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MASS-TRANSFER EFFECTS IN SOME
REFRACTORY-METAL-ALKALI-METAL-
STAINLESS STEEL SYSTEMS

J. R. DiStefano

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MASS-TRANSFER EFFECTS IN SOME REFRACTORY-METAL-ALKALI-
METAL-STAINLESS STEEL SYSTEMS

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
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FOREWORD

This report describes the results of compatibility tests completed during the period 1958 to 1961 to evaluate the behavior of niobium and stainless steels in contact with sodium. The studies were conducted as part of the Aircraft Nuclear Propulsion Project at the Oak Ridge National Laboratory and were reported in classified ANP progress reports for the appropriate periods. More recent interest in the problem of dissimilar-metal effects between Nb-1% Zr and stainless steel has arisen in conjunction with several high-temperature liquid-metal reactor concepts, including SNAP-50, some versions of SNAP-8, and liquid-metal fast breeder reactors. Therefore, we feel that test results from the (Nb-1% Zr)-Na(NaK)-stainless steel system, although obtained several years ago, are still pertinent and should be more compactly reported.

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MASS-TRANSFER EFFECTS IN SOME REFRACTORY-METAL-ALKALI-METAL-STAINLESS STEEL SYSTEMS

J. R. DiStefano

ABSTRACT

Dissimilar-metal interactions between niobium or Nb-1% Zr and type 316 or 318 stainless steel in sodium or NaK were investigated in static capsules at temperatures from 816 to 982°C. The principal interaction was the transfer of carbon and nitrogen from the stainless steel to the niobium or niobium alloy. Complex carbide-nitride layers formed on the surface of the niobium, and nitrogen but not carbon diffused appreciably into the niobium. The subsurface nitrogen pickup greatly increased tensile strength and decreased ductility. The amount of carbon and nitrogen transfer depended on temperature, exposure time, and ratio of surface areas of the dissimilar metals. The transfer was independent of stress and occurred to the same extent with types 316 and 318 stainless steels.

INTRODUCTION

The diverse requirements encountered in the design of nuclear reactors often are best satisfied by a synthesis of engineering materials rather than by a single material of construction. Where such systems employ a liquid-metal coolant, however, not only must each material be compatible with the liquid metal, but corrosive effects that occur as a result of interactions between the dissimilar materials must also be limited. It has long been known that elements of unlike alloys in contact with the same liquid metal will tend to interchange until the differences in chemical potential around the system have been eliminated. This type of interaction is known as dissimilar-alloy mass transfer and is illustrated schematically in Fig. 1. Note that this form of mass transfer can occur whether or not a temperature gradient exists in the system.

The refractory metals and their alloys are uniquely suited to the design requirements of high-temperature nuclear reactors, particularly

Fig. 1. Schematic Illustration of Steps in Dissimilar-Alloy Mass Transfer.

with regard to nuclear and mechanical properties and corrosion resistance to alkali metals. Although susceptible to air oxidation at elevated temperatures, refractory metals are nonetheless attractive in applications involving contact only with alkali metals, such as use as a fuel element cladding. In areas where oxidation resistance is a major requirement, a container material such as stainless steel is preferred. Accordingly, the present studies were initiated to examine possible dissimilar-alloy mass-transfer effects in systems of niobium or Nb-1% Zr with sodium or NaK and type 316 or 318 stainless steel under isothermal test conditions.

EXPERIMENTAL PROCEDURE AND MATERIALS

In these studies, static capsules of stainless steel contained sheet specimens of either niobium or Nb-1% Zr and of type 316 stainless steel. The test system is illustrated schematically in Fig. 2, and an exploded view of the capsule and specimens is shown in Fig. 3. Tests conducted initially to study temperature and surface area effects used sodium as the test environment. The specimen dimensions, pretest heat treatment, surface area ratios, and temperatures for these tests are listed in Table 1.

Fig. 2. Schematic of Dissimilar-Metal Test System.

Fig. 3. Components of Dissimilar-Alloy Test System.

Table 1. Summary of Conditions for Dissimilar-Alloy Mass-Transfer Tests of Niobium and Type 316 Stainless Steel with Sodium

Test	Specimens			Pretest Condition	Surface Ratio ^a	Test Temperature (°C)	Test Duration (hr)	Sodium Volume (cm ³)
	Number	Material	Size, in.					
1529	1	Niobium	0.040 × 3.25 × 0.54	Annealed 1 hr at 1100°C	13.5	927	1000	331
	1	316 stain-less steel	0.064 × 3.25 × 0.54	Stress relieved at 950°C				
1561	1	Niobium	0.040 × 3.25 × 0.74	Annealed 1 hr at 1100°C	10.1	871	1000	179
	1	316 stain-less steel	0.063 × 3.25 × 0.50	Stress relieved at 950°C				
1562	1	Niobium	0.040 × 3.25 × 0.74	Annealed 1 hr at 1100°C	10	927	900	179
	1	316 stain-less steel	0.063 × 3.25 × 0.50	Stress relieved at 950°C				
1563	1	Niobium	0.040 × 3.00 × 0.75	Annealed 1 hr at 1100°C	0.1	927	1000	80
	1	316 stain-less steel	0.030 × 3.00 × 0.50	Cold rolled 50%				
1914	1	Niobium	0.041 × 0.75 × 0.62	Annealed 2 hr at 1600°C	10	816	500	34
1915	1	Niobium	0.041 × 0.70 × 0.62	Annealed 2 hr at 1600°C	10	871	500	34
1916	1	Niobium	0.041 × 0.72 × 0.62	Annealed 2 hr at 1600°C	10	927	500	34
1917	1	Niobium	0.041 × 0.72 × 0.62	Annealed 2 hr at 1600°C	10	982	500	34

^aRatio of areas of stainless steel to niobium.

A subsequent series of tests was conducted to evaluate mass-transfer effects on mechanical properties and used NaK in place of sodium. Conditions for these latter tests are shown in Table 2.

Both sodium and NaK (44% Na-56% K) were purchased as "high-purity" grades. We further purified the sodium by cold trapping at 260°C and the NaK by cold trapping at 260°C followed by titanium gettering at 760°C. Analyses of the liquid metal before and after the purification treatments are given in Table 3. The oxygen content was lowered to a value of 20 ppm in both the sodium and NaK, as determined by the amalgamation method.

The extent of dissimilar-alloy interactions in these tests was determined from changes in specimen weight, composition, and mechanical properties. Both the test specimens and capsule were examined metallographically, and x-ray and anodic staining techniques were used to identify corrosion-product phases.

RESULTS OF SODIUM CAPSULE TESTS

Changes in Weight, Composition, and Microstructure

The first dissimilar-metal test, 1529, contained niobium and type 316 stainless steel and was operated with sodium for 1000 hr at 927°C. The weight and composition changes are summarized in Table 4. The niobium specimen, which gained 0.110 g, showed an uptake of oxygen, nitrogen, carbon, and nickel. The niobium wire used in the test showed similar composition changes and even greater increases in nitrogen and carbon. The appearance of the niobium specimen is shown in Fig. 4. An outer scaly film was scraped off and spectrographically analyzed. The major constituent was niobium, but lesser amounts of chromium and nickel were also found. Below the outer film were more adherent sublayers, which were identified by x-ray analysis as mixtures of niobium carbides and nitrides (NbC and Nb₂N were tentatively identified). The microscopic appearance of the niobium before and after test is shown in Fig. 5. Two distinct layers, both extremely hard and brittle, were present after test. The outer layer was lighter in color than the inner layer and had a hardness of 1651 DPH, compared with 2073 DPH for the inner layer.

Table 2. Summary of Conditions for Dissimilar-Alloy Mass-Transfer Tests with NaK

Test	Container Alloy	Specimens			Pretest Condition	Surface Ratio ^a	Test Temperature (°C)	Test Duration (hr)	NaK Volume (cm ³)
		Number	Material	Size, in.					
1696	316 stainless steel	3	Niobium	0.040 × 5.00 × 0.62 ^b	Annealed 2 hr at 1600°C	6.5	927	500	550
		3	Nb-1% Zr	0.040 × 5.00 × 0.62 ^b	Annealed 2 hr at 1600°C				
		3	316 stainless steel	0.040 × 5.00 × 0.62 ^b	Annealed 1 hr at 1100°C				
1697	318 stainless steel	3	Niobium	0.040 × 5.00 × 0.62 ^b	Annealed 2 hr at 1600°C	6.5	927	500	550
		3	Nb-1% Zr	0.040 × 5.00 × 0.62 ^b	Annealed 2 hr at 1600°C				
		3	318 stainless steel	0.040 × 5.00 × 0.62 ^b	Annealed 1 hr at 1100°C				
1713	316 stainless steel	3	Niobium	0.040 × 5.00 × 0.62 ^b	Annealed 2 hr at 1600°C	20	982	500	415
		3	Nb-1% Zr	0.040 × 5.00 × 0.62 ^b	Annealed 2 hr at 1600°C				
		3	316 stainless steel	0.040 × 5.00 × 0.62 ^b	Annealed 1 hr at 1100°C				
1815	316 stainless steel	4	Nb-1% Zr	0.040 × 5.00 × 0.62 ^b	Annealed 2 hr at 1600°C	11	927	500	450
1854	316 stainless steel	1	Niobium	0.3 diam × 5.00 long	Annealed 2 hr at 1600°C				
		1	Niobium	0.4 diam × 5.00 long	Annealed 2 hr at 1600°C	10	927	500	
1857	316 stainless steel	6	Nb-1% Zr	0.040 × 5.00 × 0.62 ^b	Annealed 2 hr at 1200°C				

^aRatio of areas of stainless steel to niobium.^bOverall dimensions of tensile specimens having gage width of 0.25 in. and gage length of 2.00 in. (See Fig. 2.)

Table 3. Analysis of Sodium and NaK

Element	Concentration, ppm		
	As Received	After Cold Trapping ^a	After Gettering ^b
<u>Sodium</u>			
Lithium	17	<1	
Potassium	600	190	
Magnesium	20	<1	
Calcium	200	<10	
Aluminum	<10	<7	
Iron	<20	<10	
Nitrogen	<10	<8	
Oxygen ^c	20	20	
<u>NaK</u>			
Oxygen ^c	115	60	20
Nitrogen	<10	<10	<10

^aAt 260°C.^bWith titanium sponge for 200 hr at 760°C.^cAnalyzed by amalgamation technique.

Anodic staining¹ was also used to distinguish between the layers. This technique is based on the principle that the anodic oxide film on niobium produces interference colors that depend upon the composition of the phases within the niobium specimen. The outer layer compared closely in color with that obtained by anodizing NbC and the inner layer with anodized Nb₂N. However, some Nb₂N also appeared to be intermixed with the NbC on the outer layer.

The type 316 stainless steel specimen showed a very slight weight increase (Table 4). This increase was accompanied by an increase in

¹R. S. Crouse, Identification of Carbides, Nitrides, and Oxides of Niobium and Niobium Alloys by Anodic Staining, ORNL-3821 (July 1965).

Table 4. Weight and Composition Changes in Niobium and Type 316 Stainless Steel Exposed Together to Sodium^a

Sample	Thickness (in.)	Weight (g)	Chemical Analysis, ppm						
			Oxygen	Nitrogen	Carbon	Iron	Nickel	Chromium	Niobium
Niobium Sheet	0.040								
Before		9.7941	60	45	7	1000	60	200	
After		9.9044	490	1300	330	800	200	140	
Niobium Wire	0.035								
Before			490	310	140	1300	75	60	
After			670	3350	2140	600	240	115	
Stainless Steel	0.060								
Before		14.6036		500	420				50
After		14.6064		350	300				270

^aTest conditions: 927°C for 1000 hr; surface area of stainless steel 13.5 times that of niobium.

Fig. 4. Appearance of Niobium Exposed with Type 316 Stainless Steel to Sodium for 1000 hr at 927°C.

Y-28321R

Fig. 5. Microstructure of Niobium Exposed with Stainless Steel to Sodium.

niobium content and a decrease in carbon and nitrogen concentrations. Metallographically the stainless steel was unchanged from its before-test appearance.

Effect of Temperature and Exposure Time

Subsequent tests confirmed that the transfer of carbon and nitrogen from type 316 stainless steel to niobium was the principal interaction in sodium systems. Table 5 summarizes the composition changes that were found in six sodium tests in which temperature and exposure time were varied. Although the niobium did pick up oxygen in most of these tests, the amount picked up was less than in test 1529; furthermore, the scaly nonadherent layer found on the niobium specimen from test 1529 was not found in these subsequent tests. Changes in the iron, nickel and chromium contents of niobium were also smaller and more random in the latter tests.

Figure 6 shows the temperature dependence of carbon and nitrogen pickup by niobium in these tests. The increase in nitrogen concentration exceeded that of carbon at 816, 871, and 927°C; however, at 982°C there was an abrupt increase in the rate of carbon pickup and a corresponding decrease in the rate of nitrogen pickup. The appearances of the surface layers on these specimens are compared in Fig. 7. Although two layers are visible at all temperatures, the total thickness and the proportions of the layers vary with temperature. The total layer thickness increased from approximately 0.2 mil at 816°C to approximately 0.5 mil at 927 and 982°C. At 816°C the outer layer was not continuous, and the inner layer dominated the total quantity present. At 982°C the outer layer was continuous and was over half the total quantity present. The carbon uptake by the niobium is directly related to the thickness of this outer layer, in accord with previous x-ray and anodic staining results showing the outer layer to be Nb_2C .

The effect of exposure time on carbon and nitrogen pickup at 871 and 927°C is illustrated in Fig. 8. The rate of transfer of both elements decreased after 500 hr at each temperature.

Table 5. Effect of Test Temperature and Duration on Composition Changes in Niobium and Type 316 Stainless Steel Exposed Together to Sodium

Sample	Test	Test Conditions ^a		Chemical Analysis, ppm						
		Temperature (°C)	Time (hr)	Oxygen	Nitrogen	Carbon	Iron	Nickel	Chromium	Niobium
Niobium	Before			300	85	30				
	1914	816	500	420	410	250				
	1915	871	500	600	790	390				
	1916	927	500	350	910	515				
	1917	982	500	390	770	960				
Niobium	Before			160	80	30	315	<10	<20	
	1561	871	1000	300	1100	480	285	<10	<20	
	1562	927	1000	110	1400	710	585	25	75	
Stainless steel	Before				510	420				140
	1561	871	1000		350	220				250
	1562	927	1000		380	250				270

^aStainless steel surface area 10 times that of niobium.

Fig. 6. Carbon and Nitrogen Pickup by Niobium as a Function of Test Temperature During 500 hr Exposure.

Fig. 7. Effect of Temperature on the Transfer of Carbon and Nitrogen from Type 316 Stainless Steel to Niobium. Test conditions: 500 hr, stainless steel surface 10 times that of niobium, initial concentrations in niobium 30 ppm C and 80 ppm N.

Fig. 8. Effect of Exposure Time on the Pickup of Carbon and Nitrogen by Niobium at 871 and 927°C.

Effect of Surface Area Ratio

Carbon and nitrogen transfer at 927°C showed a strong dependence on the area of stainless steel surface relative to that of niobium. The extents of transfer in three 1000-hr tests in which the surface area ratio was 0.1, 10, and 13.5 are compared in Table 6. At the lowest ratio (0.1), changes of carbon and nitrogen concentrations in the niobium were relatively small. The stainless steel specimen, however, exhibited a 1-mil-thick surface layer, as shown in Fig. 9. X-ray diffraction of this layer detected Nb, Nb₂N, NbC, and Nb₄C₃, and chemical analysis of the specimen indicated 5% Nb. Increasing the surface ratio to 10 or 13.5 significantly

Table 6. Effect of Ratio of Surface Area of Type 316 Stainless Steel to that of Niobium on Carbon and Nitrogen Transfer at 927°C

Test	Material	Test Time (hr)	Surface Ratio ^a	Carbon, ppm		Nitrogen, ppm	
				Before	After	Before	After
1563	Niobium	1000	0.1	30	140	80	60
1562	Niobium	900	10	30	710	80	1400
1529	Niobium	1000	13.5	10	330	50	1300
1563	316 stainless steel	1000	0.1	450	320	530	340
1562	316 stainless steel	900	10	420	250	500	380
1529	316 stainless steel	1000	13.5	420	300	500	350

^aRatio of areas of stainless steel to niobium.

Fig. 9. Stainless Steel Specimen after 1000-hr Exposure at 927°C with Niobium Having 10 Times the Surface Area. A 1-mil-thick niobium-rich layer is seen on the surface.

increased the amount of carbon and nitrogen transferred from the stainless steel to the niobium. Furthermore, no surface layer was found on stainless steel specimens from these latter tests.

Further data on surface area effects were generated in conjunction with NaK studies on niobium and Nb-1% Zr specimens, discussed below.

Comparative Behavior of Niobium and Nb-1% Zr

Test 1587 incorporated Nb-1% Zr specimens rather than niobium and was operated with sodium for 500 hr at 927°C. Carbon and nitrogen pickup by Nb-1% Zr was in all respects similar to that by niobium in test 1916, which operated under similar conditions of time and temperature. Results for the two tests are compared in Table 7.

Table 7. Comparison of the Behavior of Niobium and Nb-1% Zr in Sodium in Contact with Type 316 Stainless Steel for 500 hr at 927°C

Test	Surface Ratio ^a	Material	Carbon, ppm		Nitrogen, ppm	
			Before	After	Before	After
1916	10	Niobium	30	515	85	910
1587	3.2	Nb-1% Zr	310	670	200	900

^aRatio of areas of stainless steel to refractory metal.

RESULTS OF NaK CAPSULE TESTS

Effect on Mechanical Properties

The mechanical properties of a refractory metal or alloy are very responsive to changes in interstitial impurities, especially nitrogen.^{2,3} Accordingly, a series of capsule tests was operated with NaK to evaluate the changes in tensile properties resulting from interstitial mass transfer. As shown in Table 2, the tensile specimens in these tests included Nb-1% Zr and type 316 stainless steel as well as niobium and type 316 stainless steel. The alloy Nb-1% Zr was selected because it is a promising

²H. E. McCoy, R. L. Stephenson, and J. R. Weir, Mechanical Properties of Some Refractory Metals and Their Alloys, ORNL-3593 (April 1964).

³H. E. McCoy and D. A. Douglas, "Effect of Various Gaseous Contaminants on the Strength and Formability of Columbium," pp. 85-118 in Columbium Metallurgy, ed. by D. L. Douglass and F. W. Kunz, Interscience Publishers, New York, 1961.

alloy for high-temperature nuclear reactor applications, and type 318 stainless steel was included because it is similar in composition to type 316 stainless steel but contains niobium as a carbon stabilizer. To separate purely thermal effects on mechanical properties from those of mass transfer, control specimens of all materials were exposed for 500 hr in argon-filled stainless steel capsules at temperatures corresponding to those of the alkali-metal-filled capsules.

Prior to exposure in either argon or NaK the niobium and Nb-1% Zr tensile specimens were heat treated for 2 hr at 1600°C to put them in a fully annealed condition (except for specimens in test 1857, which were heat treated 2 hr at 1200°C). The types 316 and 318 stainless steel specimens were pretest heat treated for 1 hr at 1150°C.

The effect of stainless steel composition on the mechanical properties of niobium and Nb-1% Zr can be seen from comparisons of tests 1696 and 1697, both of which operated at 927°C. Chemical analyses and mechanical properties of specimens from both tests are shown in Table 8. The Nb-1% Zr specimens picked up nitrogen and carbon from each stainless steel to approximately the same degree as did niobium. Contrary to expectation, the extent of interstitial transport to the refractory metals was greater from the niobium-stabilized type 318 than from the type 316 stainless steel.

The tensile strengths of the niobium and Nb-1% Zr specimens pulled at room temperature were approximately double those of the before-test specimens. The tensile ductilities after test were lower by a factor of 2 to 4. At 927 and 982°C the increase in tensile strength and loss of ductility of the niobium were smaller than at room temperature. The niobium specimen exposed with type 316 stainless steel showed no loss of ductility at 927°C, but the ductility of the one exposed with type 318 was halved, in accord with the higher nitrogen concentration produced in the latter specimen. The types 318 and 316 stainless steel specimens showed no significant changes in either nitrogen or carbon content; accordingly, posttest mechanical properties were similar to properties of before-test specimens.

Table 8. Effect of Carbon and Nitrogen Mass Transfer in Nak on the Mechanical Properties of Niobium, Nb-1% Zr, and Stainless Steel

Material	Test	Exposure Tempera- ture (°C)	Concentration, ppm ^a							Tensile Strength (psi)			Elongation (%)		
			Nitrogen	Carbon	Niobium	Zirconium	Iron	Nickel	Chromium	25°C	927°C	982°C	25°C	927°C	982°C
										× 10 ³	× 10 ³	× 10 ³			
Niobium	Before		80	90		14	315	<10	<20	22.8	6.5	6.1	18	19	11
	1696	927	740	330		110	110	70	20	48.2	9.5		4	20	
	1697	927	2000	510		40	120	50	25	46.2	9.0		12	19	
	1713	982	940	880						50.4		7.5	6		8
Nb-1% Zr	Before		160	(b)		(c)	240	50	30	47.0	28.6	25.0	25	11	10
	1696	927	850	420		0.8%	420	60	90	86.7	42.7		10	7	
	1697	927	1500	770		1.3%	260	30	60	85.1	42.2		14	6	
	1713	982	1200	910						79.3		35.0	14		9
316 stain- less steel	Before		300	470	860	30	67.9%	11.2%	15.8%	83.7		8.1	67		46
	1696	927	280	280	250	10				80.8	19.0		63	44	
	1713	982	310	460						83.2		11.5	63		57
318 stain- less steel	Before		300	430	1.0%	3	66.1%	12.2%	16.3%	85.3			59		
	1697	927	310	450	0.9%	57				89.5	20.5		50	70	

^aUnless percentage is indicated.

^b190 ppm for test 1696, 130 ppm for tests 1697 and 1713.

^c0.6% for test 1696, 0.7% for test 1697.

Comparison of tests 1696 and 1713 shows the effect of temperature on the mass transfer of carbon and nitrogen and corresponding changes in mechanical properties. The pickup of both carbon and nitrogen was greater at 982°C than at 927°C, but as discussed previously with sodium systems there was a sharp increase in carbon pickup at 982°C. Relatively small differences in the tensile properties of specimens from these tests were found, however, indicating that carbon does not significantly contribute to the strengthening and corresponding loss in ductility that was found in after-test specimens. This conclusion was further substantiated by machining the carbide-nitride layers from some of the specimens and re-analyzing the specimens. Table 9 shows that most of the carbon was removed with the layers, but a significant amount of nitrogen was present in the bulk sample.

Table 9. Carbon and Nitrogen in Niobium and Nb-1% Zr After Exposure with Types 316 and 318 Stainless Steel in NaK

Test	Specimen Material	Concentration, ppm					
		Before Test		After Test ^a		After Machining ^b	
		Carbon	Nitrogen	Carbon	Nitrogen	Carbon	Nitrogen
1697	Niobium	90	80	510	2000	150	590
1697	Nb-1% Zr	130	160	770	1500	290	1300
1696	Nb-1% Zr	190	160	420	850	230	690

^aExposed 500 hr at 927°C.

^b0.002 in. removed from each surface after test.

To determine the effect of the surface layers on the tensile properties of Nb-1% Zr, tensile tests were conducted on specimens before and after the layers were removed. Specimens of Nb-1% Zr were annealed at 1200°C and exposed in NaK with type 316 stainless steel for 500 hr at 927°C. As shown in Table 10, chemical analyses indicated the pickup of carbon and nitrogen, and the concentration of nitrogen in these specimens remained high after they were electropolished to remove surface layers. However, removal of the layers had no significant effect on the after-test

Table 10. Effect of Surface Layer Removal on the Tensile Properties of Nb-1% Zr (Test 1857)

Specimen History	Chemical Analysis, ppm			Tensile Properties at 21°C		Tensile Properties at 927°C	
	Nitrogen	Carbon	Oxygen	Strength (psi)	Elongation ^a (%)	Strength (psi)	Elongation ^a (%)
Annealed at 1200°C	90	50	100	37,100	23.5	31,500	14.0
Control ^b				38,800	26.0	28,000	18.5
Tested 500 hr at 927°C ^(c)	920	730	250	88,500	13.5	48,000	6.5
Tested and electropolished to remove surface layers	550	120	270	80,000	10.0	43,000	4.5

^aIn 2 in.

^bAnnealed at 1200°C and then heat treated in argon for 500 hr at 927°C.

^cWith stainless steel surface area 10 times that of the Nb-1% Zr.

tensile properties. Tensile strength remained high and ductility low in tests at both room temperature and 927°C.

In some cases specimens heat treated in argon for the same time periods as those tested in NaK showed changes in tensile properties compared with before-test specimens. These changes were attributed⁴ to age hardening of the Nb-1% Zr alloy at 927°C after solution annealing 2 hr at 1600°C. Test results presented in Table 8 were on Nb-1% Zr material that did not age harden during the control heat treatment, but results from test 1815 (Table 2) were not included because the age-hardening effects prevented evaluation of the effects of carbon and nitrogen on mechanical properties. Solution annealing at 1200°C did not lead to aging effects in control specimens and was the pretest treatment for the test series reported in Table 10.

Some pickup of carbon and nitrogen was detected on niobium and Nb-1% Zr specimens after exposure in the argon-filled stainless steel containers. Mass transfer in control tests of this type is demonstrated by the data shown in Table 11. Analyses of Nb-1% Zr tabs and joining niobium wires indicated an increase in carbon and nitrogen. Oxygen content, on the other hand, decreased in some of the tests, indicating that the results could not always be explained by assuming the argon used as the control test atmosphere was contaminated. In addition, the

⁴D. O. Hobson, A Preliminary Study of the Aging Behavior of Wrought Columbium-1% Zirconium Alloys, ORNL-2995 (Jan. 6, 1961).

Table 11. Control Tests of Nb-1% Zr and Type 316 Stainless Steel Exposed Together for 500 hr at 927°C in Argon

Test	Material	Oxygen, ppm		Nitrogen, ppm		Carbon, ppm	
		Before	After	Before	After	Before	After
1589	Nb-1% Zr	435	365	200	330	200	410
1815	Nb-1% Zr	190	150	70	710	50	560
1857	Nb-1% Zr	100	250	90	830	50	960
2300	Nb-1% Zr	80	160	55	370	80	85
2300	Nb (wire)	100	490	140	580	80	140
2300	316 stainless steel	50	50	390	400	480	480

specimens exhibited a very thin surface layer, less than 0.1 mil, quite similar to the mixed carbide-nitride phase observed on specimens from sodium and NaK tests.

Effect of Stress

To determine the effect of an applied load on the integrity of the carbide-nitride film and hence on the rate of carbon and nitrogen transfer to niobium, the test system shown in Fig. 10 was devised. A 200-lb load was applied to a niobium rod with sections 0.4 and 0.3 in. in diameter and resulted in stresses of 1700 and 3000 psi, respectively. An unloaded niobium rod with sections machined to 0.4 and 0.3 in. diameter, respectively, was suspended next to the stressed rod. The unstressed rod was inverted so that its 0.3-in.-diam section was opposite the 0.4-in.-diam section of the stressed rod to minimize the effect of specimen position on the results. So that the analytical results would not be biased by the different rod thicknesses, the chemical analyses were determined from 0.005-in. layers turned from the specimens after test. Results of the analyses are shown in Table 12. At 1700 psi the amount of carbon and nitrogen transfer was less for the stressed than the unstressed rod; at 3000 psi the stressed rod picked up less carbon but more nitrogen than the unstressed rod. Metallographically the stressed and unstressed samples differed little; a duplex carbide-nitride layer of approximately the same thickness was observed on both. In view of the small differences between the specimens, stress up to the limits of this test appears to have little effect on the transfer of carbon and nitrogen.

Fig. 10. Schematic of Apparatus to Test the Effect of Stress on the Rate of Carbon and Nitrogen Pickup by Niobium Exposed with Stainless Steel in NaK.

Table 12. Effect of Stress on Transfer of Carbon and Nitrogen to Niobium^a

Stress (psi)	Rod Diameter (in.)	Analysis, ^b ppm	
		Carbon	Nitrogen
0	0.3	1010	1330
0	0.4	860	1100
1700	0.4	620	835
3000	0.3	660	1500

^aExposed 500 hr at 927°C with the stainless steel surface area 10 times the niobium surface area.

^bAverage analysis of four 0.005-in. layers turned from the surface.

Surface Area Effects

Results from NaK systems generally agreed with those from capsule tests containing sodium. Surface area ratios employed for the mechanical properties studies varied from 6.5 to 11; and, as shown in Table 13, no consistent differences were found in the amounts of carbon and nitrogen transferred.

Table 13. Effect of Surface Area of Type 316 Stainless Steel Compared with Surface Area of Nb-1% Zr on Carbon and Nitrogen Transfer in NaK for 500 hr at 927°C

Test	Alloy	Surface Ratio ^a	Carbon, ppm		Nitrogen, ppm	
			Before	After	Before	After
1696	Nb-1% Zr	6.5	190	420	160	850
1857	Nb-1% Zr	10	50	730	90	920
1815	Nb-1% Zr	11	50	300	76	1000
1696	316 stainless steel	6.5	470	280	300	280

^aSurface area ratio of stainless steel to niobium.

DISCUSSION AND CONCLUSIONS

These studies have demonstrated that transfer of interstitial impurities and, to a lesser extent, metallic constituents will occur between niobium or Nb-1% Zr and type 316 or 318 stainless steel in a sodium or NaK system at temperatures from 816 to 982°C. The rate of transfer of these elements depended upon system temperature and test time. When the amount of stainless steel surface in the system was much larger than that of Nb-1% Zr, the predominant mass-transfer reaction involved the transfer of carbon and nitrogen from the stainless steel to the Nb-1% Zr. The pickup of carbon by Nb-1% Zr was primarily restricted to a surface layer, but nitrogen diffused into the material, reducing its ductility. In a predominantly niobium system the principal reaction is the transfer of niobium to the stainless steel, and this results in the formation of complex carbide-nitride layers on the surface of the stainless steel.

The surface area effects found in these tests afford indirect evidence that, under the conditions examined, diffusion of interstitial impurities into the refractory metal was a more significant rate-controlling step in the transport process than diffusion through the stainless steel. If diffusion to the stainless steel surface was rate limiting, then one would expect a correlation of the amount of impurities picked up by niobium with surface-area ratio. Increasing the stainless steel surface area from 3 times that of niobium to 13 times did not significantly change the amount of carbon and nitrogen picked up by the niobium. The slower diffusion step on the refractory-metal side of the system may be associated with the formation of a carbide-nitride layer on the surface of refractory metal, which eventually limits the flow of carbon and, to a lesser extent, nitrogen into the metal.

Dissimilar alloy studies with potassium⁵ have given evidence that permeation of nitrogen through stainless steel may provide a significant source of this species in systems at 800 to 900°C for times exceeding

⁵Allison Division, General Motors, Progress Report, Investigation of Bimetallic Liquid Metal Systems, (1 February-31 May 1966), GMAD-3643-5 p. 4-1.

1000 hr. Data from the present tests were inconclusive with regard to this source of nitrogen. Chemical analyses completed on the test specimens and capsules, although extensive, were not sufficient to permit a direct mass balance to be made between interstitial changes in stainless steel and those in the refractory metal. As mentioned previously, the net loss of nitrogen by the stainless steel did not appear sensitive to the surface-area ratio, indicating that there might be some external source of nitrogen. However, certain of the tests employed a refractory metal capsule within a protective outer stainless steel can (Fig. 3) and were, therefore, not directly exposed to an external air environment; nevertheless, the amount of nitrogen transferred was about the same as in those in which only a stainless steel vessel was used.

Some evidence of the transfer of metallic elements of the stainless steel to the niobium was detected in spectrographic analyses of the niobium specimens. As in the case of nitrogen and carbon, the diffusion rate of metallic species into the niobium may be substantially reduced as carbide-nitride layers are produced. When these layers are absent, as might be the case in systems with relatively small amounts of stainless steel, metallic element transfer could predominate, especially at higher temperatures where diffusion rates are faster.

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