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STUDIES OF THE OXIDATION AND CONTAMINATION
RESISTANCE OF BINARY NIOBIUM ALLOYS

by

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1

STUDIES OF THE OXIDATION AND CONTAMINATION RESISTANCE OF BINARY NIOBIUM ALLOYS

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BMI-1169

A study of the effects of binary alloying additions on the oxidation and contamination resistance of niobium has been conducted. The alloys contained up to 35 a/o titanium, chromium, and zirconium, 25 a/o vanadium, molybdenum, tantalum, and tungsten, and 5 a/o beryllium, boron, cobalt, iron, manganese, nickel, and silicon. The oxidation and contamination studies were conducted in air at 600, 800, and 1000 C.

Four elements, titanium, vanadium, molybdenum, and chromium, improved oxidation resistance. The concentrations for optimum oxidation resistance at 1000 C were 25 a/o titanium, 10 a/o vanadium, 5 a/o molybdenum, and 25 a/o chromium. Titanium was most effective in reducing the rate of oxidation; at 600 to 1000 C, the niobium-25 a/o titanium alloy oxidized one-tenth to one-twentieth as rapidly as pure niobium.

Contamination was investigated by hardness-penetration measurements on all oxidized alloys except those containing beryllium or boron. Zirconium and titanium markedly reduced the depth of oxygen contamination resulting from exposure to air. Diffusion coefficients for oxygen in the niobium binary alloys were calculated, and related by activation-energy plots where possible. Zirconium, titanium, chromium, and vanadium were most effective in reducing oxygen diffusion into niobium.

INTRODUCTION

Niobium metal is of great interest as a potential high-temperature construction material for nuclear reactors and jet engines. However, like molybdenum, niobium oxidizes excessively when in contact with air at elevated temperatures. Reduction of the high oxidation rate of both of these metals is very desirable, and would greatly increase their usefulness.

Major effort in the past has been to protect molybdenum from oxidation by alloying to form a chemically and thermally stable protective oxide film, principally because the most common oxide, MoO_3 , is volatile at temperatures of interest. The possibility of increasing the oxidation resistance of niobium by alloying is more promising, because of the relatively refractory nature of the oxide formed, Nb_2O_5 . Accordingly, an investigation has been undertaken to determine the effect of binary alloying additions on the air oxidation rate, and also on the contamination rate of niobium. The latter is of importance because of the embrittling effect produced by diffusion of oxygen from the oxide scale.

The present work is concerned with air oxidation only. It was hoped that additions of appropriate alloying elements would lower the oxidation rate of niobium by formation of a protective complex oxide with the alloying element such as a niobate or a spinel. To

present as complete a picture as possible, no attempt was made to rule out potential alloying additions on the basic factors such as atomic size fit or volume. Common transition metals in the program included chromium, cobalt, iron, manganese, molybdenum, nickel, tantalum, titanium, tungsten, vanadium, and zirconium. Aluminum, beryllium, and silicon were included because of their tendencies to form tight protective self-oxides. Boron was also studied.

BACKGROUND INFORMATION

The open literature contained no information on the oxidation of niobium alloys. However, some pertinent information on the niobium oxides exists. For instance, niobium pentoxide, Nb_2O_5 , has been found to be stable up to at least 1200 C. (1, 2) According to Orr⁽³⁾, niobium pentoxide melts at 1512 C. Kubaschewski and Hopkins⁽⁴⁾ report a melting point of 1460 C.

One part of the present program on niobium was an investigation of the oxidation of pure niobium metal in air and in oxygen. The results of this study are presented separately.⁽⁵⁾ The procedure used in studying the oxidation of pure niobium in air was identical with the procedure used to evaluate binary alloys described in the present report. The specimens were exposed to undried air in a muffle furnace, removed at various times, and the weight gain measured. Reaction was due primarily to oxygen; nitrogen was found to have little effect. The oxide formed on pure niobium occurred as a nonprotective white solid, and although the measurements obtained by intermittent weighing were not suitable to establish the mode of oxidation, they were consistent with linear oxidation rates.

Data in the text show that pure niobium oxidizes in air at a higher rate at 800 C than at 1000 C, an effect which has been verified by measurements made after removal of the scale. This phenomenon may be the result of sintering of the oxide at the higher temperature, preventing ready access of air to the metal oxide interface. The characteristic voluminous white oxide formed on pure niobium at 1000 C is also pictured in this report. The appearance of pure niobium specimens oxidized at 800 C is essentially same as those oxidized at 1000 C, although specimens oxidized at 600 C form visibly less oxide.

The study on pure niobium⁽⁵⁾ also presented data on the contamination hardening of niobium in air. It was shown that air contamination is primarily due to oxygen, and that nitrogen has little effect.

PROCEDURE

The niobium-base alloys containing binary additions of up to 35 a/o were arc-melted as small buttons in a helium-atmosphere furnace on a water-cooled copper

(1) References at end of report.

hearth. The buttons were machined into rectangular specimens, about 0.1 by 0.2 by 0.45 in. For oxidation testing, the specimens were placed on inverted porcelain crucible covers and supported by 1/2-in. -diameter porcelain rings so that minimum contact was maintained between the specimen and the support. The specimens were exposed to air at 600, 800, and 1000 C in a muffle furnace for periods up to 20 hr, depending on the oxidation rate. No attempt was made to control humidity. Weight data were recorded initially and after 1, 5, 10, 15, and 20 hr of exposure. The weight-gain data were plotted for each alloy. As an example of typical weight-gain data, the behavior of pure niobium and the niobium binary alloys with 1.0, 5.0, 10.0, 25.0, and 35.0 a/o titanium at 600, 800, and 1000 C is shown later in Figure 1. Oxidation rates were then calculated from the curves. Photographs were taken to record oxide appearance. In addition to the weight-gain data, the specimens were descaled after the final exposure and weight-loss data recorded.

The scale was removed by a mechanical means to measure it for analysis, so it was often difficult to remove completely. It is believed that portions of a thin layer of oxide, possibly NbO, remained on some of the specimens following scale removal. Selected oxides were then analyzed chemically and by X-ray diffraction to study the oxidation behavior of the alloys compared with pure niobium.

Following completion of the oxidation measurements, hardness traverses were taken on sections of the oxidized but unreacted alloys to determine the extent of oxygen contamination (diffusion) during oxidation. Contamination-rate constants and diffusion constants were then calculated, and where possible, these rates were related by Arrhenius plots. Diffusion of oxygen in the most promising diffusion-resistant alloys was compared with behavior in pure niobium.

RESULTS AND DISCUSSION

Weight-Change Studies

Table 1 lists the numerical weight-change data for all of the alloys. Figure 1 presents results graphically for niobium-titanium alloys with up to 35 a/o titanium and shows that they oxidize in a substantially linear manner. Linear oxidation rates generally result in slablike oxidation products on rectangular specimens, as is verified by the appearance of the specimens in Figure 2. The formation of the voluminous white oxide, shown in Figure 2, is inhibited somewhat as the titanium content is increased to 25 a/o. Increasing the titanium content beyond 25 a/o does not appear to further improve the oxidation resistance. Table 1 and Figure 3 give the air-oxidation rates of niobium-titanium binary alloys calculated from weight-gain data, and show that the oxidation rate for these alloys at all temperatures reaches a minimum at about 25 a/o titanium. The oxidation rates at 800 C and 1000 C are essentially the same. This fact is further verified by oxidation rates of the titanium alloys calculated from weight-loss measurements after descaling, given in Table 1.

The oxidation rate of the niobium-titanium alloys appears to be linear from the present data; however, as mentioned previously, the intermittent method of measuring weight gain used in this work requires that the specimen be removed from the furnace for weighing at definite time intervals. Thus it would be difficult to detect parabolic oxidation rates if they occurred, since the protective film which was formed during

- Legend**
- Pure niobium (5%)
 - 1% Titanium
 - × 5% Titanium
 - △ 10% Titanium
 - 25% Titanium
 - + 35% Titanium

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FIGURE 1. OXIDATION OF NIOBIUM(5) AND NIOBIUM-TITANIUM ALLOYS AT 600, 800, AND 1000 IN AIR

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FIGURE 2. AIR OXIDATION OF ARC-MELTED NIOBIUM-TITANIUM ALLOYS FOR VARIOUS TIMES AT 1000 C

TABLE 1. WEIGHT-GAIN OXIDATION RATES, FINAL WEIGHT-LOSS
OXIDATION RATES(a), AS-CAST HARDNESSES, AND
EXPOSURE TIMES FOR BINARY NIOBIUM ALLOYS

Alloy Composition, a/o	As-Cast Hardness, VHN	Weight-Gain Oxidation Rate, mg/(cm ²)(hr), at			Descaled Weight-Loss Oxidation Rate, mg/(cm ²)(hr), at			Time of Exposure, hr, at Indicated Temperature		
		Indicated Temperature			Indicated Temperature					
		600 C	800 C	1000 C	600 C	800 C	1000 C	600 C	800 C	1000 C
100 Nb(b)	115	5.7	33.7	24.2	18.4	72.8	32.0	--	--	--
Nb-1.0 Ti	108	5.8	21.6	26.0	11.7	52.0	61.7	10	5	5
-5.0 Ti	115	4.7	21.0	15.7	7.6	45.7	35.4	10	5	5
-10 Ti	135	0.2	7.5	7.7	0.0	17.8	17.9	20	10	10
-25 Ti	156	0.1	0.6	1.9	0.0	0.9	5.0	20	20	20
-35 Ti	181	0.2	0.7	4.3	0.0	0.3	7.9	20	20	20
Nb-1.0 Mo	126	1.7	12.0	13.2	5.9	5.3	19.4	5	5	5
-5.0 Mo(c)	166	0.3	2.1	4.6	--	--	--	20	20	20
-10 Mo	201	0.4	1.9	10.1	0.4	17.8	167.2	5	5	5
-25 Mo	299	2.0	3.8	42.5	0.7	26.4	143.6	5	5	5
Nb-1.0 Cr	120	3.4	29.8	33.1	7.0	56.6	64.0	5	5	5
-5.0 Cr	124	3.5	24.2	28.1	4.7	31.9	58.6	5	5	5
-10 Cr	147	1.3	24.4	26.2	0.7	44.4	55.6	5	5	5
-25 Cr	345	0.5	5.1	6.1	3.7	4.6	32.4	5	5	5
-35 Cr	429	0.1	0.4	22.3	0.0	0.9	48.0	20	20	20
Nb-1.0 V	114	3.6	6.3	13.8	7.4	7.3	32.3	10	5	5
-5.0 V	160	0.9	1.4	4.6	1.3	0.6	11.0	10	10	10
-10 V	172	0.1	0.7	3.5	+(d)	+	7.0	10	10	10
-25 V	194	0.2	6.1	193	+	13.9	398.4	10	5	1
Nb-1.0 Zr	176	7.1	64.8	71.0	11.0	104.2	106.9	5	5	5
-5.0 Zr	167	3.8	41.2	135	9.8	77.8	142.5	5	5	5
-10 Zr	209	0.3	25.2	101	0.0	55.0	137.8	5	5	5
-25 Zr	272	4.7	10.7	49.5	19.3	26.5	86.4	5	5	5
-35 Zr	289	0.2	2.2	30.0	1.2	2.1	60.5	20	20	5
Nb-1.0 W	127	6.1	41.0	59.0	14.2	95.3	132.2	10	5	1
-5.0 W	165	3.1	12.3	54.0	7.2	33.2	139.7	10	5	1
-10 W	196	2.9	17.0	26.0	7.0	43.8	72.5	10	5	5
-25 W	299	8.3	31.0	94.0	27.1	86.9	253.4	10	1	1
Nb-1.0 Ta	125	6.2	29.0	68.2	15.3	70.0	161.5	10	5	1
-5.0 Ta	122	8.4	34.7	25.5	19.0	79.6	54.6	10	5	5
-10 Ta	120	7.5	39.7	20.3	17.6	96.0	38.7	10	5	5
-25 Ta	130	2.0	26.3	61.3	5.0	70.4	51.8	10	5	1
Nb-0.2 Mn	140	7.8	40.0	21.8	15.6	90.1	51.0	10	5	5
-1.0 Mn	139	4.3	38.0	22.1	8.9	88.7	52.3	10	5	5
-5.0 Mn	140	4.5	39.3	23.9	9.6	90.6	57.8	10	5	5
Nb-0.2 Fe	114	6.6	32.0	35.6	15.1	72.9	77.6	10	5	5
-1.0 Fe	146	7.0	40.5	25.0	16.3	94.0	54.0	10	5	5
-5.0 Fe	178	5.5	22.0	25.0	12.0	48.5	54.7	10	5	5

TABLE 1. (Continued)

Alloy Composition, a/o	As-Cast Hardness, VHN	Weight-Gain Oxidation Rate, mg/(cm ²)(hr), at			Descaled Weight-Loss Oxidation Rate, mg/(cm ²)(hr), at			Time of Exposure, hr, at Indicated Temperature		
		Indicated Temperature			Indicated Temperature					
		600 C	800 C	1000 C	600 C	800 C	1000 C	600 C	800 C	1000 C
Nb-0.2 Co	136	5.2	40.8	43.8	10.8	94.0	54.4	10	5	5
-1.0 Co	165	3.7	41.9	37.6	8.5	104.9	129.6	10	5	1
-5.0 Co	249	4.1	39.2	38.5	9.0	102.5	70.1	10	5	5
Nb-0.2 Ni	144	7.2	27.3	30.3	16.9	65.3	67.3	10	5	5
-1.0 Ni	147	5.2	26.5	58.5	12.9	68.9	141.1	10	5	5
-5.0 Ni	230	5.1	31.5	46.3	14.8	82.2	112.5	10	5	5
Nb-0.2 Al	132	7.5	39.2	19.8	16.2	89.9	49.7	10	5	5
-1.0 Al	131	8.0	37.2	22.5	17.3	85.2	55.0	10	5	5
-5.0 Al	114	7.1	44.2	19.4	15.8	99.8	47.5	10	5	5
Nb-0.2 Si	156	6.9	52.0	21.4	15.5	93.8	53.9	10	5	5
-1.0 Si	186	6.1	53.3	46.5	12.9	96.4	96.9	10	5	1
-5.0 Si	330	10.3	67.0	103.8	23.3	148.2	231.1	10	1	1
Nb-0.2 Be	122	5.7	27.6	24.0	12.5	63.3	54.4	5	5	5
-1.0 Be	113	6.9	31.1	21.5	15.0	72.2	48.8	5	5	5
-5.0 Be	110	6.5	40.6	18.0	14.6	94.4	39.9	5	5	5
Nb-0.2 B	103	5.8	39.3	19.9	12.8	90.7	45.0	5	5	5
-1.0 B	111	3.8	27.8	20.2	7.8	63.7	45.0	5	5	5
-5.0 B	160	3.0	10.3	15.1	5.8	19.0	66.0	5	5	5

(a) Final specimen area used in weight-loss oxidation-rate calculation.

(b) Average values from 1, 5, and 10 hr of exposure time.

(c) Specimen lost at end of weight-gain determinations.

(d) + = Specimen showed a weight gain after cleaning.

FIGURE 3. AIR OXIDATION RATES OF NIOBIUM ALLOYS CONTAINING TITANIUM, MOLYBDENUM, CHROMIUM, AND VANADIUM, CALCULATED FROM WEIGHT-GAIN DATA

exposure might crack and spall while the specimens were cooling prior to each weighing operation. Therefore, for the niobium-titanium alloys and for all of the other alloys studied in this work, the present studies show relative oxidation rates but are not presumed to establish the mode of oxidation.

Similar data were obtained for all of the niobium-alloy systems studied. The results are presented as weight-gain oxidation rates in graphical form in Figures 3, 4, 5, 6, and 7. The appearance of selected specimens following oxidation is shown in the photographs of Figures 8 and 9.

Figure 3 shows the weight-gain oxidation rates found for alloys of niobium with up to 25 a/o molybdenum and 25 a/o vanadium. Behavior of these alloys is quite similar. Both alloy systems exhibit rather sharp minima in oxidation at about 5 a/o molybdenum and about 10 a/o vanadium. Above the minimum concentrations, oxidation rates increase very rapidly and reached catastrophic proportions at 1000 C. This is not unexpected in view of the poor oxidation properties of high-molybdenum and -vanadium alloys, which are well known. The oxidation-rate data calculated from weight loss after descaling for the molybdenum and vanadium alloys verify these findings. The appearance of some of the oxidized specimens is shown in Figure 8. Although the best niobium-molybdenum alloy, 5 a/o molybdenum, is not quite so oxidation resistant as the niobium-25 a/o titanium alloy, molybdenum is the most efficient alloying addition for oxidation resistance found in this study in that only small amounts are required.

Chromium additions, shown in Figure 3, improve the oxidation resistance only slightly up to 10 a/o chromium, but considerable improvement occurs at 25 a/o and above for 600 and 800 C. However, a minimum in oxidation rate at 1000 C occurs at 25 a/o chromium.

Tungsten and tantalum additions to niobium, shown in Figure 4, do not improve the oxidation resistance of niobium. At 800 and 1000 C, small additions of tungsten and tantalum (~1 a/o) cause a marked increase in oxidation rate followed by a minimum at moderate concentrations. In both systems, the minimum is only sufficient to reduce the oxidation rate about to that of pure niobium.

Zirconium additions (Figure 4) improve oxidation resistance quite markedly at 600 C, but improvement at 800 C is noted only at about 35 a/o zirconium and above. At 1000 C, a catastrophic maximum in oxidation rate occurs at about 5 to 10 a/o zirconium. Oxidation rates for these alloys based on weight losses after descaling are given in Table 1, and support the results of the weight-gain measurements. Tantalum, tungsten, or zirconium up to 25 to 35 a/o appear to have no promise for improving the oxidation resistance of niobium metal. Visual appearance of some of these alloys is shown in Figure 9.

Eight other alloying elements, aluminum, beryllium, boron, cobalt, iron, manganese, nickel, and silicon also were evaluated. Additions were limited to a maximum of 5 a/o because of the lower expected useful amounts of the addition elements. The oxidation rate curves based on weight-gain data are shown in Figures 5, 6, and 7. None of these alloying additions decreased the oxidation rate of niobium significantly. Nickel and silicon increased oxidation at 800 or 1000 C. All eight alloy systems, except niobium-nickel, showed a greater oxidation rate at 800 C than at 1000 C for several alloy concentrations, usually 0.1 and 1.0 a/o. None of these alloy systems appear to warrant further study for oxidation-resistance purposes.

FIGURE 4. AIR OXIDATION RATES OF NIOBIUM ALLOYS CONTAINING TUNGSTEN, TANTALUM, AND ZIRCONIUM, CALCULATED FROM WEIGHT-GAIN DATA

FIGURE 5. AIR OXIDATION RATES OF NIOBIUM ALLOYS CONTAINING MANGANESE, IRON, AND COBALT, CALCULATED FROM WEIGHT-GAIN DATA

FIGURE 6. AIR OXIDATION RATES OF NIOBIUM ALLOYS CONTAINING NICKEL, ALUMINUM, AND SILICON, CALCULATED FROM WEIGHT-GAIN DATA

FIGURE 7. AIR OXIDATION RATES OF NIOBIUM ALLOYS CONTAINING BORON AND BERYLLIUM, CALCULATED FROM WEIGHT-GAIN DATA

FIGURE 8. APPEARANCE OF SELECTED MOLYBDENUM, CHROMIUM, AND VANADIUM ALLOYS OF NIOBIUM AFTER 5 HR OF EXPOSURE TO AIR AT 1000 C

FIGURE 9. APPEARANCE OF SELECTED MISCELLANEOUS NIOBIUM ALLOYS FOLLOWING 5 HR OF EXPOSURE TO AIR AT 1000 C

Examination of Oxidation Scales

Following weight-gain measurements, the Nb₂O₅ oxidation scale was removed and oxidation weight loss determined as discussed above. The scale was removed by mechanical picking and scraping, so that chemical analyses of the scale could be obtained. During this procedure, visual inspection indicated that a thin subscale may have been present on all of the alloys. This occurred between the Nb₂O₅ scale and the alloy base metal, and was difficult to separate from the alloy. Although it was not positively identified, it is believed that this was a layer of NbO or NbO-type oxide as found during the oxidation of pure niobium.⁽⁵⁾

Results of chemical analysis for binary alloy additions and for oxygen in the scale, and results of some calculations to estimate oxygen content of the scale, are given in Table 2. Oxygen content of the scales will be discussed first.

The alloys of greatest interest are the most oxidation-resistant ones, but as shown in Table 2, oxygen contents are not reported for some of these alloys. Too little scale was available for chemical analysis, and weight gains and losses were too low to provide accurate estimations. As pointed out earlier, the weight-loss measurements may be low, because of adherence of subscale to the base metal. The scale oxygen contents of the alloys determined chemically are close to the theoretical oxygen content of pure Nb₂O₅, 30.1 w/o. Scale oxygen content of the tantalum, tungsten, and zirconium alloys decreases with increasing alloy content. The oxides of these metals (Ta₂O₅, WO₃, ZrO₂) all contain less than 26 w/o oxygen, which may indicate that some Ta₂O₅, WO₃, and ZrO₂ is present in the scale. However, the 5 and 10 a/o titanium alloy and the 5 a/o chromium alloy also show a decrease in scale oxygen content, even though chromium and titanium oxides (Cr₂O₃ and TiO₂) contain more than 40 w/o oxygen. Scales from all of the 1 a/o alloys were determined by chemical analysis to contain very close to the stoichiometric amount of oxygen for Nb₂O₅, substantiating the negligible effect of these small additions on the oxidation of niobium.

The oxygen content of the scale was also estimated by calculation from the weight-gain and weight-loss oxidation data. In this method, the percentage of oxygen in the scale is obtained by dividing the weight gain (total oxygen absorbed) by the weight loss (total weight of scale formed). However, a portion of the absorbed oxygen diffused into the unreacted alloy specimen and it was necessary to correct the weight gain for this effect. Seybolt⁽⁶⁾ gives a relationship between hardness increase and oxygen content for pure niobium. Seybolt's relationship was assumed to be true for niobium alloys also, and data for the correction were obtained from the hardness-penetration graphs shown under "Contamination Studies". The following relationship may be used to calculate the amount of dissolved oxygen:

$$W = \frac{M s p}{100}, \quad (1)$$

where

W = weight of dissolved oxygen per unit area,
g per cm²

M = percentage oxygen in alloy as related to
hardness increase, after Seybolt

TABLE 2. ANALYSIS OF NIOBIUM AND NIOBIUM ALLOY

Alloy Composition (Balance Niobium)				Exposure Time, hr	Oxidation Rates			
					Determined By Weight Gain		Determined By Weight Loss	
Alloy Addition	Nominal Addition		Estimated(a) Actual Addition, w/o		Rate, mg/(cm ²)(hr)	Total Absorbed in Test, mg per cm ²	Rate, mg/(cm ²)(hr)	Total Lost in Test, mg per cm ²
	a/o	w/o						
None	100	100	100	5	33.7	158.5	72.8	364.0
Ti	5	2.6	2.4	5	21.0	105	45.7	228.5
	10	5.4	4.7	10	7.5	75	17.8	178
	25	14.7	13.6	20	0.6	12	0.9	18.0
V	5	2.8	2.4	10	1.4	14	0.6	6.0
	10	5.8	5.0	10	0.7	7.0	+	+
	25	15.5	13.2	5	6.1	30.5	13.9	69.5
Mo	5	5.2	5.2	20	2.1	42	--	--
	25	25.6	22.5	5	3.8	19.0	26.4	132.0
Cr	5	2.9	1.7	5	24.2	121.0	31.9	158
	25	15.7	9.1	5	5.1	25.5	4.6	23.0
Ta	5	9.3	9.3	5	34.7	143.5	79.6	398
	25	39.3	39.3	5	26.3	131.5	70.4	352
W	5	9.4	9.4	5	12.3	61.5	33.2	166
	25	39.8	39.8	1	31.0	31.0	86.9	86.9
Zr	5	4.9	4.9	5	41.2	206.0	77.8	389
	25	24.6	24.6	5	10.7	53.5	26.5	134
Al	5	1.51	<0.2	5	37.2	186.0	99.8	499
Fe	1	0.60	0.23	5	40.5	207.5	94.0	470
Si	1	0.30	0.23	5	53.3	265.5	96.4	482
Mn	1	0.59	0.04	5	38.0	190.0	88.7	443
Co	1	0.64	0.30	5	41.9	209.5	104.9	524
Ni	1	0.63	0.30	5	26.5	132.5	68.9	344

(a) Estimated from weight-loss data during melting.

(b) By wet chemical analysis.

(c) By vacuum-fusion analysis.

OXIDATION SCALE FOLLOWING EXPOSURE TO AIR AT 800 C

Chemical Analysis of Scale			Calculated Scale Oxygen Analysis, w/o		Remarks
Alloy ^(b) Addition, w/o	Oxygen ^(c) , w/o	Niobium ^(b) , w/o	Uncorrected	Corrected for Diffusion Into Base Metal	
0	27.3	Balance	46.3	43.3	Nb ₂ O ₅ contains 30.1 w/o oxygen
1.40	28.0	"	45.9	44.8	
4.02	23.7	"	42.1	39.2	
10.0	--	--	66.7	52.1	
1.34	--	--	235	198	Sample too small for accurate calculations
--	--	--	--	--	Sample gained weight; insufficient oxide for chemical analysis
8.1	18.1	52.7	43.9	40.0	
1.50	--	--	--	--	Sample lost following oxidation
4.03	24.2	Balance	14.4	13.2	MoO ₃ probably volatilized
0.22	28.4	67.8	76.0	75.6	
2.56	--	--	111	103	Sample too small for accurate calculations
9.4	30.0	Balance	43.6	35.7	
40.0	23.4	"	37.3	36.7	
6.0	27.6	"	37.0	33.2	
21.2	23.3	"	36.1	33.7	
4.5	25.5	"	53	52.8	
24.0	21.8	"	40.2	39.8	
0.05	Balance	69.3	37.3	37.2	
0.31	"	68.2	44.7	42.3	
0.60	"	67.9	55.3	54.2	
0.09	"	68.1	42.8	42.5	
0.01	"	67.5	39.9	39.5	
0.04	"	69.0	38.6	38.1	

s = average contamination depth, cm

ρ = density of niobium, 8.57 g per cm³.

As shown in Table 2, correction for oxygen content of the unreacted alloy decreased the estimated scale oxygen content by 1 to 10 w/o. The calculated scale-analysis results show that oxide scale from pure niobium contains 43.4 w/o oxygen, which is much higher than the stoichiometric amount present in Nb₂O₅, 30.1 w/o.

Oxygen content of the alloy scales determined by calculation and by chemical analysis does not agree closely. Oxygen content by calculation varied from 33.2 to 75.6 w/o compared with a variation from 21.8 to 32.5 w/o oxygen determined by chemical analysis. Low oxygen content found for the 25 a/o molybdenum alloy is due to volatilization of MoO₃ during oxidation testing. The calculated scale analyses all show scale oxygen contents greater than the theoretical amount of oxygen in pure Nb₂O₅ (with the exception of one 25 a/o molybdenum specimen). This would suggest excess oxygen in the scale, probably by solution of oxygen in the oxide scale. However, failure to remove all of the Nb₂O₅ scale by the mechanical methods used would tend to give lower weight-loss oxidation rates, resulting in an apparently high oxygen content in the scale in the calculations. Since considerable dissolved oxygen would be required to give the rather large increase in scale oxygen content noted, and because of the mechanical scale-removal methods, oxygen content of the scales obtained by calculation may not be reliable. The chemical analyses of the scale for oxygen are probably more nearly correct.

Chemical analyses of the scale for the binary alloying element and for niobium, in some cases, were obtained. In all instances, the binary alloying element was found present in the scale. It usually was present in an amount directly related to the binary content of the alloy whether the alloy was oxidation resistant or not. Exceptions were scales from 5 and 25 a/o chromium, 5 a/o aluminum, and 1 a/o cobalt, which contained considerably less than the expected amount of binary element based on the behavior of other alloys.

X-ray diffraction studies were conducted on the oxide scales removed from the most promising oxidation-resistant alloy systems exposed at 1000 C, as given in Table 3. The oxide scales were principally composed of the outer layers of oxide. If a thin layer of NbO-rich material were located underneath, it was not included in the X-ray analysis. The results must be considered preliminary, because the exact crystal structure of M-type Nb₂O₅, the allotropic modification stable from 900 to 1100 C⁽⁷⁾, has not been firmly established. The data in Table 3 indicate rather conclusively that the binary oxide formed on the niobium alloys studied is an Nb₂O₅ type. Most of the specimens formed either M-type or H-type (stable above 1100 C) Nb₂O₅. This behavior is particularly consistent in the molybdenum alloys where a good atomic size fit between molybdenum (Mo⁴⁺ = 0.66 Å, Mo⁶⁺ = 0.62 Å) and niobium (Nb⁵⁺ = 0.70 Å) suggests that molybdenum may be substituting in the Nb₂O₅ lattice. The X-ray data also indicate the same situation may exist for 25 a/o titanium (Ti⁴⁺ = 0.66 Å) and 5 and 25 a/o chromium (Cr⁶⁺ = 0.60 Å). The low-titanium alloys, all of the vanadium alloys, and 10 a/o chromium have oxides with new crystal structures similar to M- and H-type Nb₂O₅, but with greater symmetry. This indicates that a mixed oxide may be occurring in the majority of the less oxidation-resistant alloys. The most promising oxidation-resistant alloys, 25 a/o chromium, 5 a/o molybdenum, 25 a/o titanium, and 10 a/o vanadium, all show M- and H-type Nb₂O₅ with the exception of the latter. The 10 a/o vanadium alloy produces an oxide structure with less tendency to form a new structure

TABLE 3. X-RAY DIFFRACTION EXAMINATION OF
OXIDATION SCALE ON NIOBIUM ALLOYS
EXPOSED IN AIR

Alloy Content (Balance Niobium), a/o	Color	Exposure Time at 1000 C, hr	Results
Pure Nb		1.6	M-type Nb ₂ O ₅ ^(a)
5 Ti		5	A pattern closely related to both M- and H-types but of slightly higher symmetry
10 Ti		10	Same as 5 a/o titanium
25 Ti	White Black Yellow	20	M-type M-type M-type
1 Mo	White Black	5	H-type, well crystallized M-type, poorly crystallized
5 Mo	White Black Pink	20	M-type M-type M-type, very slight shift in the position of some lines
10 Mo	White Black	5	M-type, a marked shift in some lattice parameters Mixture of M- and H-types
5 V	Pink Black	10	Same as 5 a/o titanium Same as 5 a/o titanium
10 V	White Black	10	Related to 5 a/o titanium but more complex Same as 5 a/o titanium
25 V		1	Same as 10 a/o vanadium
5 Cr		5	M-type
10 Cr		5	Same as 5 a/o titanium
25 Cr	Yellow Brown White	5	M-type Related to 5 a/o titanium M-type

(a) M-type Nb₂O₅ is the allotropic modification stable from 900-1100 C; H-type is stable above 1100 C⁽⁶⁾. Pure niobium was exposed in oxygen.

than the alloys with poor oxidation resistance. Thus, improvement in the oxidation resistance of niobium apparently is consistent with the presence of an alloying element that will substitute for niobium in the outer scale, which retains the Nb_2O_5 structure.

In studies of the oxidation of pure niobium⁽⁵⁾, it was found that a thin, dense layer, rich in NbO, also containing oriented Nb_2O_5 , formed adjacent to the niobium metal. Presumably, oxidation proceeded in a parabolic manner, and the NbO-rich layer reached limiting thickness. Thick, relatively fluffy Nb_2O_5 formed at the NbO-gas interface in a linear manner. In all probability, oxygen diffused to the NbO- Nb_2O_5 reaction interface through pores and cracks in the Nb_2O_5 , making outward diffusion of cations from the NbO- Nb_2O_5 interface unnecessary for oxidation to proceed. In this situation, diffusion through the NbO layer was rate controlling, and the oxidation of NbO to Nb_2O_5 would only occur as fast as niobium ions were supplied through the NbO-rich layer to the NbO- Nb_2O_5 interface. Since the over-all oxidation reaction occurs at a linear rate after NbO formation is complete, niobium ions must diffuse rather rapidly through NbO.

X-ray analysis showed that the outer scale formed in the more oxidation-resistant alloys was of the Nb_2O_5 type, which forms in the same Maltese-cross manner as in free scaling of pure niobium. Although NbO was not positively identified as present in this work, visual inspection of oxidized alloys during Nb_2O_5 removal indicated a separate phase adhered to the alloy under the Nb_2O_5 -type layer. Thus, an NbO or NbO-type oxide probably forms on the alloys as well as on pure niobium, and is probably the rate-controlling factor.

If NbO is considered as a metal-excess semiconductor (stable with more than the stoichiometric amount of niobium), it is characterized by a location of excess Nb^{+2} at interstitial lattice positions as shown by the Wagner theory⁽⁴⁾. An equal amount of electrons is also located interstitially. Additions of cations of higher valency than Nb^{+2} will replace Nb^{+2} ions in normal lattice sites, causing a decrease in Nb^{+2} at interstitial lattice sites and an increase in free electrons. Since diffusion of Nb^{+2} through NbO is the rate-determining factor, and it is reduced by the decrease in interstitial niobium, oxidation will then be reduced. This may be the case in the present studies when V^{+5} , Mo^{+5} , Cr^{+6} , and Ti^{+4} ions are present in the NbO lattice, causing alloys of niobium with these metals to be oxidation resistant. However, anomalously, additions of other metals with higher ionic valences than Nb^{+2} , such as Ta^{+5} , Zr^{+4} , W^{+4} , Al^{+3} , Mn^{+4} , Si^{+4} , and B^{+3} , do not appear to inhibit oxidation. In fact, small additions (approximately 1 a/o) of many of these elements and also of titanium and chromium promote oxidation compared to higher percentages of the same addition.

Contamination Studies

Following completion of the oxidation measurements, Knoop hardness traverses were made on transverse sections of the unreacted portions of the specimens to measure the depth to which contamination (or diffusion) by oxygen* penetrated during air oxidation testing. All of the alloys were studied except those with boron and beryllium.

*Work on the contamination of pure niobium⁽⁵⁾ has shown that the principal contamination in air is oxygen. Nitrogen has only a minor effect, and, for the purposes of this study, is ignored.

Data for hardness versus depth of contamination were plotted for each alloy and temperature. Figure 10 shows the hardness-penetration curves for the niobium-25 a/o titanium alloys at 600, 800, and 1000 C, plotted on the original hardness data. Hardness-penetration curves for the other alloys studied are given in Figures 11 through 16. The original data points have been removed from these plots to improve the clarity of the data. In the depth measurements, zero baseline depth was taken as the surface of the oxidized alloy following scale removal. The hardness-penetration curve for most of these alloys does not meet the uncontaminated base-metal hardness value sharply, so a finite point for maximum hardness penetration is difficult to obtain. Therefore, maximum depth of contamination is arbitrarily taken as the point where the hardness-penetration curve reaches the base-metal hardness value plus 50 KHN. Data on the depth of contamination obtained in this manner are given in Table 4 for the alloys studied.

Figure 10 shows that hardness near the surface was greater at 800 C than at 1000 C for the niobium-25 a/o titanium alloys. These alloys oxidize more rapidly at 1000 C than at 800 C, and it may be that the reversal in surface hardness is due to the relatively rapid manner in which the metal was consumed at 1000 C compared with 800 C, so that the oxidation reaction surface tended to overtake the hardening effect of oxygen diffusing into the metal. At about a 0.01-cm distance from the surface, a crossover occurs and contamination becomes greater at 1000 C than at 800 or 600 C. Inspection of Figures 11 through 16 will show that similar effects occur in a number of other alloy systems.

The data on contamination depth in Table 4 and the contamination curves of Figures 11 through 16 show that most of the alloys studied are hardened seriously by internal contamination. The behavior of pure niobium in oxygen is given in a separate report.⁽⁵⁾ Binary additions of titanium and zirconium, however, appear to markedly reduce contamination. Increasing titanium additions progressively reduce oxygen contamination up to 35 a/o. Zirconium alloys appear to be more resistant to contamination than any of the alloys studied. The niobium-titanium alloy system was of particular interest since alloys in the range of niobium-25 a/o titanium show marked improvement in both oxidation and contamination resistance compared with pure niobium. A niobium-35 a/o zirconium alloy was virtually free of contamination. However, with this alloy system, as with most of the alloys that show poor oxidation resistance, oxidation occurred rapidly at 1000 C so that the reacting metal surface tended to overtake the portions of the specimens becoming contaminated with oxygen, which diffuses inward in a parabolic manner. This may result in fictitiously low depth-of-contamination values for the highest temperature. Thus, Table 4 should be compared with the oxidation-rate curves of Figures 3, 4, 5, and 6, or with the weight-loss data of Table 1, before conclusions are drawn concerning contamination effects.

The 25-35 a/o chromium alloys also show promising behavior compared with pure niobium. At 600 C and 800 C, 35 a/o chromium alloys are not so contamination resistant as 35 a/o titanium but, at 1000 C, 35 a/o chromium appears to be better than 35 a/o titanium.

The hardness-penetration data were first evaluated by assuming that the maximum depth of contamination varied with the square root of time, so that a contamination-rate constant could be calculated:

FIGURE 10. DEPTH OF OXYGEN CONTAMINATION IN NIOBIUM-25 a/o TITANIUM ALLOY AS DETERMINED BY KNOOP HARDNESS READINGS

FIGURE 11. DEPTH OF OXYGEN CONTAMINATION IN NIOBIUM-TITANIUM AND -CHROMIUM ALLOYS

FIGURE 12. DEPTH OF OXYGEN CONTAMINATION IN NIOBIUM-MOLYBDENUM AND -VANADIUM ALLOYS

FIGURE 13. DEPTH OF OXYGEN CONTAMINATION IN NIOBIUM-ZIRCONIUM AND -TUNGSTON ALLOYS

FIGURE 14. DEPTH OF OXYGEN CONTAMINATION IN NIOBIUM-TANTALUM ALLOYS

FIGURE 15. DEPTH OF OXYGEN CONTAMINATION OF NIOBIUM MANGANESE, -IRON, AND -COBALT ALLOYS

FIGURE 16. DEPTH OF CONTAMINATION OF NIOBIUM-NICKEL, -ALUMINUM, AND -SILICON ALLOYS

TABLE 4. CONTAMINATION DEPTH AND HARDNESS OF
NIOBIUM AND NIOBIUM-BASE ALLOYS EXPOSED
TO AIR AT 600, 800, AND 1000 C

Alloy Composition, a/o	Hardness of Uncontaminated Metal, KHN(a)	Depth of Contamination ^(b) After Indicated Exposure, cm					
		600 C Exposure	Time, hr	800 C Exposure	Time, hr	1000 C Exposure	Time, hr
100 Nb	155	0.006	1	0.032	1	0.067	1
	155	0.013	5	0.049	5	>0.12	5
	165	0.013	10	--(c)	10	>0.10	10
Nb-1.0 Ti	115	0.014	10	0.056	5	0.154	5
-5.0 Ti	125	0.006	10	0.037	5	0.065	5
-10 Ti	145	0.007	20	0.036	10	0.063	10
-25 Ti	157	0.008	20	0.018	20	0.058	20
-35 Ti	195	0.007	20	0.021	20	0.040	20
Nb-1.0 Mo	130	0.012	5	0.053	5	>0.10	5
	-5.0 Mo	155	20	~0.14	20	>0.14	20
	-10 Mo	215	5	0.070	5	--	5(c)
	-25 Mo	345	5	0.024	5	--	5(c)
Nb-1.0 Cr	132	0.016	5	0.054	5	~0.12	5
	-5.0 Cr	132	5	0.052	5	>0.14	5
	-10 Cr	165	5	0.043	5	~0.10	5
	-25 Cr	405	5	0.015	5	0.05	5
	-35 Cr	315	>0.1	>0.1	20	<0.005	5
Nb-1.0 V	125	0.009	10	0.042	5	~0.12	5
	-5.0 V	165	10	0.044	10	>0.14	10
	-10 V	200	10	0.037	10	~0.10	10
	-25 V	283	10	0.018	5	0.01	1
Nb-1.0 Zr	185	0.008	5	0.050	5	0.100	5
	-5.0 Zr	180	5	0.012	5	--	5(c)
	-10 Zr	210	5	0.013	5	0.006	5
	-25 Zr	295	5	0.0	5	0.006	5
	-35 Zr	334	<0.005	<0.005	20	<0.005	5
Nb-1.0 W	145	0.030	10	0.076	5	0.068	1
	-5.0 W	190	10	0.084	5	>0.1	1
	-10 W	177	10	>0.1	5	>0.1	5
	-25 W	385	<0.002	0.029	1	0.054	1
Nb-1.0 Ta	127	0.007	10	0.045	5	0.063	1
	-5.0 Ta	119	10	0.042	5	>0.1	5
	-10 Ta	104	10	0.032	5	>0.1	5
	-25 Ta	150	10	0.052	5	0.050	1

TABLE 4. (Continued)

Alloy Composition, a/o	Hardness of Uncontaminated Metal, KHN ^(a)	Depth of Contamination ^(b) After Indicated Exposure, cm					
		600 C Exposure	Time, hr	800 C Exposure	Time, hr	1000 C Exposure	Time, hr
Nb-0.2 Mn	137	0.018	10	0.040	5	>0.1	5
-1.0 Mn	147	0.015	10	0.049	5	>0.1	5
-5.0 Mn	164	0.015	10	0.048	5	>0.1	5
Nb-0.2 Fe	115	0.020	10	0.045	5	>0.1	5
-1.0 Fe	163	0.019	10	0.068	5	>0.12	5
-5.0 Fe	212	0.013	10	0.055	5	>0.10	5
Nb-0.2 Co	142	0.016	10	0.053	5	>0.1	5
-1.0 Co	175	0.024	10	>0.1	5	>0.1	1
-5.0 Co	280	0.022	10	>0.1	5	>0.1	5
Nb-0.2 Ni	134	0.008	10	0.037	5	>0.1	5
-1.0 Ni	176	0.009	10	0.028	5	>0.1	5
-5.0 Ni	250	0.033	10	0.044	5	>0.1	5
Nb-0.2 Al	128	0.016	10	0.075	5	>0.1	5
-1.0 Al	138	0.013	10	0.067	5	>0.1	5
-5.0 Al	132	0.013	10	0.041	5	>0.1	5
Nb-0.2 Si	172	0.013	10	0.031	5	>0.1	5
-1.0 Si	266	0.004	10	>0.1	5	>0.1	1
-5.0 Si	391	0.028	10	>0.1	1	>0.1	1

(a) Hardness of the as-melted alloy.

(b) Taken from the hardness-penetration curve at the hardness of the uncontaminated metal plus 50 KHN.

(c) Sample completely oxidized.

$$\frac{S^2}{t} = K' D_0 e^{-\frac{Q}{RT}} = (K)_T \text{ const} , \quad (2)$$

where

S = contamination depth, cm

t = contamination time, hr

K = contamination-rate constant, cm^2 per hr
(a diffusion coefficient).

This expression has been found to correlate contamination of titanium alloys.⁽⁸⁾ In the present study, it was only found possible to correlate the niobium-titanium alloys by this equation. An Arrhenius-type plot of the contamination rate, K , for niobium and the niobium-titanium system is shown in Figure 17. The family of curves obtained shows that 1 a/o titanium has virtually no effect on contamination, but that larger titanium additions reduce contamination considerably. The activation energy for oxygen contamination in this system was calculated to be $29,010 \pm 400$ cal per mole. This compares with the value of 25,700 cal per mole found in studies of the air contamination of pure niobium.⁽⁵⁾

Oxygen-Diffusion Studies

The hardness-penetration data may also be utilized to calculate the diffusion of oxygen in niobium and the alloys studied. Diffusion and contamination are very closely related, since contamination hardening is dependent on the rate at which oxygen diffuses into the metal. The solution of Fick's second law for diffusion states that a diffusing element accumulates in the diffusion medium at a rate equal to the difference between the inward and outward diffusion flux. Stated mathematically, Fick's second law is:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) , \quad (3)$$

where

c = concentration of diffusing element

t = diffusion time

x = distance diffusion occurs

D = diffusion coefficient.

D is equivalent to K in Equation (2).

The Van Ostrand-Dewey solution⁽⁸⁾ to Fick's second law was applied and may be stated as follows:

FIGURE 17. OXYGEN CONTAMINATION RATES OF NIOBIUM AND NIOBIUM-TITANIUM ALLOYS

$$\frac{c-c_o}{c_m-c_o} = 1 - \phi \left(\frac{x}{2\sqrt{Dt}} \right) , \quad (4)$$

where

c_o = original concentration of diffusing element
in the diffusion media

c_m = diffusing-element concentration at the surface

c = diffusing-element concentration at a given
distance from the surface

ϕ = probability (or error) function

x = distance from surface, cm

D = diffusion coefficient, cm^2 per hr

t = diffusion time, hr.

If the diffusing-element concentration is expressed in terms of hardness and Equation (3) is solved for D , then

$$D = \frac{x^2}{4 \left(\phi^{-1} \left[\frac{H_m - H}{H_m - H_o} \right] \right)^2 t} . \quad (5)$$

Data were taken for three points on each of the depth-of-contamination curves in Figures 11 through 16. H_m , hardness of the contaminated alloy at the alloy-air interface, was estimated by extrapolation of the depth-of-contamination curves to zero depth. Table 5 lists the average of the three values for each alloy composition and temperature. These values of the oxygen-diffusion coefficient, D , may be compared with the depth-of-contamination coefficient, K , in Table 5.* The assumption that depth of contamination varies with the square root of time [Equation (2)] is generally supported by the more exact calculations of Equation (4).

Consideration of the diffusion data in Table 5 shows that chromium, titanium, vanadium, and zirconium binary additions slow oxygen diffusion in niobium, although not all binary compositions in these systems are equally effective. The most effective additions appear to be 35 a/o chromium, 10-35 a/o titanium, 25 a/o vanadium, and 20-35 a/o zirconium. The 35 a/o zirconium alloy showed zero oxygen diffusion at 600 and 800 C, and very low diffusion at 1000 C.

*The diffusion coefficient, D , is approximately equal to one-half the depth-of-contamination coefficient, K .

TABLE 5. CONTAMINATION-RATE COEFFICIENTS, K,
AND DIFFUSION-RATE COEFFICIENTS, D,
FOR NIOBIUM AND NIOBIUM BINARY ALLOYS
EXPOSED IN AIR

Alloy Content (Balance Niobium), a/o	Contamination-Rate Coefficient, K, at Indicated Temperature, 10 ⁻⁴ cm ² per hr			Diffusion-Rate Coefficient, D, at Indicated Temperature, 10 ⁻⁴ cm ² per hr		
	600 C	800 C	1000 C	600 C	800 C	1000 C
100 Nb	0.137	9.16	16.3	0.0865	1.26	7.56
1 Ti	0.196	6.28	47.5	0.0680	2.97	9.41
5 Ti	0.036	2.64	8.45	0.0134	0.496	1.64
10 Ti	0.025	1.30	3.98	0.0062	0.289	0.711
25 Ti	0.032	0.162	1.68	0.0052	0.030	0.244
35 Ti	0.025	0.221	0.80	0.0058	0.024	0.486
1 Mo	0.288	5.62	>20.0	0.0848	1.93	4.69
5 Mo	0.721	~9.80	>9.80	0.143	2.01	(0.0287) ^(a)
10 Mo	0.722	10.1	--	0.153	1.50	--
25 Mo	0.098	1.25	--	0.0254	0.329	--
1 Cr	0.512	4.43	~28.8	0.162	1.51	8.01
5 Cr	0.578	5.00	~39.2	0.188	1.49	9.20
10 Cr	0.450	3.53	~20.0	0.0981	0.900	6.11
25 Cr	0.0	0.45	5.0	1.07	0.145	0.920
35 Cr	>5.0	>5.0	<0.05	0.0902	(0.555) ^(a)	0.0449
1 V	0.081	3.54	~28.8	0.0222	0.990	6.70
5 V	0.064	1.94	~19.6	0.0124	0.508	4.21
10 V	0.016	1.37	~10.0	0.0106	0.344	2.20
25 V	0.144	0.65	1.0	0.0785	0.0801	0.127
1 Zr	0.128	5.00	10.0	0.0476	0.384	3.38
5 Zr	0.072	0.288	--	0.0268	0.0638	--
10 Zr	0.128	0.338	0.180	0.0346	0.0232	0.0119
25 Zr	0.512	0.0	0.180	0.0870	0.0644	0.0659
35 Zr	<0.012	<0.012	<0.012	0.0	0.0	0.0120
1 W	0.900	11.6	46.4	0.118	1.82	8.40
5 W	0.785	14.2	>100.0	0.115	1.81	8.02
10 W	0.900	>20.0	>20.0	0.0902	2.00	(0.709) ^(a)
25 W	<0.004	8.4	2.92	0.0	2.01	5.09
1 Ta	0.049	4.05	39.7	0.0217	1.10	10.9
5 Ta	0.064	3.54	>20.0	0.0246	1.09	(9.42) ^(a)
10 Ta	0.169	2.05	>20.0	0.565	1.04	(1.31) ^(a)
25 Ta	0.400	5.41	25.0	0.116	1.34	6.40

TABLE 5. (Continued)

Alloy Content (Balance Niobium), a/o	Contamination-Rate Coefficient, K, at Indicated Temperature, 10^{-4} cm ² per hr			Diffusion-Rate Coefficient, D, at Indicated Temperature, 10^{-4} cm ² per hr		
	600 C	800 C	1000 C	600 C	800 C	1000 C
0.2 Mn	0.325	3.20	>20.0	0.198	1.30	(11.2)(a)
1 Mn	0.225	4.81	>20.0	0.131	1.74	(5.70)(a)
5 Mn	0.225	4.60	>20.0	0.104	1.63	(5.96)(a)
0.2 Fe	0.400	4.05	>20.0	0.159	1.48	(13.4)(a)
1 Fe	0.361	9.27	>29.0	0.0988	2.09	(7.28)(a)
5 Fe	0.169	6.05	>20.0	0.0411	1.68	(2.98)(a)
0.2 Co	0.256	5.62	>20.0	0.123	1.95	(11.6)(a)
1 Co	0.578	>20.0	>100.0	0.166	1.13	(9.21)(a)
5 Co	0.485	>20.0	>20.0	0.158	(0.100)(a)	(1.77)(a)
0.2 Ni	0.072	2.74	>20.0	0.0590	0.788	(6.48)(a)
1 Ni	0.081	1.57	>20.0	0.0215	0.394	(0.346)(a)
5 Ni	1.90	3.87	>20.0	0.107	0.780	(2.04)(a)
0.2 Al	0.256	11.2	>20.0	0.146	2.84	(14.1)(a)
1 Al	0.169	9.00	>20.0	0.134	2.92	(1.18)(a)
5 Al	0.169	3.39	>20.0	0.104	0.790	(8.20)(a)
0.2 Si	0.169	1.93	>20.0	0.0398	0.613	0.411
1 Si	0.016	>20.0	>20.0	0.0341	3.20	19.7
5 Si	0.783	>100.0	>100.0	0.562	3.80	18.4

(a) Specimen contaminated from opposite side, giving falsely high baseline hardness. D-values not used in Arrhenius-type plots.

Figure 18 shows Arrhenius-type plots of diffusion-rate coefficient, D , against reciprocal temperature for niobium and the niobium-titanium system. The activation energy for diffusion of oxygen in niobium-titanium alloys was calculated from Figure 18 to be 30,800 cal per mole, which is in good agreement with 29,000 cal per mole found for contamination by oxygen for the same alloys. These values are somewhat higher than the activation energy of 24,900 cal per mole found for diffusion of oxygen in pure niobium⁽⁵⁾, as shown in Figure 18.

It was possible to correlate oxygen-diffusion rates in most of the other alloy systems by Arrhenius-type plots, also. These data are given in Figures 19 through 27. Molybdenum, silicon, and zirconium were not correlated because of excessive scatter in the data, and, in the data presented, it was also not possible to correlate all compositions. At higher binary concentrations, marked deviations from the family of curves established were often noted. In these cases the points are plotted, but not utilized in the Arrhenius curves.

In addition, a source of error is evident in a number of the systems from failure of the hardness-penetration curve to reach the base-alloy hardness. This appears in Figures 11 through 16, where it can be seen in a number of instances that oxygen diffusing from the opposite side of the specimen reached the center, meeting oxygen diffusing from the side on which measurements were taken, so that the entire specimen was contaminated. Calculations based on this type of data result in false diffusion coefficients. In these cases, the coefficients have been reported in parentheses in Table 5, and are not included in the Arrhenius plots.

The Arrhenius plots show that chromium, titanium, and vanadium additions inhibit oxygen diffusion in niobium. Nickel also has a slight effect, 1.0 a/o nickel alloys having the best resistance to oxygen diffusion of the binaries added in 0.1 to 5.0 a/o amounts. They are roughly equivalent to a 5-10 a/o titanium alloy. The 0.1 and 5.0 a/o nickel alloys do not support the behavior of 1.0 a/o nickel. Activation energies for oxygen diffusion for all of the systems plotted are summarized in Table 6. Elements added in major quantities, which form extended solid solutions with niobium, raise the activation energy compared with pure niobium except for chromium. The minor addition elements have activation energies close to pure niobium.

The diffusion of oxygen in pure niobium and in selected promising diffusion-resistant alloys is also compared in Figures 28, 29, and 30 by use of Equation (5). The alloys chosen for comparison were niobium-25 a/o titanium, niobium-25 a/o vanadium, niobium-35 a/o zirconium, and niobium-35 a/o chromium. Values of the diffusion coefficient, D , were taken from Table 5. Exposure time was chosen as 10 hr, and the

alloys were compared at 600, 800, and 1000 C. Values of the function $\frac{H_m - H}{H_m - H_0}$ were chosen from 0.2 to 0.95, and substituted with the constants in Equation (5) to find diffusion depth. $\frac{H - H_0}{H_m - H_0}$, which is equal to $1 - \frac{H_m - H}{H_m - H_0}$, was then plotted against depth for the various temperatures.

The data of Figures 28 through 30 show that addition of 35 a/o zirconium prevents oxygen diffusion more than any other alloying addition at all temperatures. At 600 and 800 C, no diffusion was found for this alloy. At 600 C, 25 a/o titanium also decreases diffusion, but 25 a/o vanadium and 35 a/o chromium have no effect. At 800 and 1000 C,

FIGURE 18. OXYGEN-DIFFUSION RATES IN NIOBIUM⁽⁵⁾ AND NIOBIUM-TITANIUM ALLOYS

FIGURE 19. OXYGEN-DIFFUSION RATES IN NIOBIUM-CHROMIUM ALLOYS

FIGURE 20. OXYGEN-DIFFUSION RATES IN NIOBIUM-VANADIUM ALLOYS

FIGURE 21. OXYGEN-DIFFUSION RATES IN NIOBIUM-TUNGSTEN ALLOYS

FIGURE 22. OXYGEN-DIFFUSION RATES IN NIOBIUM-TANTALUM ALLOYS

FIGURE 23. OXYGEN-DIFFUSION RATES IN NIOBIUM-MANGANESE ALLOYS

FIGURE 24. OXYGEN-DIFFUSION RATES IN NIOBIUM-IRON ALLOYS

FIGURE 25. OXYGEN-DIFFUSION RATES IN NIOBIUM-COBALT ALLOYS

FIGURE 26. OXYGEN-DIFFUSION RATES IN NIOBIUM-NICKEL ALLOYS

FIGURE 27. OXYGEN-DIFFUSION RATES IN NIOBIUM-ALUMINUM ALLOYS

TABLE 6. ACTIVATION ENERGIES FOR OXYGEN
DIFFUSION FROM AIR IN NIOBIUM-
RICH BINARY ALLOYS

Alloy System	Activation Energy, Q , cal per mole
Pure niobium	24,900 ^(a)
Niobium-titanium	30,800
Niobium-chromium	21,300
Niobium-vanadium	31,600
Niobium-tantalum	35,100
Niobium-tungsten	24,400
Niobium-manganese	23,000
Niobium-iron	26,600
Niobium-cobalt	21,700
Niobium-nickel	24,000
Niobium-aluminum	28,000

(a) See Reference (5).

FIGURE 28. COMPARATIVE OXYGEN-DIFFUSION HARDENING OF NIOBIUM AND NIOBIUM ALLOYS IN AIR AT 600 C

FIGURE 29. COMPARATIVE OXYGEN-DIFFUSION HARDENING OF NIOBIUM AND NIOBIUM ALLOYS IN AIR AT 800 C

FIGURE 30. COMPARATIVE OXYGEN-DIFFUSION HARDENING OF NIOBIUM AND NIOBIUM ALLOYS IN AIR AT 1000 C

all of the alloying additions have a marked effect. As temperature increases, the effect of vanadium increases relative to titanium additions, which are most effective at lower temperatures.

CONCLUSIONS

Conclusions from the experimental work on the effect of binary alloying on the air oxidation and contamination of niobium metal at 600, 800, and 1000 C are as follows:

- (1) Binary additions of titanium decrease the oxidation rate of niobium. The oxidation resistance improves with increasing titanium content up to at least 25 a/o titanium. The present data appear to show that niobium-titanium alloys oxidize in a linear manner like pure niobium. Chromium, molybdenum, and vanadium additions also reduce the oxidation rate of niobium. Optimum oxidation resistance is found at 25 to 35 a/o chromium, 5 a/o molybdenum, and 5 to 10 a/o vanadium for these binary alloys. Niobium-35 a/o zirconium alloys show a reduced oxidation rate compared with pure niobium, at temperatures of 600 and 800 C.
- (2) Binary additions of up to 25 a/o tantalum and tungsten give no significant improvement in oxidation resistance. Binary additions up to 5 a/o of aluminum, beryllium, boron, cobalt, iron, manganese, nickel, and silicon do not significantly increase or decrease the oxidation rate of niobium metal.
- (3) Alloying additions of up to 35 a/o titanium reduce internal contamination of niobium by oxygen significantly. Within this range, increasing titanium content increases the contamination resistance for all temperatures. Alloys with up to 35 a/o zirconium also showed improved contamination resistance at all temperatures. The niobium-35 a/o zirconium alloy was exceptional. At 1000 C, niobium-35 a/o chromium possesses equal or better contamination resistance than the best titanium alloys and is equal to the 30 a/o zirconium alloy. Vanadium additions also produce some improvement in contamination resistance.
- (4) Alloy additions of up to 25 a/o molybdenum, tantalum, and tungsten, and up to 5 a/o aluminum, cobalt, iron, manganese, nickel, and silicon were found to result in negligible improvement in contamination resistance.
- (5) Diffusion-rate constants for oxygen diffusion were determined from the contamination data for most of the alloys studied. Zirconium alloys show the most resistance to oxygen diffusion; 35 a/o zirconium shows a zero diffusion rate at 600 and 800 C, and a very low rate at 1000 C. Titanium additions also reduce oxygen diffusion, and 25 to 35 a/o titanium is nearly as effective as 35 a/o zirconium. Niobium-25 a/o vanadium and niobium-35 a/o chromium alloys also significantly reduce oxygen-diffusion rates, vanadium becoming increasingly effective with increasing temperature.

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