

## NIOBIUM IN HIGH TEMPERATURE APPLICATIONS

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### Abstract

A critical review of the literature shows that niobium alloys have potential aerospace applications to 1316 C (2400 F) in closed cycle power systems in the uncoated state or for glide re-entry vehicles and rocket nozzles in the coated state. The survey shows that technical feasibility depends principally on controlling the oxidation and/or coating-substrate reactions as they severely degrade alloy mechanical properties. Data are presented to illustrate these instabilities and the technology developed is summarized to show how the incompatibility problems were or could be resolved.

## Introduction

In the U.S.A., the decade of the 1960's marked a period of extensive government sponsored research and development on materials for defense and space needs. Advanced concepts for the aerospace field provided the pre-dominant consideration of refractory alloys for use in solid propellant rockets, lifting and guidance structures for re-entry vehicles, compact and high power density nuclear power systems, and gas turbine components for hypersonic aircraft (1). Solid propellant nozzles require materials having high melting points, corrosion-erosion resistance to propellant combustion products, and capability of being manufactured in large diameters. Molybdenum can be used for flame temperatures up to 2650 C (4800 F) while tungsten is used when flame temperatures approach 3316 C (6000 F). Tantalum and niobium alloys have been used as nozzle extensions where flame temperatures are under 1650 C (3000 F).

Heat shields for aerodynamically-heated surfaces in glide re-entry vehicles represent a potentially new use for refractory metals. In the Space Shuttle Orbiter the applicable areas totalling about  $930 \text{ m}^2$  ( $10^4 \text{ ft}^2$ ) are found in the forward sections and in the leading edges of the guidance components where the temperatures exceed 1193 C (2000 F). The artist's conception of the vehicle is depicted in Figure 1(a) (2). To maximize payloads, construction of the heat shield dictates the use of sheet material welded into a lightweight and stiffened structure similar to that shown in Figure 1 (b) (3). Because the fabrication of high quality sheet from tungsten and molybdenum alloys is difficult and their welds tend to be brittle at low temperatures, they are less reliable than the niobium and tantalum alloys. For re-entry temperatures to 1371 C (2500 F), niobium alloys are preferred; however, above this temperature niobium alloys rapidly lose strength and the tantalum alloys become more appropriate. The metallic thermal protection system (TPS) concept adopted for the space shuttle is schematically shown in Figure 1 (c) (3). In this arrangement the heat shield which radiatively dissipates the aerodynamic heat is separated from the load carrying substructure by insulation.

Refractory alloys in space nuclear power systems show promise in containing circulating alkali metals in Rankine cycle systems or a pressurized inert gas in Brayton cycle systems. For either system, tubing and sheet for heat exchangers and headers, respectively, are the major mill products. As in the case of heat shields, the reliability factor desired in these complex structures dictated the exclusive consideration of the more fabricable niobium and tantalum alloys.

Refractory metals were initially considered for gas turbine applications. Interest originally centered on molybdenum turbine blades, but because of its tendency for catastrophic oxidation failure, attention shifted to niobium alloys. Because of the improved performance brought about by internally cooling superalloy blades and the requirement for impact damage and erosion resistance, the application of refractory metals for gas turbines has not been realized.

This report reviews the technology developed for using uncoated niobium alloys in applications where the environmental constraints are perceived to be minimal due to low oxygen pressures as exemplified by a closed cycle Brayton system and then considers uses under environmental conditions that would rapidly oxidize the alloys without the protection of coatings (e.g., re-entry vehicles). Both applications depend on the ability of the alloys to be fabricated into complex shapes.

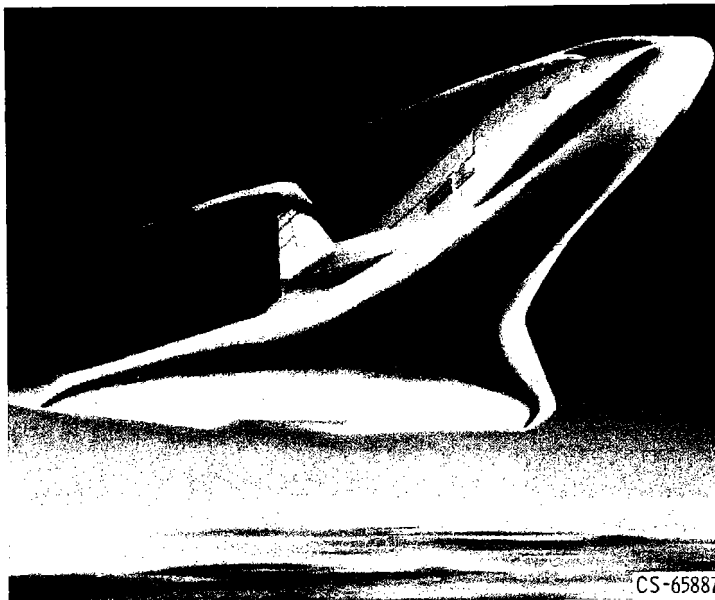


Figure 1(a) - Artists Conception of Space Shuttle Orbiter on Atmospheric Re-Entry. Aerodynamic heating raises about 15 percent of vehicle surface to 2012-2400 F (1100-1316 C). (From Levine (2)).

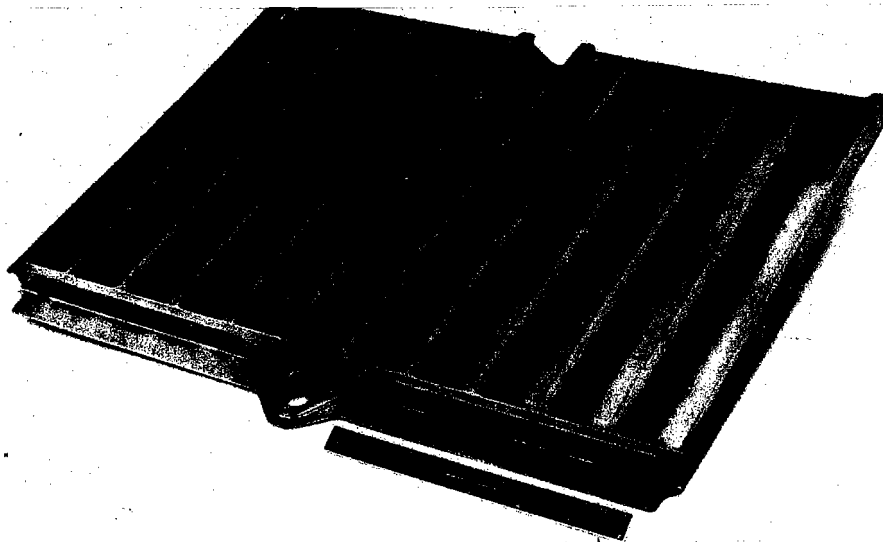
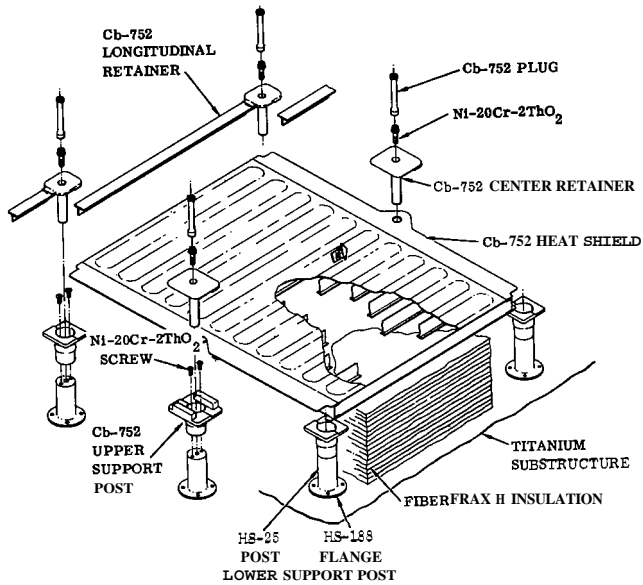


Figure 1(b) - Interior View of Electron-Beam Welded Niobium Heat Shield. Strong lightweight structure requires a fabricable and weldable alloy (from Black (3)).



**Figure 1(c) - Coated Cb 752 (Nb-10W-2.5 Zr-0.004C) Protects Heat Shield from Oxidation and Radiates Heat During Re-Entry. Removable panel concept permits inspection and field repairs (from Black (3)).**

Niobium readily reacts with  $O_2$ ,  $H_2O$ ,  $CO$ ,  $CO_2$ ,  $N_2$ , and  $H_2$  at high temperatures. These gases are the components of air, the residual gases in vacuum systems, impurities in inert gases, and frequently are the decomposition products of compounds. By far the most persistent and probably one of the more difficult reactions to control at high temperatures is that which occurs between the metal and the oxygen containing gas species. As will be discussed later, the niobium-oxygen reaction is also the most important reaction from the standpoint of practical applications because of its profound effect on mechanical properties.

Effect of oxygen pressure

It has been conceded that the oxidation of niobium cannot be eliminated at the anticipated service temperatures but can be reduced to acceptable rates by controlling the  $P_{O_2}$  over the metal. Figure 2, which shows the effect of the oxygen pressure on the oxidation rate of Nb illustrates this dependence. This curve shows that the oxidation rate can be reduced by four orders of magnitude on going from 100 psi oxygen to  $10^{-9}$  kg/mm<sup>2</sup> ( $10^{-6}$  psi) at 1200 C. Below about  $10^{-4}$  kg/mm<sup>2</sup> ( $10^{-4}$  psi) the oxidation rate is proportional to the pressure and varies approximately as  $\sqrt{P_{O_2}}$  above this pressure

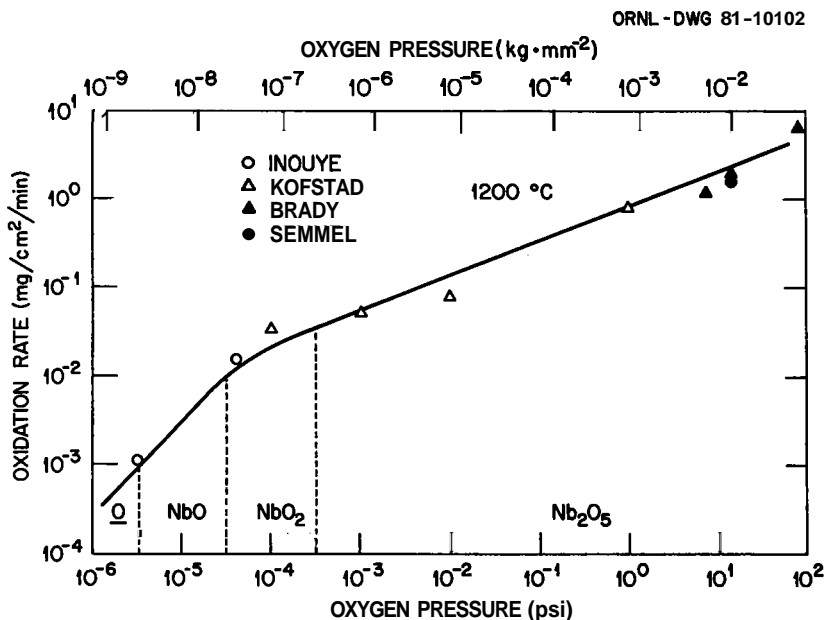


Figure 2 - Oxidation Rate of Niobium Varies Linearly with  $P_{O_2}$  Below About  $10^{-4}$  psi and as  $\sqrt{P_{O_2}}$  Between  $10^{-4}$  and 10. Oxide reaction products also depend on  $P_{O_2}$  (from Inouye, Kofstad, Semmel, and Brady (4, 5, 6, 7)).

(4, 5, 6, 7). The vertical dashed lines indicate the approximate pressure boundaries that favor the formation of Nb-O solid solutions (designated as  $\theta$ ),  $\text{NbO}$ ,  $\text{NbO}_2$ , and  $\text{Nb}_2\text{O}_5$  as the principal reaction products. These boundaries shift to higher pressures with increasing temperatures and move in the opposite direction with increasing exposure time. Oxidized niobium can form one or more of these oxides on the surface depending on the exposure conditions, but because oxygen rapidly diffuses into niobium, Nb-O solid solutions form below the oxide surface under most conditions.

Uncoated niobium alloys have always been considered for closed cycle systems and structures fabricated from them are designed on the basis of their creep strength. Typically these applications project a component life of several thousand hours and assume that the  $\text{P}_{\text{O}_2}$  in the system has been reduced to insignificant levels by using components with low oxygen content, thoroughly outgassing of all hot structures, and by the use of sacrificial getters to absorb oxygen released during service. In contrast, a re-entry vehicle experiences a pressure-temperature profile similar to that shown in Figure 3 (3). In this case, each mission exposes the niobium structure to oxygen pressures that favors the conversion of Nb to  $\text{Nb}_2\text{O}_5$  for period of under 1 h. Because this application anticipates a re-use capability of about 100 missions, and the effects of the oxidation reactions are cumulative, the application requires the use of oxidation-resistant or coated niobium alloys.

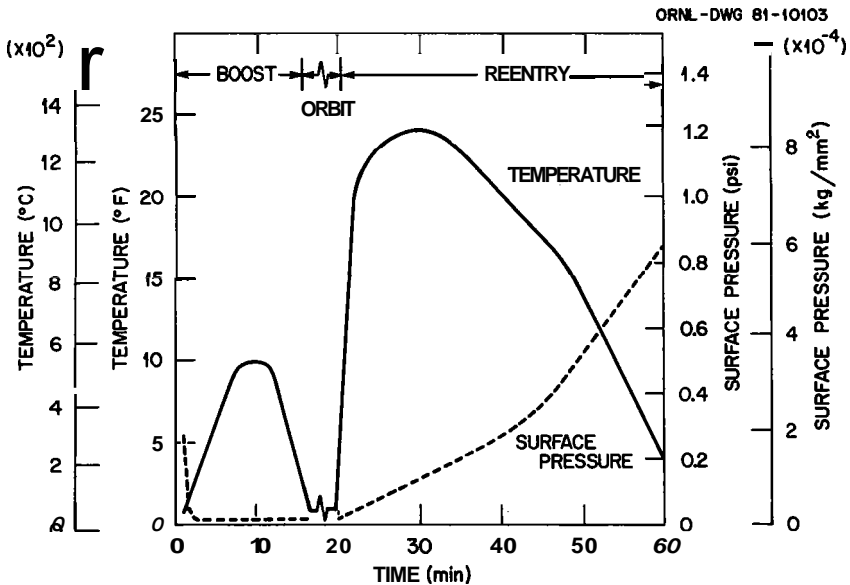


Figure 3 - Typical Temperature-Pressure Profile for a Glide Re-Entry Vehicle Exposes Heat Shield Protected Surfaces to 2400 F (1316 C) at Low Pressures (from Black (3)).

## Oxidation resistant niobium alloys

The oxidation rate of niobium is reduced by alloying with the elements shown in Figure 4 (6). In several binary alloys, the rate goes through a minimum (Figures 4(a) and 4(c)) and at the optimum alloying concentration is about a factor of 5 lower than niobium. Alloying with both chromium plus cobalt produced the alloy with the lowest oxidation rate (Figure 4(b)). Combination of alloying elements such as aluminum plus vanadium at levels of - 3 wt percent each were effective in reducing the oxidation rate by a factor of over 10 (8). Further modification of the ternary alloy with both Ti and Cr resulted in added oxidation resistance (Figure 5). While significant, these reductions in the oxidation rate are still too low to allow consideration of these materials as practical oxidation-resistant alloys. Also as it usually happens, alloying for maximum oxidation resistance is obtained at the expense of strength as shown in Figure 6 (9).

The work directed toward the development of oxidation-resistant alloys while not culminating in satisfactory alloys did, however, show that coatings were necessary for the oxidation protection of niobium. Further, the identification of the reaction products and characterization of their morphology on oxidized alloys showed which elements should be incorporated into the coating and their probable functions. As an example, the reaction products on oxidized Nb-Al-V alloys showed the absence of both aluminum and vanadium

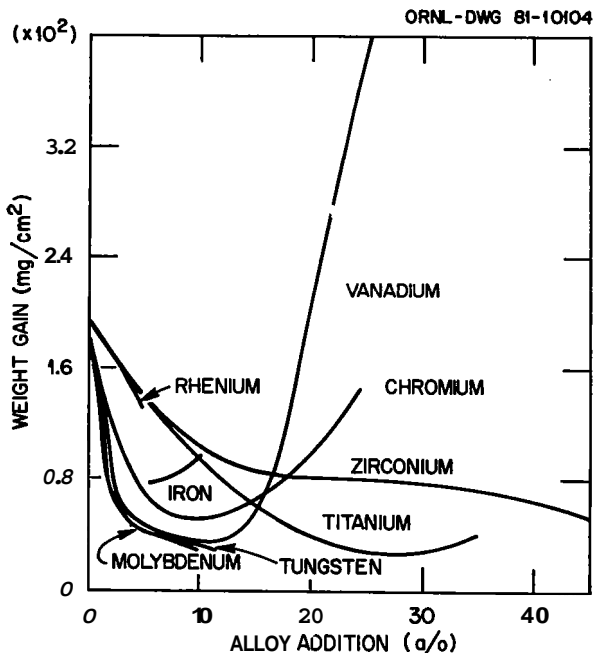


Figure 4(a) - Niobium Alloys are Not Oxidation Resistant (from Semmel (6)). Weight Gain for 2 h Exposure at 2193 F (1200 C) Versus Composition Goes through Minima.

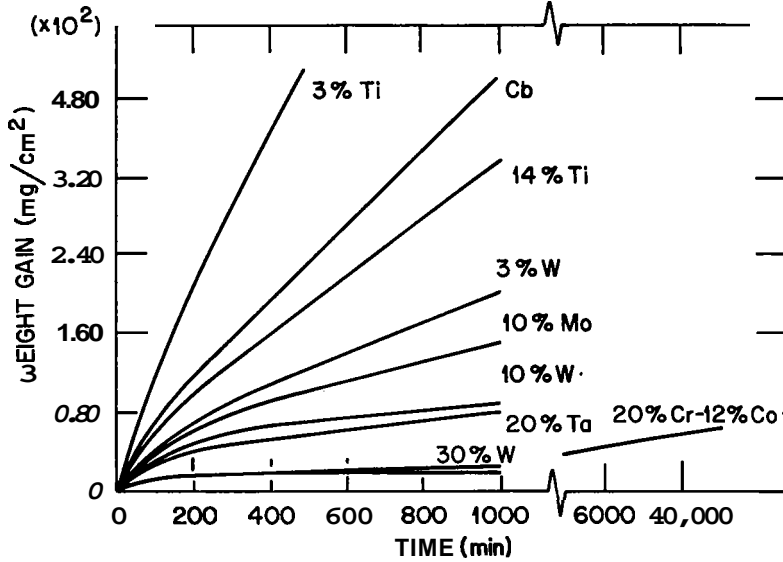


Figure 4(b) - Niobium Alloys are not Oxidation Resistant (from Semmel (6)). Oxidation Rates of Nb Alloys at 2000 F (1093 C) are Lower than Nb.

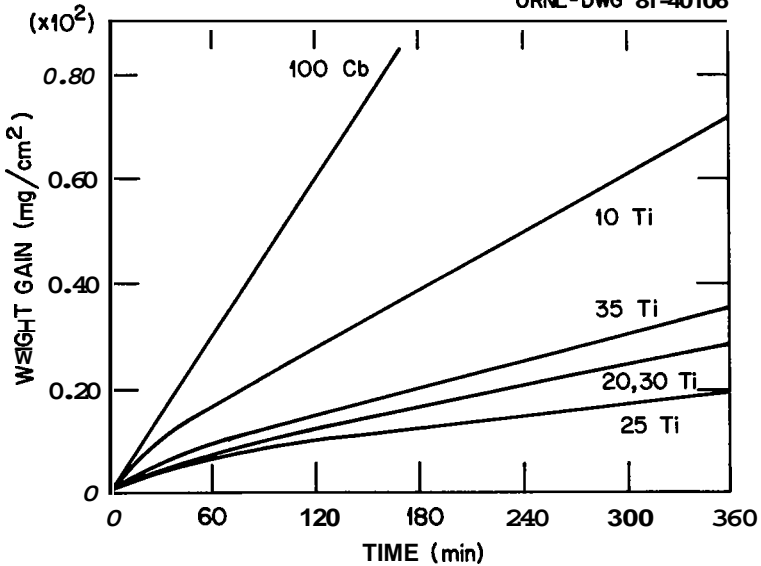


Figure 4(c) - Niobium Alloys are not Oxidation Resistant (from Semmel (6)). Alloys Containing 25 a/o Ti Improve Oxidation of Nb by a Factor -6 at 1832 F (1000 C).



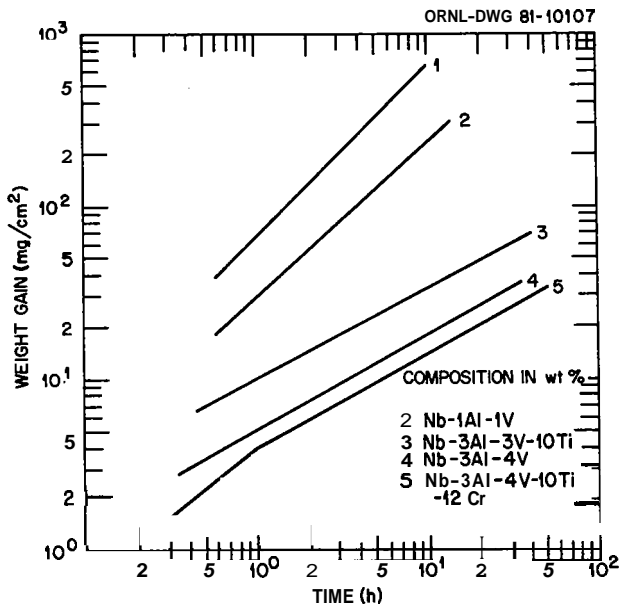


Figure 5 - Oxidation of Niobium Alloys at 1832 F (1000 C) in Oxygen (from Wlodek (8)). Al and V additions lower the oxidation rate by improving the plasticity of  $Nb_2O_5$ . Cr additions to Nb-Al-V-Ti improves oxidation resistance by forming  $Nb_2O_5 \cdot TiO_2$  at metal-oxide interface.

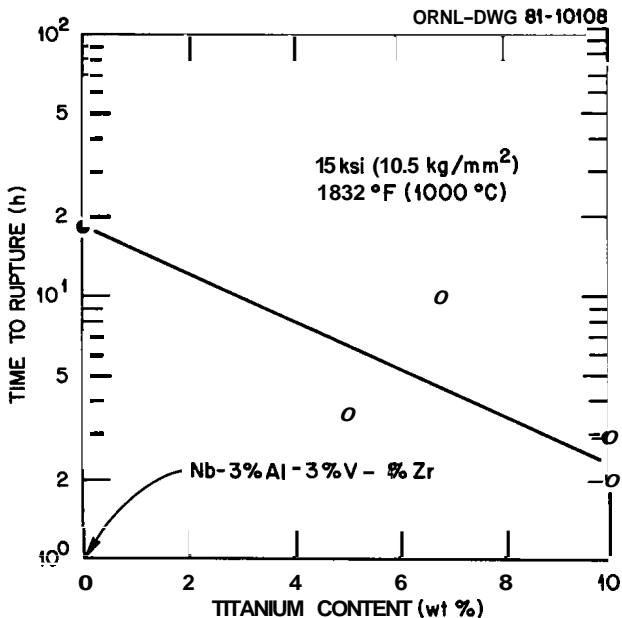


Figure 6 - Titanium Lowers the Rupture Life of a Nb Alloy (from Sheely (6)).

oxide, but the formation of greater than normal amounts of  $NbO$  and  $NbO_2$  below the outer  $Nb_2O_5$  scale. This result in combination with that shown in Figure 2 shows that alloying niobium with aluminum and vanadium had the same effect as reducing the  $P_{O_2}$  to about  $10^{-3}$ - $10^{-4}$   $kg/mm^2$  ( $10^{-4}$  to  $10^5$  psi) from  $1.47 \times 10^{-2}$   $kg/mm^2$  (14.7 psi). It is believed that this occurs because the small amounts of Al and V which dissolve in the  $Nb_2O_5$  delays or eliminates its periodic fracture by improving the plasticity (6, 8).

In the case of the titanium modified Nb-Al-V alloy, the titanium which appears as  $Nb_2O_5 \cdot TiO_2$  in the outer scale degrades the oxidation resistance of the ternary alloy (Figure 5, curves 3 and 4). However, when chromium is added with the titanium, the  $Nb_2O_5 \cdot TiO_2$  also forms at the metal-oxide interface, chromium oxides are not formed, and according to Figure 5, curve 5, improves the oxidation resistance. These diagnostic studies suggest that coating performance can be improved by elements that enhance the mechanical properties of the oxide and also indicates that the protective capacity of a surface oxide does not necessarily depend on its composition but also on where it forms.

### Coatings for the Protection of Niobium Alloys from Oxidation

#### Coating systems

The preferred niobium alloys for constructing components for complex structures are listed in Table I. Characteristically, they possess excellent fabricability, weldability, have moderate strength, but oxidize at rates comparable to unalloyed niobium (Figure 7) (10). Their use at high temperatures under oxidizing conditions require coatings applied by one of the techniques listed in Table II (1). Of the numerous options available it has been determined that intermetallic coatings based on silicides and aluminides applied by pack cementation and the slurry paint methods produced the best coatings.

In the pack cementation process, the article to be coated is heated in a powder mixture of an inert material (usually  $Al_2O_3$ ), the powder of the element to be deposited (e.g., Al or Si), and a halide salt activator (e.g., KF) in a closed retort. On heating to the reaction temperature, a volatile metal halide (e.g.,  $SiF_4$ ) forms and reacts with the metal to form a coating whose thickness is governed by the reaction temperature and time. This process is capable of coating small parts uniformly but becomes increasingly difficult to control as the size and complexity of the part increases due to poor heat transfer through the  $Al_2O_3$  powder.

Table I. Composition of Fabricable and Weldable Niobium Alloys

Alloy Designation	Composition
D-14	5 Zr - .006C-bal Nb
C-129	10 Hf - 10W-.015C-bal Nb
C-129y	10 Hf-10W-.015C-.2Y-bal Nb
CB-752	10 W-2.5 Zr-.004C-bal Nb
D43	10 W-1Zr-0.1C-bal Nb
B66	5 Mo-5V-1Zr-.006C-bal Nb
D31	10 Mo-10 Ti-.015C-bal Nb
C-103	10 Hf-1Ti-0.7 Zr-.015C-bal Nb
D-36	10 Ti-5 Zr-.015C-bal Nb

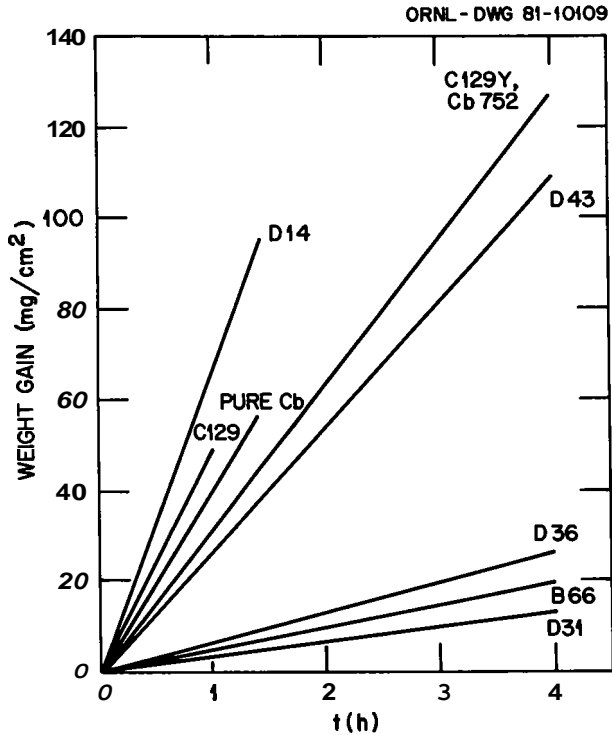


Figure 7 - Oxidation Resistance of Fabricable and Weldable Nb Alloys are not Significantly Better than Unalloyed Nb (from Metcalfe (10)).

Table II. Coating Application Techniques (from Krier (11))

<u>Plating from Liquids</u>	<u>Chemical Deposition</u>
Electroplating Electrophoretic	Vapor Plating Pack cementation Exothermic reaction
<u>Hot Spraying</u>	<u>Other</u>
Flame spraying Detonation Plasma	Vacuum metallizing Cladding Hot dipping Slurry paint

The slurry method consists of painting or dipping the article to be coated with a powder suspension of the coating, drying, then sintering/diffusing it into the substrate. This process provides precise control over the coating composition if prealloyed alloyed powders are used, can be conducted in standard furnaces with an inert cover gas, and is adaptable to repairing defects.

Chemical and structural compatibility of coatings and substrates

Coatings based on silicides or aluminides usually contain microcracks formed during cooling below or heating above the coating temperature due to thermal expansion mismatch. One approach to minimizing the cracking problem in coatings is to match their thermal expansivities with the substrate; however, even this falls short of that desired under conditions of rapid heating and cooling due to thermal gradients. Another coating design extensively explored is to accept the mechanical incompatibility due to thermal expansion mismatch but incorporate a repair mechanism in the coating to heal the inevitable cracks or defects. As an example, the disilicides of Mo, W, and V are very oxidation resistant but oxidize at too low a rate to heal cracks. Modifying these compounds with Ti and/or Cr improves their crack healing capacities. The stable phases in multicomponent coatings unfortunately change with temperature and leads to another variation of mechanical incompatibility called "pecking." Briefly, this is a phenomena characterized by accelerated oxidation rates at intermediate temperatures. As an example,  $\text{MoSi}_2$  is exceptionally oxidation resistant at 1371 C (2500 F) by oxidizing to form a continuous film of  $\text{SiO}_2$ ; however, this compound exhibits pest failure at about 704 C (1300 F) due to the formation of molybdenum oxides in addition to  $\text{SiO}_2$ . The failure is caused by the mechanical stresses generated by thermal expansion mismatch in the surface reaction products (12). Boron additions to the disilicides reduces the stresses by forming glassy phases with the  $\text{SiO}_2$ .

Finally, the thermal expansion mismatch problem was approached by devising a system whereby the stresses in the coating would be relaxed by a reservoir which formed a liquid phase at temperature and was also ductile at room temperature. Typical examples are Sn-Al and Ag-Al-Si which are equal in oxidation resistance to the disilicides. At high temperatures, the Al and Si in the coating form oxidation resistant oxides over liquid phases enriched with Sn or Ag (10). These coatings resist thermal cycle failure but vaporize the liquid phase component at reduced pressures and high temperatures and rapidly debond under hypervelocity gases due to aerodynamic shear.

Chemical incompatibility is the other major cause of failure in coated systems. Reactions between the coating and substrate reduce the load-carrying ability of the substrate by reducing its thickness and/or by removing critical strengthening elements. At the same time the coating-substrate and the coating-environment reactions increase the failure probability by changing the coating to a less oxidation-resistant composition. Whatever the coating composition, niobium will be one of the components due to its diffusion from the substrate alloy. Thus, serviceable coatings must be tolerant of niobium.  $NbSi_2$  and  $Nb_5Si_3$  are not oxidation resistant; however, when combined with Ti-Mo, Ti-W, V-Cr, or Ti-Cr have oxidation rates comparable to the disilicides of Mo, W, and V.

A survey of coatings developed by industry therefore shows that they are not simple formulations but are basically silicides or aluminides modified by one or more specific elements to improve their mechanical and chemical compatibility with the substrate alloy. The specific composition of the coatings depends on the niobium alloy to be coated and is generally proprietary, however, analysis of forty-five different coatings shows that silicon, aluminum, chromium, and titanium are the principal elements (Figure 8). A sectional view of a typical coated alloy representing the current technology subjected to the anticipated service condition has been found to consist of microcracks and three principal zones depicted by Figure 9. The thin outer oxide is the primary oxygen barrier which formed on oxidizing the disilicide coating. A secondary oxygen barrier is the coating itself whose function is to supply a reservoir of elements that repair the primary oxide when damaged. The diffusion zone results from the reaction of the coating with the alloy. Coating thicknesses of about 0.076 mm (0.003-in.) are applied but increase somewhat during service.

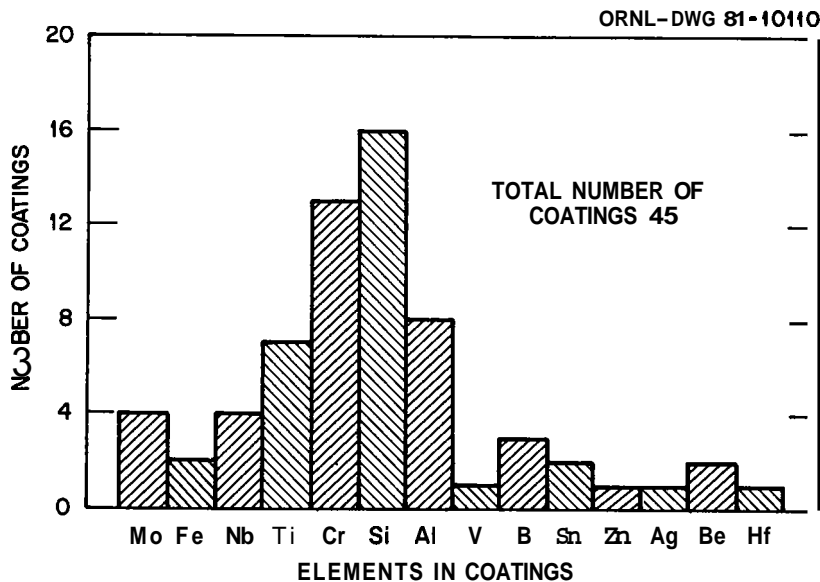


Figure 8 - Histogram of 45-Coatings Developed for the Protection of Nb Alloys from Cyclic Oxidation to 2500 F Show Strong Preference for Ti, Cr, Al, and Si (from Krier (9)).

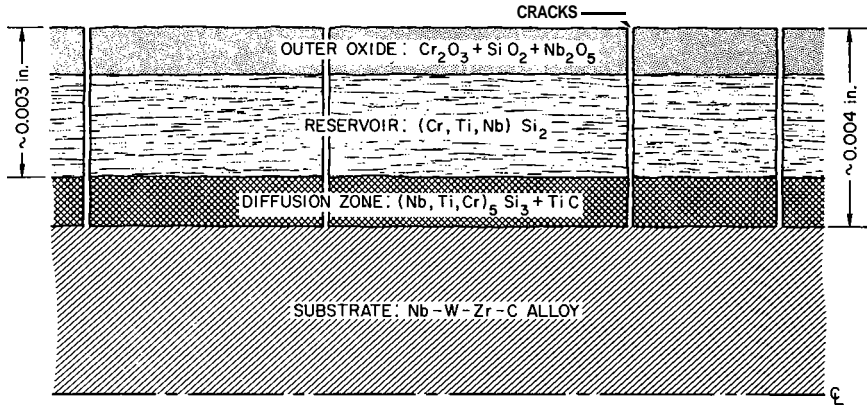


Figure 9 - Schematic of a Disilicide Coated D43 (Nb-10 W-1 Zr-0.1 C) that Formed Three Zones During Cyclic Oxidation. Cracks are caused by thermal expansion mismatch between coating and substrate (from Metcalfe (10)).

### Performance of Niobium Alloys at High Temperatures

#### Uncoated niobium alloys

The mechanical properties of niobium alloys are impaired when they absorb trace levels of active gases from the environment in which they are heated. As an example, the ductility of C-103 (Nb-10 Hf-1 Ti-0.7 Zr) is progressively reduced in the manner shown in Figure 10 as it absorbs oxygen and carbon from CO at pressures of  $10^{-10}$  kg/mm<sup>2</sup> ( $10^{-7}$  psi). The separate curves for each reaction temperature are caused by differences in the internal reactions between the absorbed gases and the Hf, Ti, and Zr in the alloy.

In addition to severe embrittlement, gas absorption significantly lowers the creep strength of niobium alloys. Under hard vacuum conditions where gas absorption does not occur  $10^{-13}$  kg/mm<sup>2</sup> (e.g.,  $10^{-10}$  psi), the creep rupture life of C-103 would be several thousand hours; however, in the presence of only  $10^{-10}$  kg/mm<sup>2</sup> ( $10^{-7}$  psi) of H<sub>2</sub>O, rupture occurs in a fraction of the expected life (see Figure 11). It has been determined that the creep acceleration is caused by the generation of large internal stresses as the alloy absorbs oxygen from the H<sub>2</sub>O (13).

Thus, uncoated niobium alloys would be restricted at high temperatures to systems where gross gas metal reactions are inhibited by using closed cycle systems such as exemplified by either the Rankine or Brayton system. Even this design feature does not guarantee freedom from problems because hot structures degas, components decompose, and complex structures may lead to raise impurity gas levels over the estimated ideal level of  $10^{-13}$  kg/mm<sup>2</sup> ( $\sim 10^{-10}$  psi). It has been suggested that getters would resolve this problem; however, their practicality has not been demonstrated.

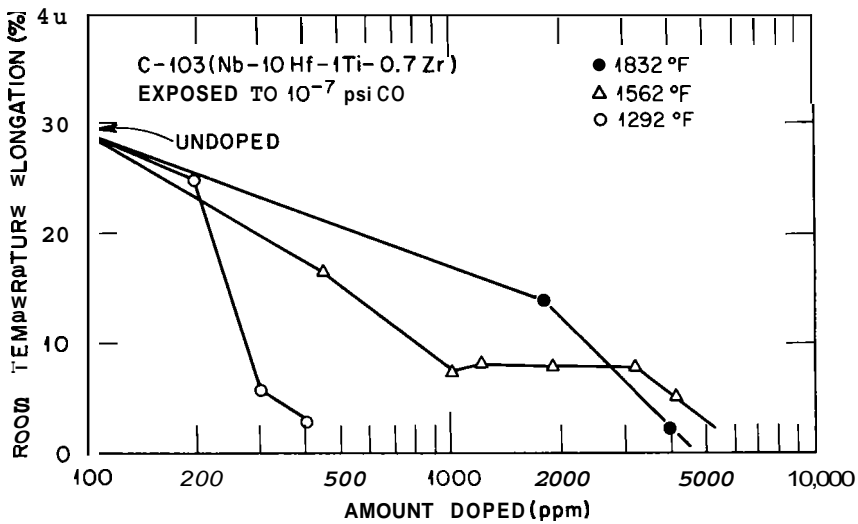


Figure 10 - Doping with Carbon and Oxygen (CO) Embrittles C-103 (Nb-10 Hf-1 Ti-0.7 Zr). Effect of dopants depends on their state in the alloy and thus varies with reaction temperature and amount doped (from Liu and Inouye (13)).

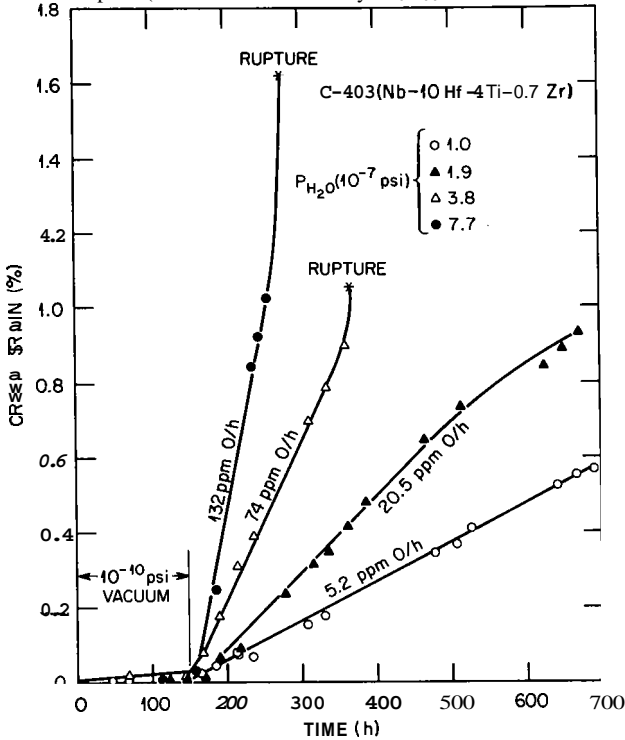


Figure 11 - C-103 (Nb-10 Hf-1 Ti-0.7 Zr) Absorbs Oxygen from  $H_2O$ . The oxidation reaction at 1600 F generates high internal stresses and when superimposed on a creep stress accelerates creep rates and promotes early failure (from Liu and Inouye (13)).

Procedures and techniques for evaluating coated alloys are not standardized; consequently, comparison of results from different organizations are difficult and are considered to be misleading. Detailed accounts of test results, however, show that certain properties or effects such as those described below are common to all systems and in many cases limit the application or the design of a structure.

Figure 12 compares the mechanical properties of a coated alloy under compressive and tensile loading (10). The upper curve in Figure 12(b) reflects the compression behavior and represents the closing of hairline cracks in the silicide coating. In tension the pre-existing cracks eliminate any strength contribution from the coating so that the strength is equal to the uncoated alloy in either compression or tension. The difference between the upper and lower curves represents the compressive strength of the coating (Figure 12(a)),

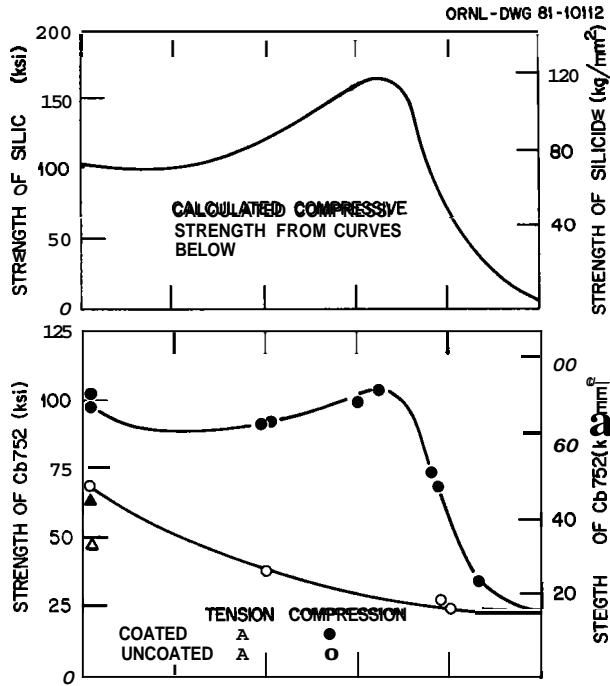


Figure 12(a) - Compressive Strength of Silicide Coating; (b). The Ultimate Strength of Silicide Coated Cb752 (Nb-10 W-2.5 Zr-.004C) is Greater in Compression than in Tension Due to Microcracks in the Coating (from Metcalfe (10)).



The room temperature yield strength of coated alloys is about 70-90 percent of the uncoated specimens due to the reductions in substrate thickness during the coating process. On the other hand, the ductility is markedly lowered because plastic deformation is localized at the roots of hairline cracks. Figure 13 shows the effects of coating heat treatment and oxidation exposure on the bend transition temperature of a coated alloy (14). The increase in the transition temperature is attributed to the presence of coating cracks, oxygen contamination at coating defects, and grain growth in the substrate.

Silicide coatings lose weight in the manner shown in Figure 14 when heated to high temperatures and low pressures. At  $10^{-7}$  kg/mm<sup>2</sup> ( $10^{-4}$  psi) the chromium and silicon in the coating vaporize leaving Nb<sub>2</sub>O<sub>5</sub> as the surface oxide. At a higher pressure of  $10^{-6}$  kg/mm<sup>2</sup> ( $10^{-3}$  psi), the external oxides are NbCrO<sub>4</sub> and Nb<sub>2</sub>O<sub>5</sub>. Not until the pressures exceed  $10^{-5}$  kg/mm<sup>2</sup> ( $10^{-2}$  psi) do the oxidation resistant oxides SiO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> form (15). These surface losses lower the emissivity of the coating to 0.5-0.6 from about 0.8 and promote coating failure by increasing the surface temperatures in re-entry vehicles above that shown in Figure 3.

Two reactions occur at the coating-substrate interface. First, the reservoir, usually consisting of disilicides, is consumed by its reaction with the substrate to form silicides of the M<sub>5</sub>Si<sub>3</sub> type with lower oxidation resistance. The conversion does not compromise the protective capacity of the coating if the coating contains Ti and Cr modifiers. Decarburization of the alloy by the titanium in the coating (16) is the second reaction and results in a significant reduction in the creep and yield strengths of the substrate as shown in Figure 15 and 16, respectively. The reaction rate of this "interstitial sink" effect is controlled by the diffusion of zirconium from the carbide phase in the alloy into the niobium alloy matrix. The process occurs when the titanium content in the coating exceeds about 10 percent and is reduced by vanadium additions to the coating.

### Reliability and Defects in Coated Alloys

Statistical procedures are vital aspects of establishing the reliability of protective coatings for refractory alloys, and has been quite effective in determining the effects of coating thickness, coating heat treatments, and substrate preparation on performance. Such work has conclusively shown that a coating system (i.e., the coating and substrate) optimized for one thermal environment does not perform equally well under a different thermal environment. As expected, the performance data from small laboratory type specimens cannot be extrapolated to actual service conditions or to hardware of large dimensions.

Reviews of well-established commercial practices indicate that the attainment of good coating adhesion is not a science but is an art; however, recent findings show that strong chemical bonds develop between the coating and substrate only when the coating contained the ion of the metal in the substrate. While NDE methods such as eddy current and thermoelectric measurements have been useful in determining coating thicknesses and uniformity during manufacture, visual examination has been relied on to detect coating breakdown after oxidation exposure. While the latter inspection technique can be readily accomplished on external surfaces, the detection of defects on internal surfaces require the removal of the component from the substructure to which they are attached for inspection and possible repair. The design of coated panels in Figure 1(c) is based on this restriction.

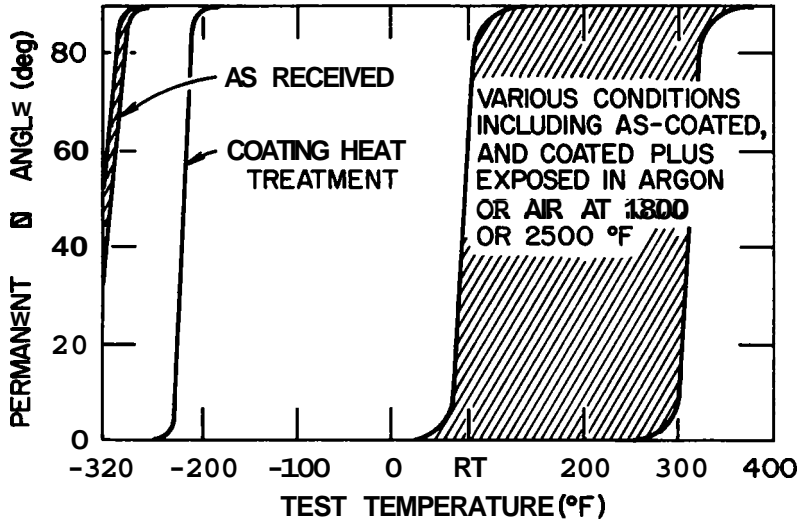


Figure 13 - The Bend Transition Temperature of B-66 (Nb-5 Mo-5V-1 Zr-.006C) Increases with Grain Size, Coating-Substrate, Reactions, and Oxygen Contamination when Subjected to Coating Process and Cyclic Oxidation Exposures (from Gibeaut (4)).

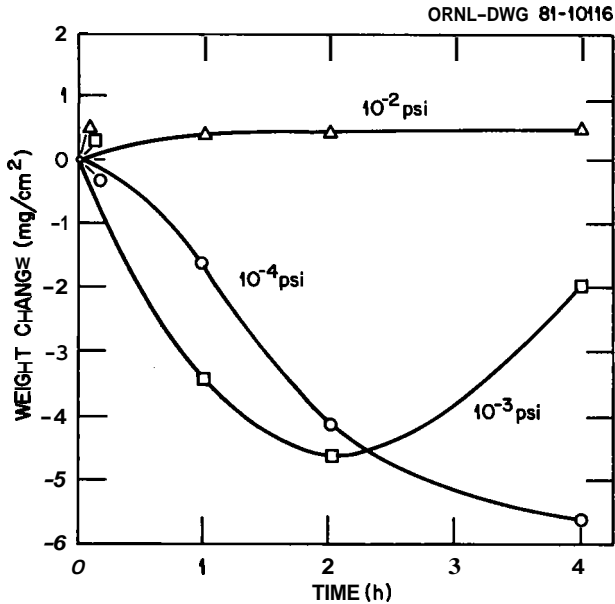


Figure 14 - A Si-25 Cr-5 Ti Coating Oxidized at 10<sup>-4</sup> or 10<sup>-3</sup> psi and 2500 F (1371 C) in Air Loses Weight Due to Vaporization of Si and Cr. SiO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> form in 10<sup>-2</sup> psi Air (from Priceman (15)).

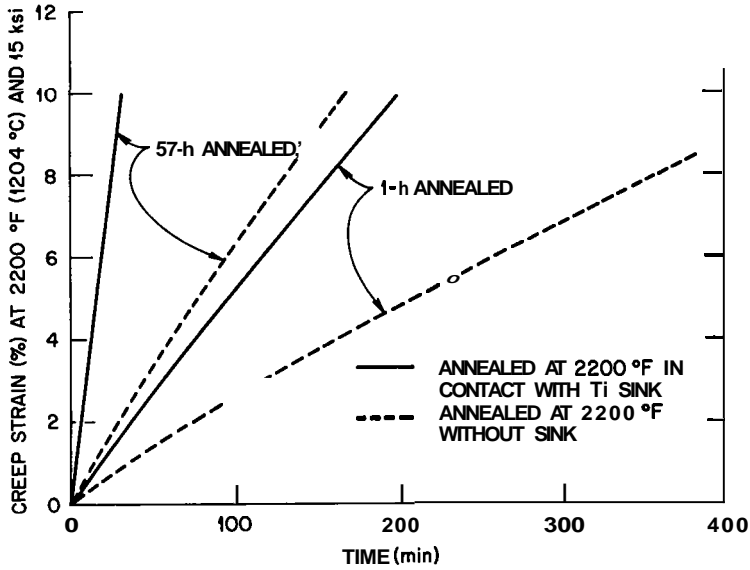


Figure 15 - The Interstitial Sink Effect (i.e., Decarburization) Occurs when D-43 (Nb-10W-1 Zr-0.1C) is Annealed in Contact with a Coating Containing More Than 10%Ti. The reaction reduces the creep strength of the alloy (from Brentnall (16)).

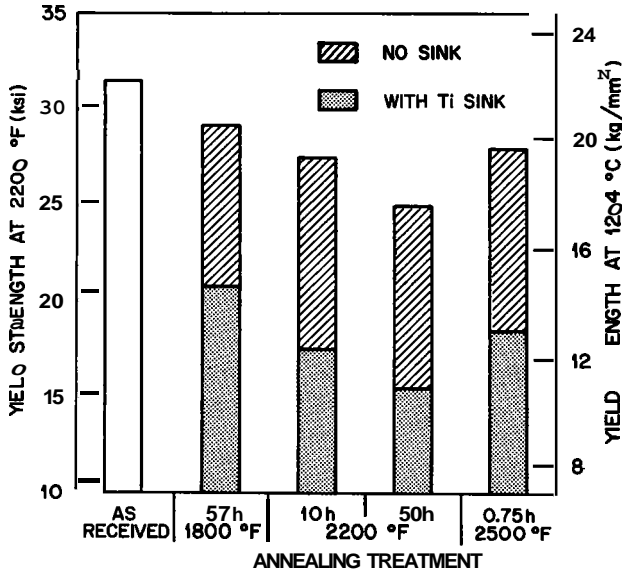


Figure 16 - The Interstitial Sink Effect Reduces the Yield Strength of D-43 (from Brentnall (16)).

Defects occur under conditions of physical and chemical cleanliness and is a constant source of trouble on the edges of coated sheet. This problem has been minimized by applying a second coating using a slurry paint technique to beveled edges. Defect growth rates of the order of  $2.5 \times 10^{-3}$  mm/min ( $10^{-4}$  in./min) have been measured at the maximum projected use temperatures of 1250-1300 C (2282-2372 F) but abruptly increase to  $2.5 \times 10^{-2}$  mm/min ( $10^{-3}$  in./min) at 1350 C (2462 F) (2). A larger area consisting of an oxygen contaminated zone encircles the defects. Specimens containing intentional defects after cyclic oxidation exposures to re-entry conditions similar to that shown in Figure 3 retain a significant fraction of their initial tensile strength and limited ductility as shown in Figure 17. Severely damaged sites such as punctures survived numerous additional cyclic exposures after being field repaired. Catastrophic failures characteristic of coated molybdenum are thus not observed in coated niobium alloys.

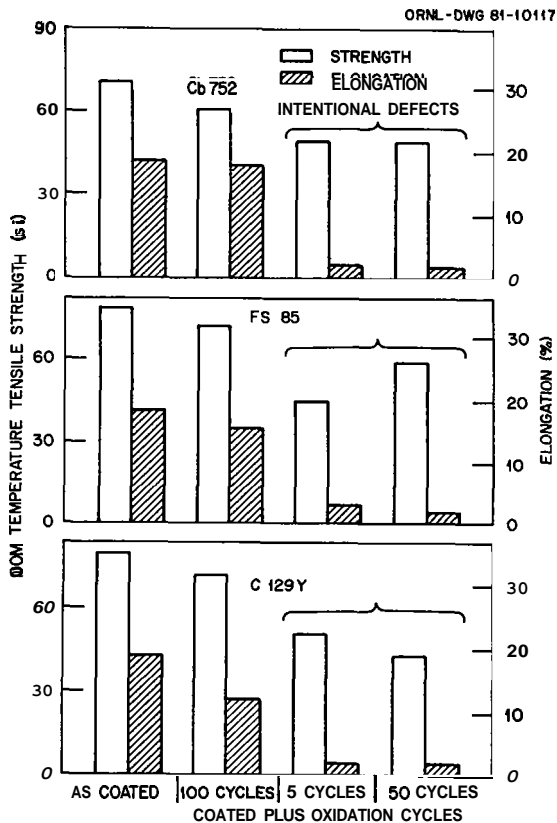


Figure 17 - The Tensile Strength of Defected Silicide Coated Nb Alloys are Modestly Lower than Defect-Free Coated Alloys. Oxygen contamination of zone encircling defects embrittles alloys. Defect diameters are about 12 percent of gage width (from Levine (2)).

## Summary and Conclusions

Niobium alloys have potential applications under two radically different conditions to temperatures of 1315 C -2400 F. In the uncoated state they could contain the working fluid in the Rankine or Brayton cycle systems but require an environment essentially free of reactive gases. When they are protected from oxidation with coatings, they have the potential of being used as rocket nozzle parts or the protective skin of glide re-entry vehicles to dissipate the aerodynamic heat generated at the surfaces. Since these applications require complex structures, the alloys need to be readily fabricable and weldable. The state of the technology, while it does not have the benefit of extensive practical experience, is now developed well enough to arrive at the following technical limitations and general conclusions.

Uncoated niobium alloys are embrittled and their creep strength reduced when they absorb trace levels of oxidizing gases from the environment in which they are heated. The extent of the impairment of their ductility and strength closely parallels the amount absorbed and absorption rate, respectively. Thus, the life of an uncoated component is expected to be strongly dependent on the  $P_{O_2}$  in the environment since the reaction rates show a strong pressure dependence. Deleterious environmental effects on mechanical properties have not been detected at  $P_{O_2}$  levels of about  $10^{-14}$  kg/mm<sup>2</sup> ( $10^{-10}$  psi) but are severe at  $10^{-10}$  kg/mm<sup>2</sup> ( $10^{-7}$  psi).

Niobium alloys are not oxidation resistant and therefore require coatings when the application subjects them to strongly oxidizing environments. For cyclic oxidation protection, coatability, and reliability, complex silicide coatings containing chromium, titanium, and silicon as the principal elements applied by a slurry paint technique have been found to be optimum. Coated systems, however, degrade due to mechanical incompatibility promoted by the thermal expansion mismatch between the coating and substrate and also by the chemical incompatibility which results from the reactions of the coating with the environment and the substrate. Coating defects have been concluded to be inevitable; however, they do not cause catastrophic failure in components designed for the Space Shuttle Orbiter.

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