40. C. A. Hampel, Corrosion - NACE, 14 (1959) p. 557t.

41. C. R. Bishop, Corrosion - NACE, 19 (1963) p. 308t.

42. D. Lupton, W. Schiffmann, F. Schreiber and E. Heitz, Proc. 8th Int. Cong. on Metallic Corrosion, Mainz, Sept. 1981.

43. D. Lupton and F. Aldinger, Proc. 10th Plansee Seminar, Reutte/Austria, June 1981.

44. H. Braun, K. Sedlatschek and R. Kieffer, J. Less-Common Metals, 1 (1959) p. 413.

45. A. V. Moselev, et al., Tr. Gos. Nauchno-Issled. Proektn. Inst. Azotn. Prom-sti. Prod. Org. Sint. 18 (1973) p. 154.

46. D. F. Taylor, Industrial and Engineering Chemistry, 42/4 (1950) p. 639.

47. M. G. Fontana, ibid. 44/7 (1952) p. 71A.

48. M. Krehl, Diploma Thesis, Max-Planck-Institut fur Metallforschunp and University of Stuttgart, 1981.

49. D. A. Prokoshkin and E. V. Vasil'eva, "Alloys of Niobium", Israel Program for Scientific Translations, Jerusalem 1965.

50. R. Kieffer, K. Sedlatschek and H. Braun, Auslegeschrift 1123836, FRG Patent Office, filed 6.4.1959.

51. R. T. Bepley, W. N. Platte, A. I. Lewis and R. L. Ammon, WADC Techn. Report 57-344, Part V, Sept. 1961.

52. E. F. Duffek, U. S. Patent 3 186 837, filed 28.2.1961.

53. A. H. Barber, Chemical and Process Engineering 42 (1961) p. 451.

54. R. L. Barto and D. T. Hurd, Research/Development (November 1966) p. 26.

55. M. G. Barker, Rev. int. hautes Temper. Refract., Fr., 16 (1979) p. 237.

56. W. C. Thurber, J. R. DiStefano, T. G. Kollie. H. Inouye. H. E. McCoy and R. L. Stephenson, pp. 59-77 in "High Temperature Refractory Metals", ed. R. W. Fountain. J. Maltz and L. S. Richardson, Gordon and Breach. New York, 1966.

57. R. L. Klueh, Met. Trans., 5(1974) p. 875.

58. R. L. Klueh, Trans. Am. Nuc. Soc., 15 (1972) p. 746.

59. A. G. Arakelov, V. V. Vavilova, A. F. Gekov and A. M. Zel'tser, Fiziko Khim. Mekh. Mater. (Kiev), 13 (1977) p. 45.

60. W. Rockenbauer, Chem.-Ing.-Techn. 41 (1969) p. 159.

61. Cl. Decroly, A. Mukhtar and R. Winand, J. Electrochem. Soc. 115 (1968) p. 905.

62. S. Senderoff and G. W. Mellors, Science 153 (1966) p. 1475.

63. G. J. Janz, Molten Salts Handbook, Academic Press, New York, 1967.

64. R. Baboian, Mater. Perform., 18 (1979) p. 9.

65. S. Steinemann and S. Perren, Patentschrfit 21 34 926, FRG Patent Office filed 13.7.71.