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Study of the Potential Use of Carburized Niobium in Plutonium Processing

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Abstract

Carburized refractory metals, especially tantalum, have been shown to possess properties useful for application as hardware in the plutonium-processing environment. These applications are driven in part by a desire to minimize the production of radioactively contaminated waste. The current use of ceramics as containment materials for Pu processing are not ideal due to the short service life of the hardware, placing an additional burden on the contaminated waste stream. Carburized niobium has been examined for use as an improved hardware material. The Nb-C system is analogous to the previously studied Ta-C system. The low density of niobium relative to tantalum will improve the ergonomics of the glovebox environment. The choice of the Nb-C system will be supported by a thermodynamic and kinetic analysis. Preliminary results of the processing investigation also will be presented.

Introduction

The plutonium processing environment has been shown to be extremely corrosive to traditional pyrometallurgical processing hardware materials. The service environment includes repeated exposure to high temperatures, liquid metals, molten salts, and corrosive gasses. Metals typically fail through accelerated grain boundary attack of the liquid plutonium before their bulk solubility in $Pu_{(L)}$ is reached. Ceramics either are reduced by the liquid metal or are broken through thermal stresses. Fixtures and crucibles must be discarded after only a short time in service, placing a considerable burden on the radioactive contaminated waste stream that then must be disposed of at great cost.

The primary objective of this study is to develop a hardware material that is physically robust and chemically inert with respect to the service environment. It is desired that the corrosion resistant character be distributed throughout the bulk of the material. Coatings can be unsatisfactory in these applications because a small uniform thickness reduction through corrosion or any surface damage would expose the unprotected substrate, leading to a catastrophic failure. An approach based on thermodynamics was used to select the niobium-carbon system as a candidate. Computer modeling of the process environment was performed first to indicate the potential inert character of the Nb-C system. Coupons of niobium then were carburized under

low pressure in a packed carbon bed to achieve the desired extent of carbon saturation. Scanning Electron Microscopy was used to evaluate the developed microstructures.

Background and Theory

Previous studies have shown the tantalum-carbon system to be a successful substitute material [1]. After carburization and subsequent aging there is an extensive network of carbide precipitates at the tantalum grain boundaries. These grain boundary precipitates were shown to effectively stop the penetration of liquid plutonium along the grain boundaries. Niobium has physical and chemical properties similar to those of tantalum, as is suggested by their relative positions in the periodic table. One suspects that the niobium-carbon system also will have similar beneficial properties in the plutonium processing environment.

Nb-C System

A series of carbide layers will form at the niobium surface while the bulk of the material increases in carbon concentration during carburization. The two carbide phases examined in this study are Nb_2C and NbC .

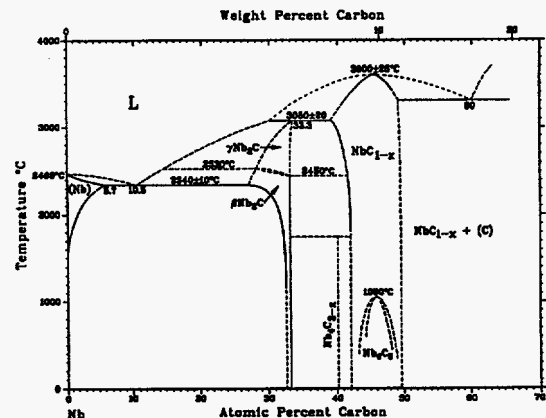


Figure 1. Niobium-carbon phase diagram

Carbon has very little solubility in niobium at room temperature. However, it is seen in Figure 1 that the solubility increases to 5.7 atomic % at the Nb-rich eutectic temperature of 2340°C. The high temperature solid solubility limit of carbon in niobium, C_s (at. %), has been determined to be valid for 1500°C < T < 2200°C [2]:

$$C_s = 4190 \cdot \exp\left(\frac{-17200}{T}\right)$$

Upon cooling, the niobium is supersaturated with carbon that precipitates as Nb_2C on the grain boundaries and within the grains. The cooling and subsequent precipitation produce the grain boundary carbides desired for improved corrosion resistance.

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Chemical Stability of Nb-C system in Pu environment

Comparing the standard Gibbs free energies of formation for potential interfering species can help predict which phases will be present in a system at equilibrium. Note that in Figure 2 the niobium carbides have lower free energies of formation and therefore Pu will not react with the niobium carbides.

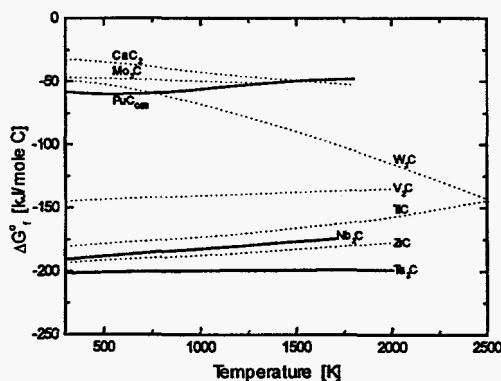


Figure 2. Standard Gibbs free energies of formation for various carbides normalized to 1 mol carbon.

Thermodynamic Simulations

The thermodynamic modeling package MTDATA, obtained from the National Physical Laboratory, Teddington, UK, was used to calculate the equilibrium phases distributions in complex heterogeneous systems. An analysis was made of this system under an $Ar_{(g)}/Cl_{2(g)}$ mixture. A 'typical' argon feed was simulated as 10 PPM each of $H_2O_{(g)}$, $O_{2(g)}$, and $N_{2(g)}$. Table 1 shows the results of the simulation. In neither case were the Nb_2C or Nb predicted to react with the ambient or the liquid plutonium.

Table 1. MTDATA results @ 1000K, 0.101325 MPa

Input Species	[mol]	Equilibrium Species	[mol]
n(Pu)	10.000	n(Pu)	9.3329
n(Nb)	1.0000	n(Nb)	1.0000
n(Nb_2C)	0.1000	n(Nb_2C)	0.1000
n($H_2O_{(g)}$)	0.0001	n($H_{2(g)}$)	0.0001
n($O_{2(g)}$)	0.0001	n($PuOCl$)	0.0003
n($N_{2(g)}$)	0.0001	n(PuN)	0.0002
n($Cl_{2(g)}$)	2.0000	n($PuCl_3$)	0.6667
n($Ar_{(g)}$)	10.000	n($Ar_{(g)}$)	10.000

Experimental Procedure

Niobium coupons 1.500" dia. x 0.060" thick were cut by EDM from annealed rod stock and a 32 rms finish was applied to each face. They were carburized to equivalent saturation conditions at various temperatures between 1400°C and 1700°C. The cooling rate from 1700°C to 1500°C was 100K/min. Each coupon was sectioned with a low speed diamond wafering blade and mechanically

polished through 1 μm alumina. Niobium carbides were resolved by secondary electron imaging in the scanning electron microscope through differential polishing effects. The size, distribution, and orientation of the carbide precipitates then could be determined. Figure 3 shows a metallographic cross section of a niobium coupon obtained in this manner. Note that in the case of Figure 3, the grain boundaries were not entirely decorated with the large carbides.

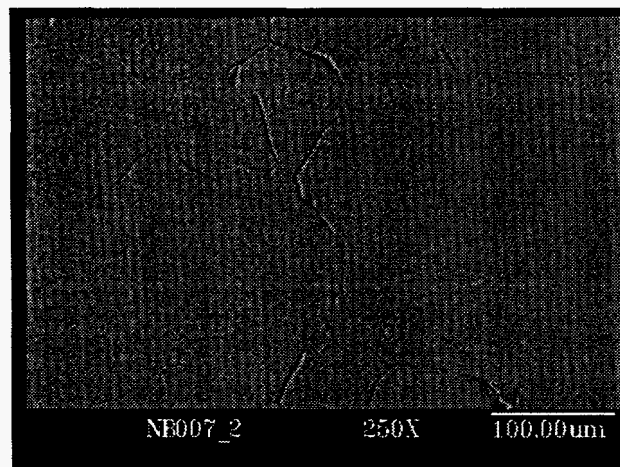


Figure 3. SEI image of a niobium coupon carburized 7.51 hours at 1400°C.

Conclusion

A systematic approach to materials selection for use in the corrosive plutonium processing environment has been shown. The utilization of both simple chemical thermodynamics and complex computer simulations can efficiently narrow the search for successful material selection. Time and effort in the laboratory devoted towards exposure tests and corrosion evaluation then can be reduced.

Future Work

Further analysis must be done to fully quantify the development of the carbide microstructure. Tests involving long term to the service environment will be run to determine the stability of the system. Tests will also be performed on the various carbide surfaces to evaluate the wettability of liquid Pu. If the preceding test are successful, an attempt will be made to fabricate, carburize, and test niobium hardware in the plutonium processing environment.

References

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2. G. Horz, K. Lindenmaier, and R. Klass, *J. Less Common Metals*, vol. 35, pp. 97, 1974