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Argonne National Laboratory

AN EXPLORATORY STUDY OF THE BEHAVIOR
OF NIOBIUM- AND VANADIUM-BASE ALLOYS
IN OXYGEN-CONTAMINATED SODIUM

by

Harry A. Levin and Sherman Greenberg

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AN EXPLORATORY STUDY OF THE BEHAVIOR OF NIOBIUM- AND VANADIUM-BASE ALLOYS IN OXYGEN-CONTAMINATED SODIUM

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ABSTRACT

Niobium- and vanadium-base alloys were exposed to oxygen-contaminated sodium at 650°C in a series of exploratory studies. The purpose of these studies was to determine if, based on corrosion (i.e., weight-change) data, any alloys in these systems may be suitable as fuel jacketing in sodium-cooled reactors operating at approximately 650°C. The tests of the niobium and vanadium alloys showed that vanadium alloys have markedly superior corrosion resistance. At oxygen concentrations below approximately 15 ppm, V-20 w/o Ti was the best alloy tested. The corrosion resistance of V-20 w/o Ti, as indicated by low weight changes, is sufficient to warrant additional study of behavior in a sodium environment to determine the usefulness of the alloy as a fuel-jacketing material.

I. INTRODUCTION

Since breeding reactors are an essential component of a viable nuclear-reactor power industry, plutonium must be extensively used as a fuel material. Metallic fuels are preferable to ceramic fuels on the basis of heat-transfer properties and considerations of nuclear physics; but many serious problems must be solved before metallic fuels can be used.

When the program discussed in this report was initiated, metallic fuels that contained plutonium were regarded as incompatible with the materials expected to have adequate corrosion resistance in reactor-grade sodium at 650°C, i.e., the stainless steels and nickel-base superalloys. Requirements of compatibility with fuels and high strength in the region of 650°C essentially restricted the choice of jacketing materials to the refractory metals and their alloys.

Nuclear and economic considerations, as applied to central-station power reactors, eliminated all but niobium, vanadium, and possibly, chromium alloys. Since the technology of chromium alloys was relatively

undeveloped, attention in the initial stages of the work has been restricted to alloys based on niobium and on vanadium. Availability of tubing, and good behavior in other liquid-metal systems made Nb-1 w/o Zr the tentative choice as the reference jacketing for plutonium-alloy fuel. The purpose of the phase of the investigation discussed in this report was to determine if any otherwise acceptable niobium- or vanadium-base alloy was, in fact, potentially useful in sodium of reactor quality at temperatures up to 650°C.

II. EXPERIMENTAL PROCEDURE

Samples were exposed in a forced-flow loop of Type 304 stainless steel. The operating temperature in the loop, which contained 26 liters of sodium, was 650°C. The samples were suspended in a test chamber upstream of zirconium (turnings) getter material. Rectangular coupons approximately 10 by 30 by 1.5 mm were exposed at a flow rate of 15 cm/sec. To ensure a uniform surface finish, the samples were wet-ground on abrasive papers through 600 grit before exposure in the loop.

Sodium samples for oxygen analysis were obtained by filling a stainless steel dip tube, which was an integral component of the sample-holder structure. Samples were analyzed by use of the mercury amalgamation technique.

Corrosion samples to be weighed were cleaned of adhering sodium and loose corrosion product by washing with alcohol and by brushing. Microhardness traverses were accomplished with a Leitz Mini-Load Tester. Bend ductility was evaluated at room temperature by stressing the test coupons in compression along the largest dimension until the coupons fractured or were bent 180°.

III. RESULTS AND DISCUSSION

A. Preliminary Tests in Low-oxygen Sodium

In 1960, the Reactor Engineering Division undertook a program to evaluate experimental niobium-base (fabricated at Battelle) and vanadium-base (fabricated at Armour Research Foundation) alloys as potential jacket materials for EBR-II fuels. Sheet samples, 200-250 μ thick, were exposed to flowing sodium (61 cm/sec) at 650°C for 21 days. Oxygen concentration was controlled by the use of uranium as a getter. The reported oxygen concentration was 1-5 ppm by weight. This concentration was estimated from the change in hardness of tantalum tabs and confirmed by visual inspection of uranium tabs (i.e., no visible tarnish produced) exposed to the sodium during the test. Sample evaluation was limited to measurement of

weight change and visual (macroscopic) inspection of the surfaces at the end of the test. These results are summarized in Table I.¹ These samples have been subjected to a more extensive evaluation, including metallographic examination, microhardness measurements, and chemical analysis.

TABLE I. Some Results of Exposure of Niobium- and Vanadium-Base Alloys to Low-oxygen Sodium at 650°C for 21 days

Material	Weight Change, mg/cm ²	Appearance
Unalloyed niobium	-0.23	Dull, dark, adherent coating.
Nb-1.84 w/o Cr (with weld)	+0.02	Weld area dull metallic; remainder dull, dark, adherent coating.
Nb-1.84 w/o Cr	±0.00	Dull, heavy discoloration.
Nb-3.21 w/o Cr	±0.00	Bright metallic; small discolored areas.
Nb-4.33 w/o Zr	+0.01	Dull metallic; some discoloration.
Nb-4.33 w/o Zr (with weld)	-0.09	Weld area dull metallic, hairline crack; remainder dull, discolored.
Nb-4.33 w/o Zr	-0.07	Dull metallic, some discoloration.
Nb-20 w/o Ti-4.28 w/o Cr	+0.23	Dull, iridescent tarnish.
Nb-20 w/o Ti-4.28 w/o Cr (foil)	-	Dull, iridescent tarnish; severely embrittled, disintegrated on handling.
Nb-20.5 w/o Ti-4.28 w/o Cr (with weld)	+0.29	Weld area dull metallic; remainder dull metallic with dark tarnish.
Nb-20.5 w/o Ti-4.28 w/o Cr	-0.28	Dull metallic, dark tarnish.
Nb-5 w/o Mo	-0.03	Bright metallic.
Nb-1 w/o V	+0.21	Covered with dull, black adherent coating.
Nb-3 w/o V	-0.06	Covered with dull, dark gray adherent coating.
Nb-5 w/o V	-0.07	Covered with dull, light adherent coating.
Nb-5.3 w/o V	-0.10	Dull metallic with adherent dark coating.
Unalloyed vanadium	-0.16	Bright metallic light gray spots.
V-10 w/o Ti-1 w/o Ta	-	Dull metallic; severely embrittled, disintegrated on handling.
V-10 w/o Ti-1 w/o Nb	+0.11	Dull metallic with adherent light gray coating.
V-10 w/o Ti-3 w/o Nb	+0.21	Dull metallic with adherent gray coating.
V-10 w/o Ti-3 w/o Nb (welded; cold-rolled)	+0.18	Dull metallic with adherent gray coating.
V-10 w/o Ti-3 w/o Ta	+0.14	Dull metallic with adherent gray coating.
V-10 w/o Ti-3 w/o Ta (welded; cold-rolled)	+0.27	Bright metallic with adherent gray coating.
V-5 w/o Ti-20 w/o Nb	+0.05	Dull metallic.
V-5 w/o Ti-20 w/o Nb (welded; cold-rolled)	+0.19	Dull metallic with adherent gray coating.

1. Niobium-base Alloys

The Nb-1.84 w/o Cr and Nb-4.33 w/o Zr samples showed no structural changes, but the edges of transverse sections were more resistant to chemical etching than the centers of the sections. Microhardness measurements showed a hardness gradient from edge to center, with the maximum hardness at the edges. Microhardness data for material exposed to sodium and for specimens that were vacuum-annealed at 650°C for 21 days are shown in Figs. 1 and 2. The center hardness of the specimens exposed to sodium was the same as the hardness of the annealed material.

Fig. 1. Effect of Low-oxygen Sodium on Hardness of Nb-1.84 w/o Cr

Fig. 2. Effect of Low-oxygen Sodium on Hardness of Nb-4.33 w/o Zr

A microhardness traverse of Nb-5 w/o Mo exposed to the low-oxygen sodium showed no hardness gradient across the sample. The sodium-tested specimen was slightly softer than the as-rolled material, an indication that some stress relief had occurred at the test temperature. Oxygen concentrations of as-rolled and sodium-tested samples of Nb-4.33 w/o Zr and Nb-5 w/o Mo are shown in Table II.

TABLE II. Effect of Exposure to Low-oxygen Sodium on Oxygen Content of Some Niobium-base Alloys

Material	Oxygen Content, ppm by weight	
	As-rolled	Sodium-tested ^a
Nb-4.33 w/o Zr	60-76	1090-1130
Nb-5 w/o Mo	190-206	270-282

^aSurface film removed.

The oxygen concentration near the surface, particularly of the Nb-4.33 w/o Zr, was probably much higher than the reported overall value.

No solubility data for oxygen in these alloys are available. The solubility of oxygen in unalloyed niobium at 600°C is 3000 ppm by weight.²

The mechanical properties of niobium are sensitive to the interstitial elements oxygen, carbon, nitrogen, and hydrogen. Bend tests have been performed on as-received and sodium-tested samples of Nb-1.84 w/o Cr, Nb-4.33 w/o Zr, and Nb-5 w/o Mo. Specimens with and without welds were tested. Welded specimens were compressed with the weld in the direction of loading; i.e., the weld was parallel to the long axis of the specimen.

The welded, as-rolled Nb-1.84 w/o Cr specimen cracked at the weld, but the base (nonheat-affected) material did not crack and survived a 180° bend. An examination at a magnification of 10X showed yielding of the base material. In the sodium-tested sample, fracture initiated in the weld section and propagated across the entire sample. The specimen failed in a brittle manner. The as-rolled Nb-1.84 w/o Cr specimen (without weld) survived a 180° bend. The sodium-tested sample fractured upon initiation of compression.

The welded Nb-4.33 w/o Zr sample exhibited the same behavior as the welded niobium-chromium sample in that the as-rolled specimen survived a 180° bend, while the sodium-tested sample failed in a brittle manner upon application of compression. The as-rolled and sodium-tested unwelded niobium-zirconium samples failed in a brittle manner, but the sodium-tested sample failed at a much smaller bend angle. The cracking of the unwelded sample is believed to have been caused by factors related to sample geometry. Tested and untested Nb-5 w/o Mo specimens survived a 180° bend without fracture.

2. Vanadium-base Alloys

The results of oxygen analyses and hardness- and weight-change measurements are shown in Table III. Each of the three alloys showed a distinct surface layer approximately 10 μ thick. Adjacent to this was a darkly etched layer, approximately 40 μ thick, which contained a second phase. This typical structure is illustrated for the V-5 w/o Ti-20 w/o Nb alloy in Fig. 3.

TABLE III. Effect of Exposure to Low-oxygen Sodium at 650°C for 21 days on Vanadium-base Alloys

Material	Weight Gain, ^a mg/cm ²	Oxygen Concentration, ppm by weight ^b		Hardness (DPH, 100-g Load)					
				Edge			Center		
		As-rolled	Exposed	As-rolled	Exposed	Annealed ^c	As-rolled	Exposed	Annealed ^c
V-10 w/o Ti-3 w/o Nb	0.21	665	1400	240	650	200	240	190	200
V-10 w/o Ti-3 w/o Ta	0.27	570	1800	240	450	200	240	195	200
V-5 w/o Ti-20 w/o Nb	0.05	530	1200	275	680	245	275	235	245

^aData repeated from Table I for completeness (21-day exposure).

^bBulk sample concentration. Average of two analyses.

^cAt 650°C for 23 hr in vacuum.

38101

Etched: 40% HNO_3 , 20% HF , 40% H_2O

640X

Fig. 3. V-5 w/o Ti-20 w/o Nb Exposed to Low-oxygen Sodium at 650°C for 21 days

An electron-diffraction study of the exposed V-5 w/o Ti-20 w/o Nb sample to determine the identity of the surface layer was unsuccessful. X-ray powder patterns of the surface layer showed the presence of two phases. One set of diffraction lines corresponded to the base material (V-5 w/o Ti-20 w/o Nb); the other could not be indexed on the basis of any of the simple oxides of the alloy constituents.

Microhardness measurements showed the edge hardness of the exposed specimens to be much greater than the center hardness. This is attributed to oxygen pickup. Since the oxygen data in Table III represent the average concentration for the entire sample, hardness data indicate a higher surface-oxygen concentration. The hardness data also indicate that some stress relief occurred at the test temperature. No tests of bend ductility were performed on the vanadium-alloy samples because of insufficient material.

B. Screening Tests in Zirconium-gettered Sodium

The niobium- and vanadium-base alloys fabricated at Argonne were exposed to zirconium-gettered sodium at 650°C in the loop described previously. The niobium- and vanadium-base alloy samples were tested at the same time, thus ensuring the validity of comparative evaluations. Samples were tested in various metallurgical conditions. Table IV summarizes the conditions of heat treatment.

The amalgamation technique of analysis for oxygen in the sodium yielded values in excess of 100 ppm by weight, but the results of subsequent

experiments, which included the use of more sophisticated sampling and analytical techniques, have led to the conclusion that the oxygen concentration in the sodium for all experiments described in this section was, in fact, less than 15 ppm by weight.

TABLE IV. Heat Treatment of Niobium- and Vanadium-base Alloys

Material	Stress-relief Temperature, ^a °C	Recrystallization Temperature, ^a °C
Unalloyed niobium	800	1100
Nb-5 w/o Mo	800	1100
Nb-10 w/o Ti	650	1100
Nb-10 w/o Ti-5 w/o Zr	600	1100
Nb-18 w/o Ti-4 w/o V	600	1050
Nb-3 w/o Mo-9 w/o Ti	600	1100
Nb-10 w/o W-2.5 w/o Zr	950	1250
Unalloyed vanadium	650	900
V-10 w/o Ti	650	900
V-20 w/o Ti	650	900

^aVacuum-annealed at 10^{-6} Torr for 2 hr.

1. Niobium-base Alloys

The behavior of a group of cold-rolled niobium-base alloys is summarized in Table V. As indicated, all alloys had high rates of metal loss. In addition, the Nb-1 w/o Zr, Nb-5 w/o Zr, Nb-5 w/o Mo, and Nb-2.37 w/o Cr samples were extensively split at the edges (as shown in Fig. 4).

TABLE V. Behavior of Cold-rolled Niobium-base Alloys in Zirconium-gettered Sodium at 650°C

Material	Exposure Time, days	Weight Loss, mg/cm ²	Equivalent Metal Loss ^a	
			cm	mils
Nb-39 w/o V-1 w/o Ti	7	17.8	2.38×10^{-3}	0.934
Nb-39 w/o V-1 w/o Ti	13	17.9	2.38×10^{-3}	0.94
Nb-39 w/o V-1 w/o Ti	14	22.8	3.04×10^{-3}	1.2
Nb-1 w/o Zr	7	85.0		
Nb-1 w/o Zr	14	62.2		
Nb-5 w/o Zr	7	51.4		
Nb-5 w/o Zr	14	37.3		
Nb-5 w/o Mo	13	11.5		
Nb-5 w/o Mo	14	28.7		
Nb-2.4 w/o Cr	13	5.5		

^aCalculated for samples that maintained reasonable integrity. Any remaining oxide film assumed negligible.

Fig. 4. Niobium-base Alloys Exposed to Zirconium-gettered Sodium at 650°C

Microhardness measurements across transverse sections of the specimens showed that the profiles of Nb-1 w/o Zr and Nb-5 w/o Mo had a constant hardness increase (about 30 DPH units center to edge), and the Nb-39 w/o V-1 w/o Ti samples had very steep hardness gradients at the surface. The Nb-2.37 w/o Cr sample showed a shallow hardness gradient from edge to center, the edge hardness being 50 DPH harder than that at the center.

Table VI summarizes the effect of metallurgical condition on a group of niobium-base alloys. These samples, with the exception of niobium and Nb-10 w/o Ti, showed varying degrees of intergranular attack. The most extreme example was that of the recrystallized Nb-10 w/o W-2.5 w/o Zr sample (as shown in Fig. 5).

The greater weight loss of recrystallized samples of Nb-10 w/o Ti-5 w/o Zr and Nb-10 w/o W-2.5 w/o Zr alloys is due to extensive grain-boundary attack and consequent physical loss of many grains, but the effect of recrystallization is not uniformly pronounced for all the alloys tested.

Microhardness measurements across transverse sections of the samples showed various profiles, but there were no distinct differences between the hardness profiles of stress-relieved and recrystallized samples.

TABLE VI. Effect of Heat Treatment and Alloying on Behavior of Niobium-base Alloys in Zirconium-gettered Sodium at 650°C with 15-cm/sec Flow Rate

Material ^a	Exposure Time, days	Weight Loss, mg/cm ²	Equivalent Metal Loss ^b	
			cm	mils
Unalloyed niobium	9	12.5	1.47×10^{-3}	0.59
Unalloyed niobium	9	15.8	1.97×10^{-3}	0.77
Nb-5 w/o Mo (SR)	7	13.0		
Nb-5 w/o Mo (Rx)	7	10.1		
Nb-10 w/o Ti-5 w/o Zr (SR)	7	4.0		
Nb-10 w/o Ti-5 w/o Zr (Rx)	7	18.8		
Nb-18 w/o Ti-4 w/o V (SR)	7	11.8		
Nb-18 w/o Ti-4 w/o V (Rx)	7	15.4		
Nb-10 w/o W-2.5 w/o Zr (SR)	7	3.1		
Nb-10 w/o W-2.5 w/o Zr (Rx)	7	8.9		
Nb-3 w/o Mo-9 w/o Ti (SR)	7	17.0		
Nb-3 w/o Mo-9 w/o Ti (Rx)	7	14.9		
Nb-10 w/o Ti (SR) ^c	9	3.0		
Nb-10 w/o Ti (Rx) ^c	9	1.3		

^aSR = stress-relieved; Rx = recrystallized.

^bCalculated for samples that maintained reasonable integrity. Corrected for oxygen pickup in the metal.

^cLower oxygen concentration in sodium than in preceding tests.

38097

Etched: 40% HNO₃, 20% HF, 40% H₂O

200X

Fig. 5. Recrystallized Nb-10 w/o W-2.5 w/o Zr Exposed to Zirconium-gettered Sodium at 650°C for 7 days

2. Vanadium-base Alloys

A group of vanadium-titanium alloys was exposed simultaneously with the unalloyed niobium listed in Table VI. Table VII summarizes the results.

TABLE VII. Effect of Heat Treatment on Behavior of V-10 w/o Ti and V-20 w/o Ti in Zirconium-gettered Sodium at 650°C with 15-cm/sec Flow Rate for 9 days

Material ^a	Weight Loss, mg/cm ²	Equivalent Metal Loss ^b	
		cm	mils
V-10 w/o Ti (SR)	0.97	2.8×10^{-2}	0.11
V-10 w/o Ti (Rx)	0.83	2.3×10^{-2}	0.088
V-20 w/o Ti (SR)	0.10	2.2×10^{-2}	0.087
V-20 w/o Ti (Rx)	0.11	2.5×10^{-2}	0.095

^aSR = stress-relieved; Rx = recrystallized.

^bCorrected for oxygen pickup in the metal.

The data in Tables VI and VII show that V-10 w/o Ti and V-20 w/o Ti lose approximately an order of magnitude less weight than is apparently typical for niobium-base alloys exposed under identical conditions.

X-ray powder patterns were taken of a nonadherent corrosion product from the vanadium-titanium specimens. The lines in the X-ray pattern correspond to $\text{VO}_{0.9}$. The presence of titanium in the oxide (in approximately the same composition as the metal) was demonstrated by chemical analysis.

A second group of vanadium and vanadium-titanium alloy samples was exposed simultaneously with the Nb-10 w/o Ti samples described in Table VI. The results are shown in Table VIII. In contrast to

TABLE VIII. Effect of Heat Treatment and Titanium Additions on Behavior of Vanadium in Zirconium-gettered Sodium at 650°C with 15-cm/sec Flow Rate for 9 days

Material ^a	Weight Gain, mg/cm ²	Material ^a	Weight Gain, mg/cm ²
Unalloyed vanadium ^b (SR)	0.466	V-10 w/o Ti (SR)	0.315
Unalloyed vanadium ^b (Rx)	0.493	V-10 w/o Ti (Rx)	0.334
Unalloyed vanadium ^c (SR)	0.568	V-20 w/o Ti (SR)	0.076
Unalloyed vanadium ^c (Rx)	0.558	V-20 w/o Ti (Rx)	0.096

^aSR = stress-relieved; Rx = recrystallized.

^b1070 ppm by weight oxygen in vanadium before test.

^c200 ppm by weight oxygen in vanadium before test.

the vanadium alloys that lost weight (Table VII), similar vanadium alloys (Table VIII) gained weight. The niobium-titanium alloys (Table VI) lost appreciably less weight than most of the other niobium alloys listed. Subsequent work showed that the oxygen concentration of the sodium was lower for the samples described in Table VIII than for the samples listed in Table VII.

Heat treatment had no effect on the corrosion behavior of the specimens tested. The effect of differences in initial oxygen concentration in the vanadium samples was small. The vanadium samples with lower initial oxygen concentration gained slightly more weight than the high-oxygen samples. The most probable reason for the difference is the greater concentration gradient for diffusion of oxygen in the metal of the initially low-oxygen sample.

Photomicrographs of vanadium, V-10 w/o Ti, and V-20 w/o Ti after 9 days of exposure to hot gettered sodium are shown in Figs. 6-8, respectively. The hardened layer at the surface of the vanadium-titanium samples is metallographically evident and is a result of differences in the mechanical polishing and etching characteristics of the alloys related to the amount of oxygen in solution. The oxygen-contaminated region is visibly thicker for the V-10 w/o Ti sample than for the V-20 w/o Ti sample. The unalloyed-vanadium hardness gradient is much less steep; this effect is presumably caused by more uniform distribution of the oxygen. An oxygen-contaminated region is not visible metallographically.

45643

Etched: 40% HNO_3 , 30% HF , 40% H_2O

600X

Fig. 6. Unalloyed Vanadium Exposed to Zirconium-gettered Sodium at 650°C for 9 days

45642

Etched: 40% HNO_3 , 20% HF , 40% H_2O

600X

Fig. 7. V-10 w/o Ti Exposed to Zirconium-gettered Sodium at 650°C for 9 days

45644

Etched: 40% HNO_3 , 20% HF , 40% H_2O

800X

Fig. 8. V-20 w/o Ti Exposed to Zirconium-gettered Sodium at 650°C for 9 days

Comparative microhardness traverses for the vanadium, V-10 w/o Ti, and V-20 w/o Ti samples listed in Table VIII are shown in Fig. 9. The hardness measurements were made with the Knoop diamond indenter at a load of 15 g. The data are plotted as a normalized hardness function, where H is the measured hardness at a given distance from the surface, H_0 is the base hardness of the uncontaminated metal, and H_s is the extrapolated surface hardness. It is evident that the titanium additions markedly reduce the depth of the contaminated region in the metal.

Fig. 9. Normalized Hardness Profiles of Vanadium and Vanadium-Titanium Alloys Exposed to Zirconium-gettered Sodium at 650°C for 9 days

of oxygen concentration up to a 6 a/o (2 w/o). From the observed gains in weight of the vanadium samples, and from values of D determined for oxygen in unalloyed vanadium, either by other investigators or in this ANL work, the maximum surface concentration was calculated to be less than 4 a/o (1.2 w/o). Therefore, the assumption of a linear relation between hardness and oxygen concentration in these experiments is justified for unalloyed vanadium. No hardness data as a function of oxygen concentration are available for the vanadium-titanium alloys, but the assumption of linearity for these alloys does not appear unreasonable.

Table IX shows the results of chemical analyses of vanadium alloys and niobium for oxygen and carbon before and after exposure. The major impurity picked up by these alloys is oxygen.

The relatively low increase in oxygen in the niobium is more a reflection of high metal loss through nonadherent oxide formation than of a low diffusion coefficient in the metal.

If increases in hardness caused by the solution of oxygen in the metal are assumed to be linear with the oxygen concentration, the profiles of oxygen concentration in the metal can be ascertained by measuring the profiles of hardness. The diffusion coefficients of oxygen in the various materials can be determined from these profiles.

Seybolt and Sumsion³ found the hardness of unalloyed vanadium to be a linearly increasing function

TABLE IX. Oxygen and Carbon Pickup of Vanadium-Titanium Alloys and Niobium Exposed to Zirconium-gettered Sodium at 650°C for 9 days

Material	Initial Bulk Concentration, ppm by weight		Final Bulk Concentration, ppm by weight	
	O	C	O	C
V-10 w/o Ti	800	486	2240	-
V-20 w/o Ti	800	435	1482	509
Unalloyed niobium	65	38	222	28

The method for the calculation of the diffusion coefficient of oxygen in vanadium and the vanadium-titanium alloys involved a solution to Fick's Second Law for two different sets of boundary conditions. For V-10 w/o Ti and V-20 w/o Ti, oxygen had not diffused to the center of the samples, and the concentration of oxygen at the center remained constant at the initial concentration. For the unalloyed vanadium, oxygen had diffused to the center, resulting in an increased concentration of oxygen at the center of these samples. In both cases, the surface concentrations of oxygen in the metal were assumed to have remained constant for the duration of each experimental run.

For V-10 w/o Ti and V-20 w/o Ti, the boundary conditions were satisfied for diffusion into a semi-infinite sheet with a constant concentration of the diffusing species at the surface.

The solution to Fick's Second Law for these boundary conditions is

$$\frac{C - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{X}{2\sqrt{Dt}}\right).$$

where

C = concentration of the diffusing species at a given distance from the surface,

C_0 = original concentration of the diffusing species in the metal,

C_s = concentration of the diffusing species at the surface,

X = distance from the surface,

and

t = time.

The assumption that the hardness is a linear function of the oxygen concentration, $H = KC$, results in the following equation:

$$\frac{H - H_0}{H_s - H_0} = \operatorname{erfc}\left(\frac{X}{2\sqrt{Dt}}\right),$$

where H , H_0 , and H_s have been previously defined.

The following equation gives D as a function of position and hardness values:

$$D = \frac{X^2}{4t \left[\operatorname{erfc}^{-1}\left(\frac{H - H_0}{H_s - H_0}\right) \right]^2}.$$

The diffusion coefficients for oxygen in V-10 w/o Ti and V-20 w/o Ti at 650°C were calculated, from the data in Fig. 9, to be 4×10^{-12} and 7×10^{-13} cm²/sec, respectively.

The calculation of the diffusion coefficient of oxygen in unalloyed vanadium required a solution to Fick's Second Law under conditions in which the surface concentration was maintained constant and diffusion had occurred over a region of finite dimensions. The solution for these boundary conditions can be found in Crank⁴ and is in the form of an infinite series. Combining this solution with the assumption that the hardness is a linear function of the oxygen concentration results in the following equation:

$$\frac{H - H_0}{H_s - H_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left[-\frac{D(2n+1)^2}{4L^2} \right] \cos \frac{(2n+1)\pi X}{2L},$$

where L is the half-thickness.

The data for vanadium from Fig. 9 were used in estimating the diffusion coefficient by means of a graphical solution of the above equation. The value of D for oxygen in vanadium was $8.0 \pm 1.9 \times 10^{-11}$ cm²/sec at 650°C.

The assumptions used for calculation of the diffusion coefficients are restated as follows:

- a. The hardness of the metals varies linearly with the concentration of dissolved oxygen.
- b. The concentration of oxygen at the surface of the metal was constant during the entire exposure. This implies that the oxygen concentration in the liquid sodium did not change throughout the duration of the experiment.
- c. The diffusivity is independent of oxygen concentration.

The diffusion coefficient of oxygen in unalloyed vanadium at 650°C was calculated to be 5.84×10^{-10} cm²/sec from the internal-friction measurements of Stanley and Wert.⁵ Powers and Doyle⁶ obtained a value of 1.77×10^{-9} cm²/sec at the same temperature from measurements of internal friction and anelastic relaxation. One would not necessarily expect the values determined from internal-friction measurements at very low oxygen concentrations to be the same as those determined from an experiment in which the average oxygen concentration was much higher. These values are reported to form a basis of comparison between values of diffusion coefficients determined at two levels of oxygen concentration.

IV. CONCLUSIONS

Under identical exposures to oxygen-contaminated sodium, vanadium-base alloys are superior to niobium-base alloys. Additions of titanium to vanadium in the range of 0-20 w/o substantially improve the corrosion behavior of vanadium, presumably by lowering oxygen-diffusion rates in the alloys. Of the alloys tested, V-20 w/o Ti had the best corrosion resistance, but adequate corrosion resistance of this material has not been demonstrated in systems of practical interest. Additional vanadium alloys and the sodium environment are being studied.

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REFERENCES

1. V. J. Rutkauskas, personal communication (Sept. 30, 1960).
2. W. Rostoker and A. S. Yamamoto, Trans. ASM 47, 1002 (1955).
3. A. U. Seybolt and H. T. Sumsion, Trans. AIME 197, 292 (1953).
4. J. Crank, The Mathematics of Diffusion, Oxford University Press, p. 45 (1956).
5. J. T. Stanley and C. A. Wert, Acta Met. 3, 107 (1955).
6. R. W. Powers and M. V. Doyle, J. Appl. Phys. 30, 514 (1959).