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EVALUATION OF NIOBIUM-VANADIUM ALLOYS FOR APPLICATION IN HIGH-TEMPERATURE REACTOR SYSTEMS

Compiled by:

T. K. Roche

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METALS AND CERAMICS

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T. K. Roche

OCTOBER 1965

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
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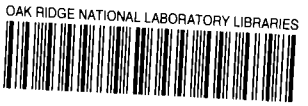

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EVALUATION OF NIOBIUM-VANADIUM ALLOYS FOR APPLICATION IN HIGH-TEMPERATURE REACTOR SYSTEMS

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ABSTRACT

Alloys in the niobium-vanadium system were evaluated for potential use in high-temperature reactor systems capable of long-time operation. These alloys were attractive because of their good tensile properties as reported by other investigators. Properties of immediate interest which were examined included fabricability, corrosion behavior in lithium, strength, weldability, aging response, and stability in high vacuums. The greatest emphasis was placed on alloys with about 40% V and small additions of titanium and zirconium. This concentration of vanadium has been shown to be near optimum for good tensile properties.

A complete evaluation of the alloys was not carried out because several drawbacks were uncovered early in the program. For example, difficulty was experienced in fabricating seamless tubing of the alloy Nb–39% V–1% Ti, and this same alloy was subject to metal losses by evaporation at elevated temperatures in high vacuums. The most disappointing result was the lack of creep strength at elevated temperatures. This report presents the results obtained to justify the conclusion that other niobium alloys presently available would be more satisfactory for this application.

INTRODUCTION

A nuclear reactor system capable of long-time high-temperature operation is being considered as the heat source for the generation of electric power for space applications Such a system would employ alkali metals as coolants and working fluids. For example, liquid lithium would flow through the reactor core, emerge, and transfer its heat by means of a heat exchanger to liquid potassium which would in turn be vaporized to operate a turbogenerator.

Reactor temperatures of interest are in the 1100 to 1370°C (2000 to 2500°F) range, which is considerably above the useful range for

conventional iron-, nickel-, and cobalt-base alloys. As an alloy base, niobium has many attractive properties which make fulfillment of the requirements placed on a material for the above application a distinct possibility. These requirements are that the material be:

1. fabricable into a variety of shapes, including tubing, plate, sheet, bar, and wire,
2. corrosion resistant to alkali metals,
3. weldable,
4. strong at elevated temperatures,
5. free from serious aging embrittlement,
6 not deleteriously affected by high vacuums.

To date, the alloy Nb–1% Zr, the first commercial alloy, has held the greatest interest for potential reactor applications of this type. Perhaps the most significant single disadvantage of this alloy is a lack of high-temperature strength, which restricts its use.

The development of advanced niobium alloys for use in the temperature range 1100 to 1370°C (2000 to 2500°F) is progressing. Emphasis is placed on improvement in strength properties consistent with good fabricability. The increased strength is achieved by precipitation hardening or solid-solution strengthening or a combination of the two techniques. Elements such as W, Mo, and V are used to provide solid-solution strengthening. Zirconium is the agent in dispersion-hardening, which is achieved by its reaction with residual oxygen and residual or intentionally added carbon.

Vanadium, which forms a continuous series of solid solutions with niobium,[1] has been found by Begley and Bechtold[2] to be one of the most potent elements for improving the tensile properties of niobium. This

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[1]H. A. Wilhelm, O. N. Carlson, and J. M. Dickerson, J. Metals 6, 915 (Aug. 1954).

[2]R. T Begley and J. H. Bechtold, J. Less-Common Metals 3, 1–12 (1961).

conclusion was also reached by Armour Research Foundation[3-6] from their extensive evaluation of vanadium alloys. Their work has shown that of the refractory metals (Nb, Ta, Mo, and W) added to vanadium, niobium was the most desirable for its effect on properties. Binary niobium-vanadium alloys exhibited a peak in tensile strength at 1100°C (2000°F) within the composition range of Nb–25 to 40% V. This peak resulted in a yield strength approximately 2 1/2 times greater than that shown by Nb–1% Zr at this temperature. Armour Research Foundation further found that a small addition of 0.5 to 1% Ti to an alloy of Nb–39% V slightly improved the 1100°C (2000°F) tensile strength of the binary composition. In fact, the alloy Nb–39% V–1% Ti was considered a very promising material by Armour from the standpoint of tensile strength, fabricability, and weldability.

The attractive properties of niobium-vanadium alloys as reported by these investigators led to the decision to include these alloys in a program for evaluating materials for application in lithium-cooled reactor systems. The evaluation procedure can be generally represented by the flow diagram shown in Fig. 1. This report describes the results of the various tests performed on the selected alloys within the framework of this program. However, work on this system was curtailed early in the program, due to the inadequacy of the creep properties. For this reason, the work reported here is not quite complete; for the most part, only indications of metallurgical behavior were obtained.

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[3] Improved Vanadium-Base Alloys (Summary Report), Armour Research Foundation ARF 2165-6 (1959).

[4] Improved Vanadium-Base Alloys (Final Report), Armour Research Foundation ARF 2191-6 (Dec. 27, 1960).

[5] Improved Vanadium-Base Alloys (Final Report), Armour Research Foundation ARF 2210-6 (Dec. 20, 1961).

[6] Pilot Evaluation of Vanadium Alloys (Bimonthly Report No. 1), ARF 2231-1 (Dec 11, 1961); (Bimonthly Report No. 2), ARF 2231-2 (Feb. 14, 1962); (Bimonthly Report No. 3), ARF 2231-3 (April 13, 1962); (Bimonthly Report No. 4), ARF 2231-4 (June 15, 1962); (Bimonthly Report No 5), ARF 2231-5 (Aug. 14, 1962); (Bimonthly Report No. 6), ARF 2231-6 (Oct 15, 1962) (Bimonthly Report No. 7), ARF-B231-7 (Dec. 14, 1962).

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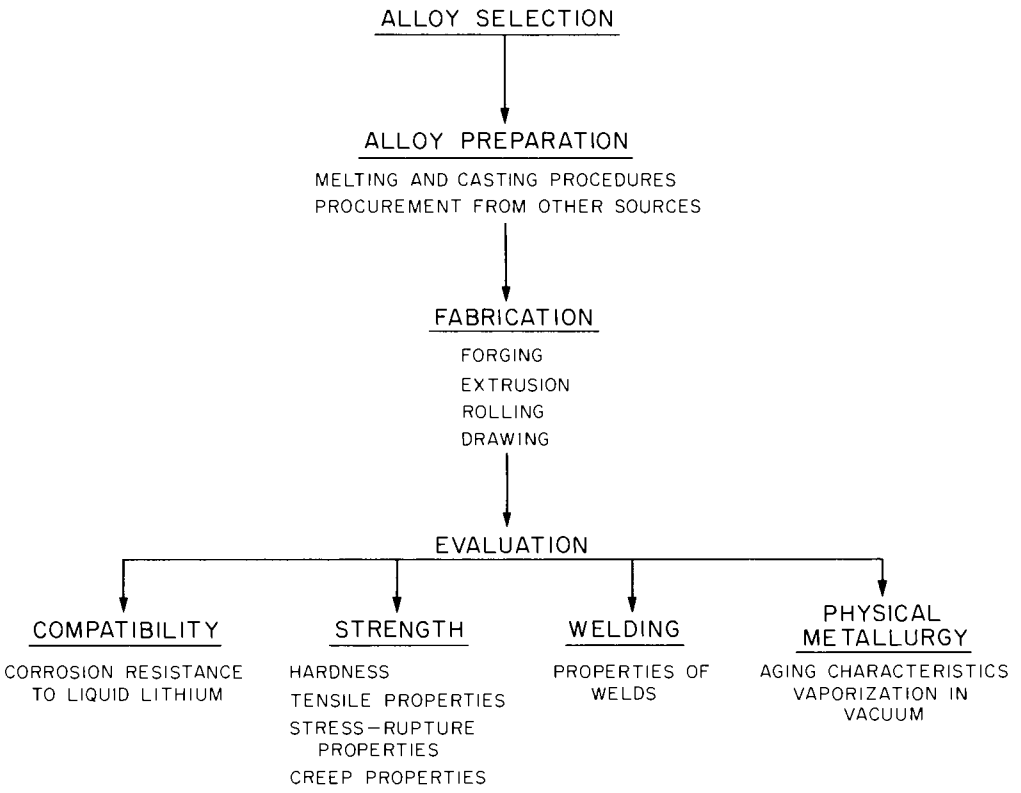

Fig. 1. A General Procedure for Evaluating Niobium-Vanadium Alloys.

ALLOY SELECTION

T. K. Roche

The specific alloy compositions selected for study are listed in Table 1. This selection was based on available property data. For example, the vanadium content of most of the alloys was between 30 and 50%, which reasonably encompassed the range of peak tensile strength, as will be shown later. The binary alloys were of interest in confirming this strength peak. From work done on pure niobium and the alloy Nb-1% Zr, it was found that zirconium enhanced corrosion resistance to lithium; therefore, this element was included as an alloying addition. As previously mentioned, Armour Research Foundation found that titanium additions were beneficial for slightly improving the tensile strength of an alloy containing about 40% V, thereby accounting for the interest of this element.

Table 1. Chemical Analyses and Fabrication Results Obtained on Niobium-Vanadium Alloys

Composition												Fabrication	
Nominal (wt %)				Analyzed (wt %)				Analyzed (ppm)				Attempted Fabrication by Cold Rolling	Results[a]
Nb	V	Zr	Ti	Nb	V	Zr	Ti	C	O	H	N		
99	1											No	
90	10			91.2	9.57	< 0.2		580	140	47	88	Yes	NT, C
80	20			80.3	19.6	< 0.2		200	150	17	180	Yes	T
70	30			70.2	29.8	< 0.2		230	190	20	150	Yes	T
60	40			59.4	39.7	< 0 1		320	290	< 1	150	Yes	T
50	50			49.9	49.2	< 0.1		290		3	170	Yes	T
40	60			40.7	59.3	< 0.2		300	330	21	190	Yes	T
30	70											Yes	T, C
20	80											Yes	NT, C
69.5	30	0.5		69.6	29.9	0.49		530	140	21	180	Yes	T, C
69	30	1.0										No	
68.5	30	1.5										No	
59.5	40	0.5		59.8	39.7	0.45		250	360	25	140	Yes	T, C
59	40	1.0		59.4	39.5	1.1		140	330	2	140	Yes	T, C
58.5	40	1.5										No	
49.5	50	0.5										No	
49	50	1.0										No	
48.5	50	1.5		49.7	48.8	1.4		680	220	27	280	Yes	T, C
69	30		1.0									No	
59	40		1.0	59.7	39.5	< 0.2	0.90	280	160	15	210	Yes	T, C
49	50		1.0									No	
68	30	1.0	1.0									No	
58	40	1.0	1.0	57.9	39.6	1.2	1.2	420	150	17	220	Yes	T, C
48	50	1.0	1.0[b]									No	
60	39		1.0[b]	60.2	Bal		1.35	260	270	4	130	c	

[a] Legend: T – twinned during rolling.
NT – did not twin during rolling.
C – cracked during rolling.

[b] Armour Research Foundation alloy.

[c] See FABRICATION, p. 7.

In addition to the alloys prepared at the Oak Ridge National Laboratory, material of the composition Nb–39% V–1% Ti was obtained from Armour. This material was supplied on a data exchange basis as the program at Armour had at that time reached a stage for evaluation of the properties of pilot size heats of several of their promising alloys. This alloy was used for seamless tubing fabrication and mechanical property studies in the ORNL program.

ALLOY PREPARATION

T. Hikido,[7] R. E. McDonald, C. F. Leitten, Jr.

ORNL Alloys

Prior to preparing the ORNL alloys, the vanadium and niobium melting stock were electron-beam melted to reduce their interstitial contents. The vanadium melting stock was in the form of arc-melted ingot with an interstitial analysis of 321 ppm C, 200 ppm O, 10 ppm H, and 280 ppm N. Electron-beam melting reduced the hydrogen and nitrogen contents but had little or no effect on the oxygen and carbon contents. The average interstitial analysis of four electron-beam melted ingots was 325 ppm C, 185 ppm O, 5 ppm H, and 36 ppm N. Significant losses of vanadium metal occurred in the electron-beam furnace. These losses amounted to about 22% of the initial ingot weight and were attributed to the relatively high vapor pressure of the metal, coupled with the high pumping capacity required for the electron-beam furnace.

Greater success was realized in purifying the niobium melting stock. The starting material was pressed pellets with an interstitial analysis of 100 ppm C, 1800 ppm O, 20 ppm H, and 580 ppm N. Approximately 500 g of pellets were electron-beam melted at one time, resulting in an ingot with an average analysis of 16 ppm C, 26 ppm O, 2 ppm H, and 50 ppm N. Niobium metal losses in the electron-beam furnace were notably less than those for vanadium, being on the order of 6% of the furnace charge.

Final preparation of the ORNL alloys was carried out by nonconsumable electrode-arc melting in a highly purified argon atmosphere. Under these conditions, the vanadium metal losses were much less than those

[7]Now with Pyromet, San Carlos, California.

encountered during electron-beam melting of the vanadium alone. The disk-type ingots prepared were 4 in. in diameter and 3/8 to 1/2 in. thick and weighed 500 to 600 g. Chemical analyses of the as-cast alloys, as shown in Table 1, indicated good control of the alloy composition, although some contamination with interstitial impurities was encountered.

Armour Alloy

The Armour alloy, Nb–39% V–1% Ti, was prepared by double consumable electrode-arc melting at Oregon Metallurgical Corporation. After melting, the ingot was about 6 in. in diameter and 11 in. long and weighed approximately 75 lb. The ingot was turned to 5.5 in. in diameter prior to fabrication. The interstitial analysis of the ingot, as shown in Table 1, was in good agreement with the predicted levels as obtained from the melting stock.

FABRICATION

D. O. Hobson, C. J. McHargue, C. F. Leitten, Jr., T. K. Roche

ORNL Alloys

The niobium-vanadium system is unique in its fabrication and deformation behavior. This system encompasses alloys that have high hardness and tensile strength compared to unalloyed niobium or vanadium, yet they are capable of being cold worked. Operative throughout most of the composition range is a twinning deformation, which apparently enhances fabricability.

Fabrication work per se on the indicated alloys in Table 1 was directed toward rolling the as-cast ingot forms into sheet specimens for alloy evaluation. After an initial homogenization treatment for 2 hr at 1200°C (2200°F), the niobium-vanadium binary alloys in the composition range of 20 to 70% V could be cold rolled to as much as 90% reduction in thickness without an intermediate anneal. These binary alloys were

characterized by an initial rapid work-hardening rate during which time profuse twinning occurred. This was followed by a slower, approximately linear increase as reductions above 20 to 25% were attained No twinning was evident at the higher reductions. Figure 2 illustrates these observations with data obtained from Nb–30% V and Nb–40% V. After 26% reduction in thickness, the hardness of both alloys was R_C40. The hardness and ductility of this system can probably be attributed to the twinning mechanism that is operative during rolling. This mechamism presumably allows a high stress to build up in the material but relieves it by twinning before fracture occurs The Nb–10% V and Nb–80% V alloys that did not twin during rolling cracked severely after approximately 10% reduction in thickness.

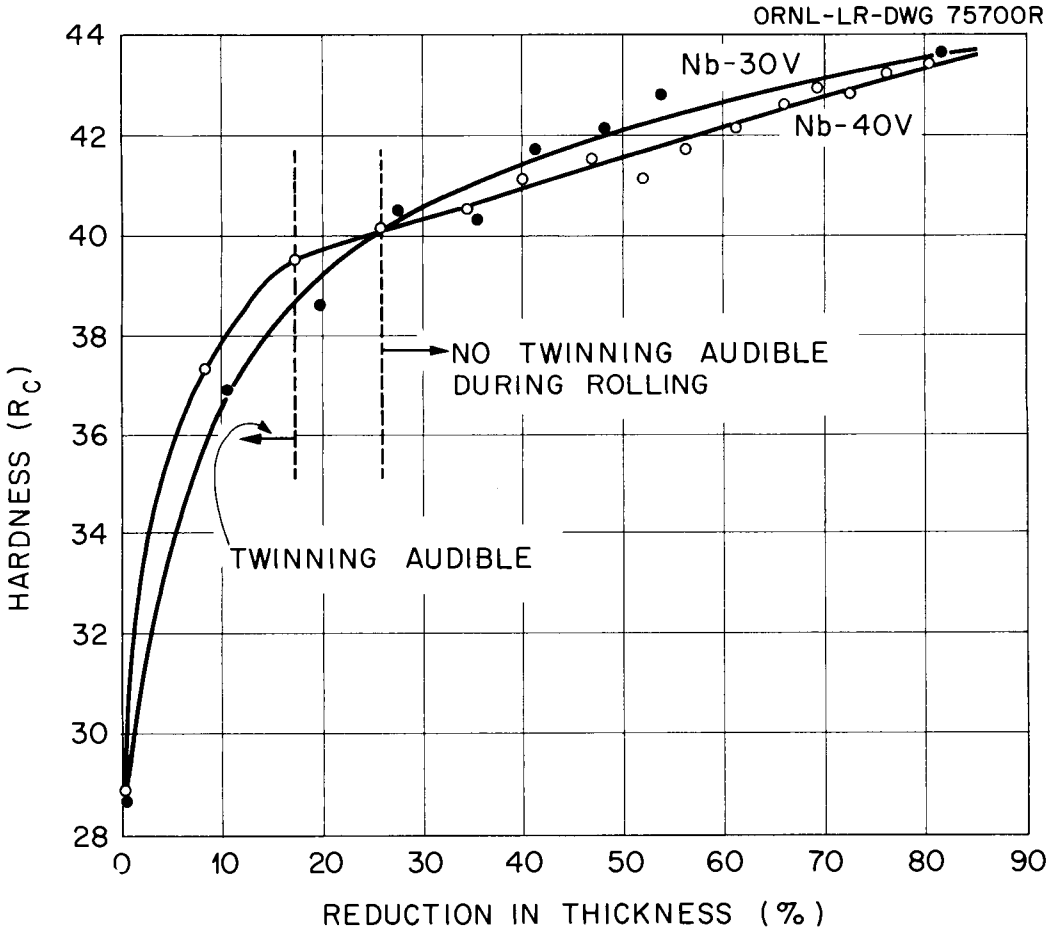

Fig. 2. Effect of Cold-Rolling Reduction on the Hardness of Nb–30% and Nb–40% V.

Metallographic examination of specimens reduced about 50% in thickness showed heavily distorted twin traces, which indicated that twinning preceded gross slip in this system.

The fabricated alloys containing zirconium and titanium listed in Table 1 were allowed to edge crack on rolling at room temperature to obtain work-hardening data. Intermediate annealing treatments would undoubtedly have eliminated or minimized this problem. These alloys also twinned and showed the same general work-hardening characteristics as previously presented in Fig. 2.

As a contribution to the technology of niobium-vanadium alloys, a more detailed study has been made of the twinning that occurs in the binary alloys.[8]

Armour Alloy

Fabrication, including extrusion and rolling, of the alloy Nb–39% V–1% Ti was performed at E. I. du Pont deNemours and Company, Inc. The 5.5-in.-diam ingot was canned and extruded to sheet bar 1.7 × 4 × 36 in. Extrusion was carried out at 1100°C (2000°F) at a ratio of 4:1. Glass was used for lubrication. Most of the material was then rolled to finish gage, but a small amount of extruded bar was retained.

For processing 0.050-in.-thick sheet, a piece of the extruded bar was warm rolled at 650°C (1200°F) to 0.3 in. thick, annealed at 1010°C (1850°F), cold rolled to 0.126 in. thick, reannealed, and cold rolled to 0.050 in. thick. Oak Ridge National Laboratory was supplied with a piece of the sheet stock, 7.5 × 8 × 0.050 in., for creep-rupture evaluation and a piece of bar stock 1.3 in. in diameter and 3.75 in. long (turned from the as-extruded bar) for the fabrication of seamless tubing.

Superior Tube Company attempted to convert the bar stock to seamless tubing after it was first vacuum annealed 1 hr at 1150°C (2100°F), then drilled and turned to 1.2-in.-OD × 0.238-in.-wall tubing. Difficulty was

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[8]D. O. Hobson, Deformation Twinning in the Columbium-Vanadium Alloy System, ORNL-3678 (Sept. 1964).

encountered throughout the processing of the tubing, and failure occurred at a size of 0.627-in.-OD × 0.046-in. wall, as shown in Fig. 3. The principal fabrication procedure up to the time of failure included alternate drawing and annealing operations as indicated in Table 2. All rod drawing operations with the exception of the first one were carried out at 315 to 370°C (600 to 700°F). For annealing, a double wrapper was placed around the tube — niobium foil adjacent to the tube, followed by iron foil. The vacuum level was 3×10^{-4} torr at temperature. The hardness survey following each annealing treatment indicated contamination of the tube as the annealed hardness continued to increase slightly with each heat treatment. This fact was corroborated by chemical analyses of specimens taken from the tube during the course of fabrication. Maximum increases of approximately 500 ppm C and 700 ppm O were found. It thus appears probable that contamination contributed to the difficulties experienced in fabrication of the tubing, but other factors such as incorrect reduction and annealing schedules should not be discounted.

Table 2. Summary of Procedure for Fabricating Nb–39% V–1% Ti Seamless Tubing

Operation	Size	Rockwell C Hardness
As-received bar	1.3-in. OD × 3.75-in. length	30/32
Drill and turn	1.2-in. OD × 0.238-in. wall	
Tube reduce (cold)	0.895-in. OD × 0.125-in. wall	41/43
Vacuum anneal 1 hr at 1100°C (2000°F)		35
Rod draw (cold)		42
Re-vacuum anneal 1 hr at 1100°C (2000°F)		37
Rod draw (warm)	0.725-in. OD × 0.075-in. wall	38/39
Vacuum anneal 1 hr at 1100°C (2000°F)		37
Rod draw (warm)	0.675-in. OD × 0.060-in. wall	40
Vacuum anneal 1 hr at 1100°C (2000°F)		
Rod draw (warm)	0.627-in. OD × 0.046-in. wall	Material failed

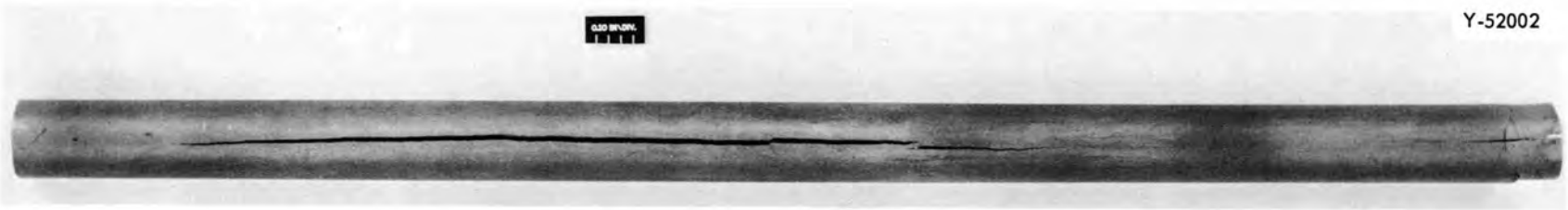

Fig. 3. Fabrication Failure in Nb—39% V—1% Ti Seamless Tubing.

LITHIUM CORROSION

J. R. DiStefano, E. E. Hoffman[9]

The use of liquid alkali metals as coolants and working fluids for high-temperature reactor systems can involve compatibility problems between the liquid metals and their containers.[10] For example, a severe type of corrosion interaction between refractory and alkali metals appears to occur as a result of the presence of oxygen as an impurity in the solid metal. It has been observed that oxygen in niobium can lead to very rapid penetration by lithium over a wide range of temperatures. The corrosive action by lithium involves penetration of the metal by lithium and the formation of a "corrosion" phase. This phase has not been identified but is suspected to contain lithium, oxygen, and niobium.

Major variables affecting the extent of lithium penetration were found to be oxygen concentration and temperature. Time was not considered a significant variable in the sense that the maximum depth of corrosion generally occurred in less than 1 hr. Although the mechanism of this corrosion process is not fully understood, it is proposed that the existence of oxygen-rich areas in grain boundaries or along crystallographic planes may result in lithium corrosion by the formation of a lithium-niobium-oxygen complex in these areas.

It has been suggested[11] that the development of corrosion-resistant niobium systems for the containment of lithium will depend ultimately on the addition to the base metal of an alloying element whose oxide is stable in lithium or at least stable in niobium. This hypothesis has been substantiated by results indicating oxygen-contaminated Nb–1% Zr shows no corrosion if the oxygen-to-zirconium atomic ratio does not exceed 2 and the alloy is properly heat treated prior to exposure to lithium.

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[9]Now with Space Power and Propulsion Section, Missile and Space Division, General Electric Co., Cincinnati, Ohio.

[10]J. R. DiStefano and E. E. Hoffman, Corrosion Mechanisms in Refractory Metal–Alkali Metal Systems, ORNL-3424 (Aug. 1963).

[11]E. E. Hoffman, The Effects of Oxygen and Nitrogen on the Corrosion Resistance of Columbium to Lithium at Elevated Temperatures, ORNL-2675, pp. 34–7 (Jan. 16, 1959) (classified).

With a background of corrosion information as cited above, the effect of oxygen on the corrosion resistance of Nb–40% V to lithium at 815°C (1500°F) was investigated. Specimens of Nb–40% V were oxidized at 1000°C (1832°F) at an oxygen pressure of 9×10^{-5} torr in a modified Sievert's apparatus. After oxidation, each specimen was homogenized for 2 hr at 1300°C (2375°F). The oxygen concentration in each specimen was determined by weight change measurements after oxidation and by vacuum-fusion analyses of samples cut from each specimen. Reasonably good correlation was obtained between the two methods as indicated in Table 3.

Table 3. Oxygen Concentration in Nb–40% V as Determined by Weight Change and Chemical Analyses

Specimen Number	Oxygen Concentration (ppm)		
	Weight Change	Chemical Analyses	Average
1	a	500	500
2	1000	900	950
3	1400	1300	1350
4	2500	2100	2300
5	4800	4200	4500

[a]As-received specimen; no oxygen added.

The specimens listed in Table 3 were then exposed to lithium in separate niobium containers for 100 hr at 815°C (1500°F), and the data obtained from these tests are summarized in Table 4. It may be seen that corrosion increased with increasing oxygen concentration. The metallographic appearance of four of the specimens after test may be seen in Fig. 4.

These results are, in general, similar to those observed for unalloyed niobium and therefore it is concluded that the addition of vanadium to niobium does not significantly alter its corrosion behavior in lithium. Under similar conditions the Nb–1% Zr alloy containing up to 3300 ppm O would be unattacked by lithium when appropriately heat treated.

Table 4. Effect of Oxygen Concentration in Nb–40% V on Its Corrosion Resistance to Lithium at 815°C (1500°F)

Specimen Number	Oxygen Concentration (ppm)		Change in Oxygen Concentration (ppm)	Metallographic Observations	
	Before[a] Test	After[b] Test		Depth of Attack (mils)	Intensity of Attack
1	500	300	–200	0	
2	950	750	–200	Complete[c]	Light
3	1350	750	–600	Complete	Moderate
4	2300	650	–1650	Complete	Moderate
5	4500	250	–4250	Complete	Heavy

[a]Average of weight change and chemical analysis.

[b]Chemical analysis.

[c]Specimen thickness: 0.060 in.

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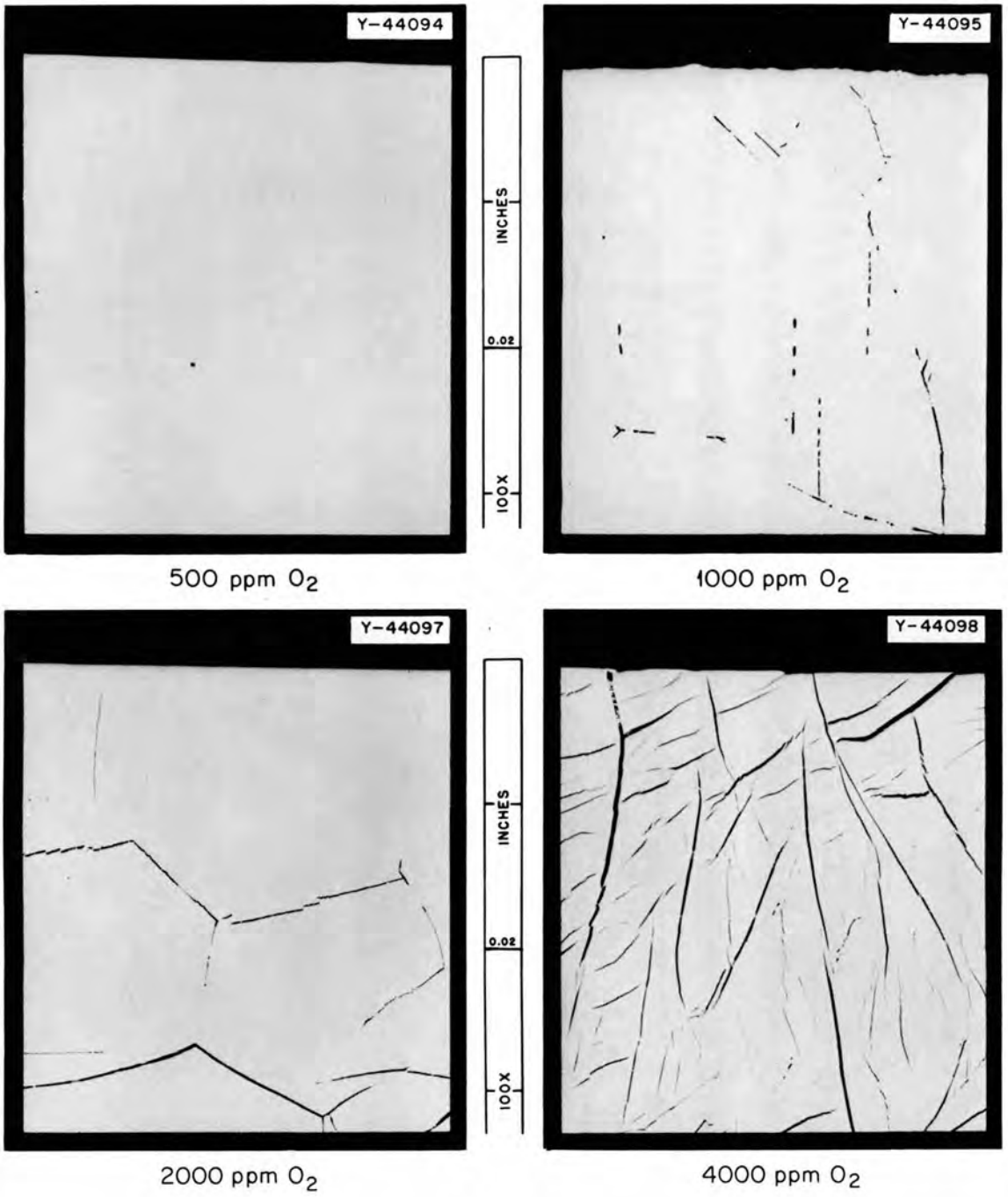

Fig. 4. Effect of Oxygen Concentration in Nb–40% V on its Corrosion Resistance to Lithium. Test conditions: 100 hr at 815°C (1500°F). As polished.

MECHANICAL PROPERTIES

G. Hallerman, R. J. Gray, R. L. Stephenson, H. E. McCoy,
J. R. Weir, T. K. Roche

Tensile Properties

Reference has already been made to the fact that alloys of the niobium-vanadium system exhibit good tensile properties at room and elevated temperatures. Typical tensile data for binary compositions at room temperature and 1100°C (2000°F), as determined by Armour, are shown in Table 5. A plot of the 1100°C (2000°F) tensile strength as a function of alloy composition is presented in Fig. 5, and the strength peak within the composition range Nb–25 to 40% V is readily apparent.

Table 5. Tensile Properties[a] of Niobium-Vanadium Binary Alloys at Room Temperature and 1100°C (2000°F)

Composition	Test Temperature (°C)	Ultimate Tensile Strength (psi)	Yield Strength (psi)	Elongation (%)
Nb–10% V	RT	117,400	96,500	20
	1100	46,000	42,500	48
Nb–15% V	1100	52,500	46,800	35
Nb–25% V	RT	142,500	128,000	12
	1100	61,700	53,400	32
Nb–40% V	RT	147,500	130,100	23
	1100	57,300	52,400	86
Nb–50% V	RT	168,000	163,500	2
	1100	41,200	37,400	5
Nb–60% V	RT	162,400	161,100	3
	1100	39,600	38,700	5
Nb–70% V	RT	110,900	92,400	25
	1100	44,300	40,200	69
Nb–80% V	RT	107,000	105,500	6
	1100	35,400	32,100	85

[a] B. R. Rajala and R. J. Van Thyne, "Vanadium-Columbium Alloys for 980°C (1800°F) to 1200°C (2200°F) Service," Paper presented at AIME High-Temperature Materials Conference, Cleveland, April 27, 1961.

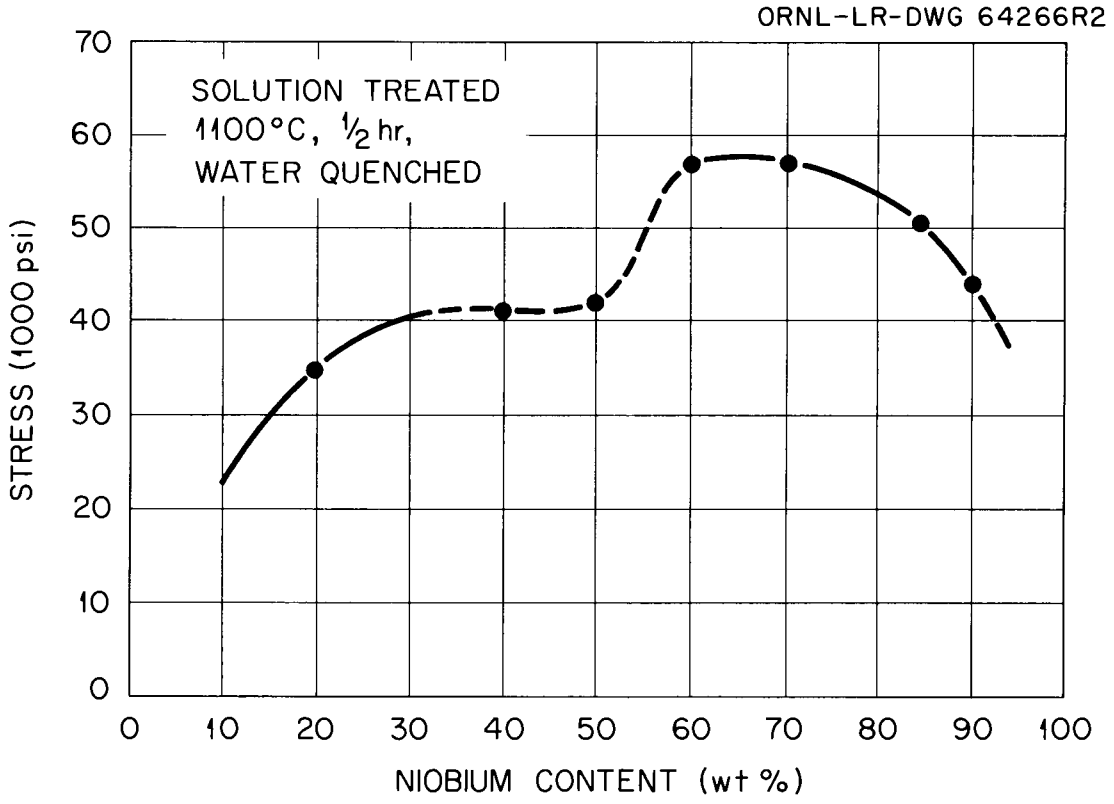

Fig. 5. Effect of Composition on the Tensile Strength of Niobium-Vanadium Binary Alloys at 1100°C (2000°F).

A comparison is made between the tensile properties of Armour's alloy Nb–39% V–1% Ti, other second-generation niobium alloys, and the alloy Nb–1% Zr in Table 6. The competitive tensile properties of niobium-vanadium alloys are clearly evident.

Table 6. Tensile Properties of Various Niobium Alloys at Room Temperature, 1100°C (2000°F), and 1200°C (2200°F)

Composition (wt %)	Test Temperature (°C)	Ultimate Tensile Strength (psi)	Yield Strength (psi)	Elongation (%)
Nb–39 V–1 Ti[a]	RT	151,000	129,700	23
	1100	59,100	53,400	87
	1200	37,800	32,300	114
Nb–5 Mo–5 V–1 Zr (B-66)[b]	RT	102,000	77,000	26
	1100	46,000	40,000	48
	1200	40,000	33,000	53
Nb–10 W–1 Zr–0.1 C (D-43)[b]	RT	88,000	73,000	19
	1100	43,000	39,000	16
Nb–10 W–2.5 Zr (Cb-752)[b]	RT	86,000	70,000	21
	1100	42,000	27,000	25
	1200	36,000	23,000	33
Nb–27 Ta–10 W–1 Zr (FS-85)[c]	RT	70,000	50,000	20
	1100	46,000	35,000	23
Nb–1 Zr[d]	RT	45,800	25,900	36
	1100	23,000	17,200	23
	1200	19,100	16,200	17

[a] Improved Vanadium-Base Alloys (Final Report), Armour Research Foundation ARF 2210-6 (Dec. 20, 1961).

[b] G. K. White and F. R. Cortes, Development of Procedures for Shape Rolling Columbium Alloys – Phase I Technical Progress Report, Aeronautical Systems Division – Air Force Systems Command (Wright Patterson Air Force Base) ASD 8-108 (June 1963).

[c] Mater. Design Eng. – Materials Selection Issue 56(5) (Mid-October 1962).

[d] Alloy Data Sheet, Columbium–0.75% Zirconium, Union Carbide Metals Company (Jan. 1, 1960).

Hot Hardness

To corroborate the strengthening effect of vanadium additions to niobium, hot-hardness measurements up to 1000°C (1832°F) were obtained on the ORNL-prepared binary alloys. The operation of the hot-hardness apparatus has been described previously.[12] As-cast specimens of the alloys containing 1, 10, 20, 30, and 50% V and a wrought specimen of the alloy containing 60% V were used for this study. The specimens were given a prior homogenization treatment for 2 hr at 1200°C (2200°F). The results shown in Fig. 6 reveal several things:

[12]George Hallerman and R. J. Gray, Equipment for Hardness Testing at Elevated Temperatures, ORNL-3448 (July 1963).

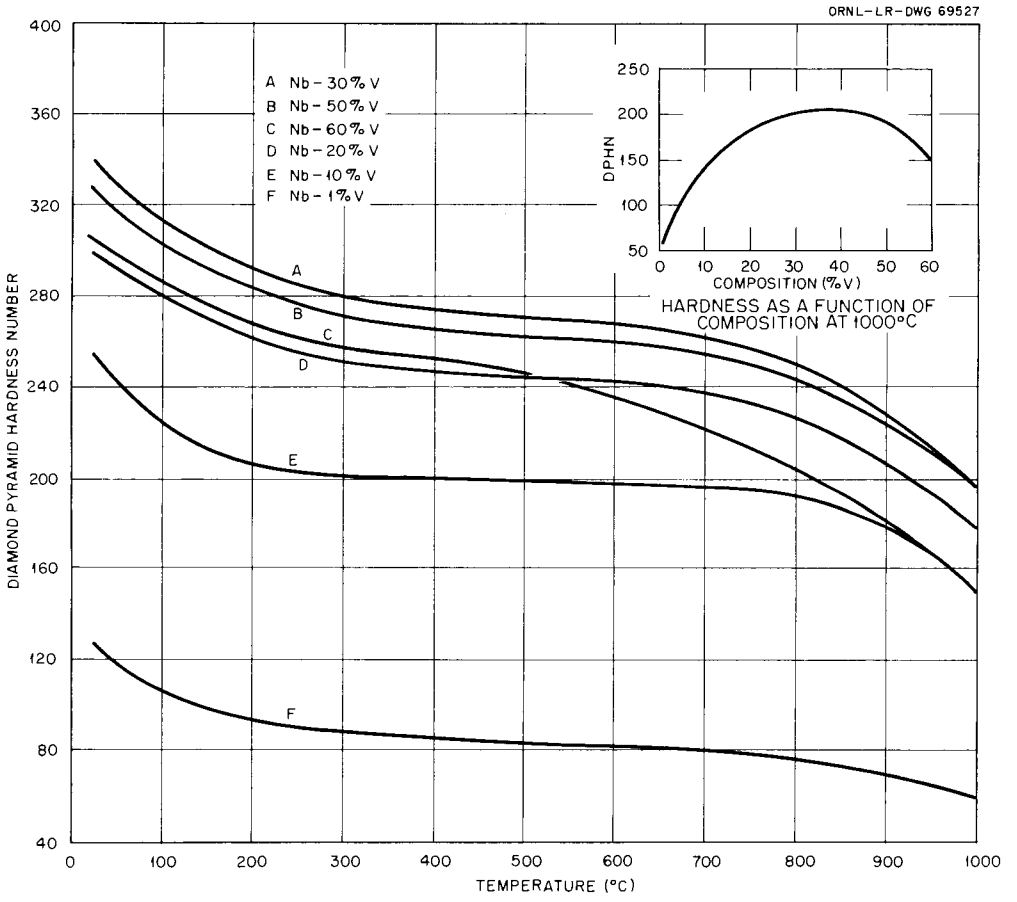

Fig. 6. Elevated-Temperature Hardness of Niobium-Vanadium Binary Alloys.

1. The hardness decreases relatively little with increase in temperature for all compositions tested.

2. The hardness increases with increasing vanadium content over the entire temperature range for alloys containing up to 30% V.

3. At 1000°C (1832°F) the hardness of Nb–60% V alloy is the same as that of Nb–10% V and lower than the hardness of the alloys containing 20, 30, or 50% V (hardness vs composition curve, Fig. 6 insert).

These results are in good agreement with the tensile data discussed previously.

Creep and Stress-Rupture Properties

The potential of niobium-vanadium alloys for long-time, high-temperature service becomes questionable when available stress and creep-rupture data are considered. These properties for niobium-vanadium alloys are inferior to those of other niobium-base alloys, as seen in Table 7.

Table 7. Stress-Rupture Properties of Various Niobium Alloys at 1100°C (2000°F)

Composition (wt %)	Stress for Rupture in 10 hr (psi)
Nb–39 V–1 Ti	~ 10,000[a]
Nb–27 Ta–10 W–1 Zr (FS-85)	25,000[b]
Nb–10 W–1 Zr–0.1 C (D-43)	23,000[b]
Nb–10 W–2.5 Zr (Cb-752)	22,000[b]
Nb–1 Zr	15,000[b]

[a] Improved Vanadium-Base Alloys (Final Report), Armour Research Foundation ARF 2210-6 (Dec. 20, 1961).

[b] G. K. White and F. R. Cortes, Development of Procedures for Shape Rolling Columbium Alloys – Phase I Technical Progress Report, Aeronautical Systems Division – Air Force Systems Command (Wright Patterson AirForce Base) ASD 8-108 (June 1963).

A qualitative assessment of the creep resistance of niobium-vanadium alloys was made by means of a cantilever-beam slow-bend test. This test procedure has been described elsewhere.[13] Figure 7 shows the deflection-time results for the alloys Nb–1% Zr, Nb–40% V, and Nb–40% V–1% Zr at 1200°C (2200°F) and an initial outer-fiber stress of 8000 psi. A lack of creep resistance by the niobium-vanadium alloys is indicated under these test conditions, even though there existed a wide difference in oxygen content between the alloys and the vacuum conditions were not equivalent for the three tests.

Because the creep properties of these alloys did not appear promising at 1200°C (2200°F), conventional creep-rupture tests were conducted at 870°C (1600°F) on the Armour alloy.

[13]T. K. Roche, Effect of Degree of Vacuum on the Slow-Bend Creep Behavior of Columbium–0.6% Zirconium at 1100°C, ORNL-3569 (June 1964).

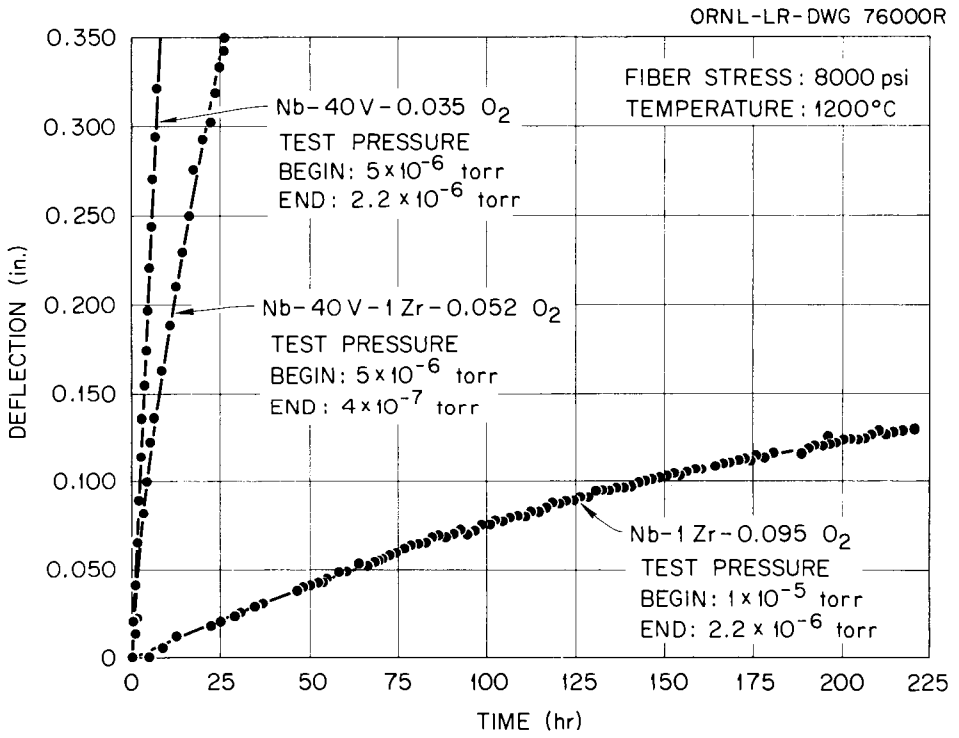

Fig. 7. Deflection-Time Curves for Nb–1% Zr, Nb–40% V, and Nb–40% V–1% Zr in a Cantilever-Beam Slow-Bend Test.

The as-received material was cold rolled to 0.040 in. thick and creep-rupture specimens were machined from this stock. Tests were conducted in a vacuum of approximately 1×10^{-6} torr at 870°C (1600°F) and stress levels of 6000, 8000, 10,000, and 12,000 psi with the material in the as-rolled condition.

The results are tabulated in Table 8 and are plotted in Fig. 8, where a comparison is made between these data and stress-rupture data[14] on cold-rolled Nb–1% Zr sheet tested at 980°C (1800°F). It can be seen that the rupture data for the two alloys are roughly equivalent for the 110°C (200°F) difference in test temperature. However, the rupture ductilities of Nb–39% V–1% Ti were greater than 150%. Realistically, a structural member would be regarded as having failed long before this elongation was reached. Thus, if stresses to produce 1 to 10% elongation were to be compared for the two alloys, the Nb–39% V–1% Ti composition would be shown in an even less favorable light.

[14]R. L. Stephenson and H. E. McCoy, Metals and Ceramics Div. Ann. Progr. Rept. May 31, 1963, ORNL-3470, p. 119.

Table 8. Creep-Rupture Properties of Nb–39% V–1% Ti at 870°C (1600°F)

Stress (psi)	Time for Indicated Creep (hr)					Secondary Creep Rate (%/hr)
	1%	2%	5%	10%	Rupture	
6,000	5.4	11.2	31.5	70.0	399.6	0.073
8,000	4.9	11.2	33.5	73.0	515.9[a]	0.16
10,000	0.35	0.9	9.6	33.6	395.9[a]	
10,000	2.4	5.6	15.4	32.3	245.4	0.3
12,000	1.3	3.4	10.5	23.0	80.4	

[a]Test discontinued.

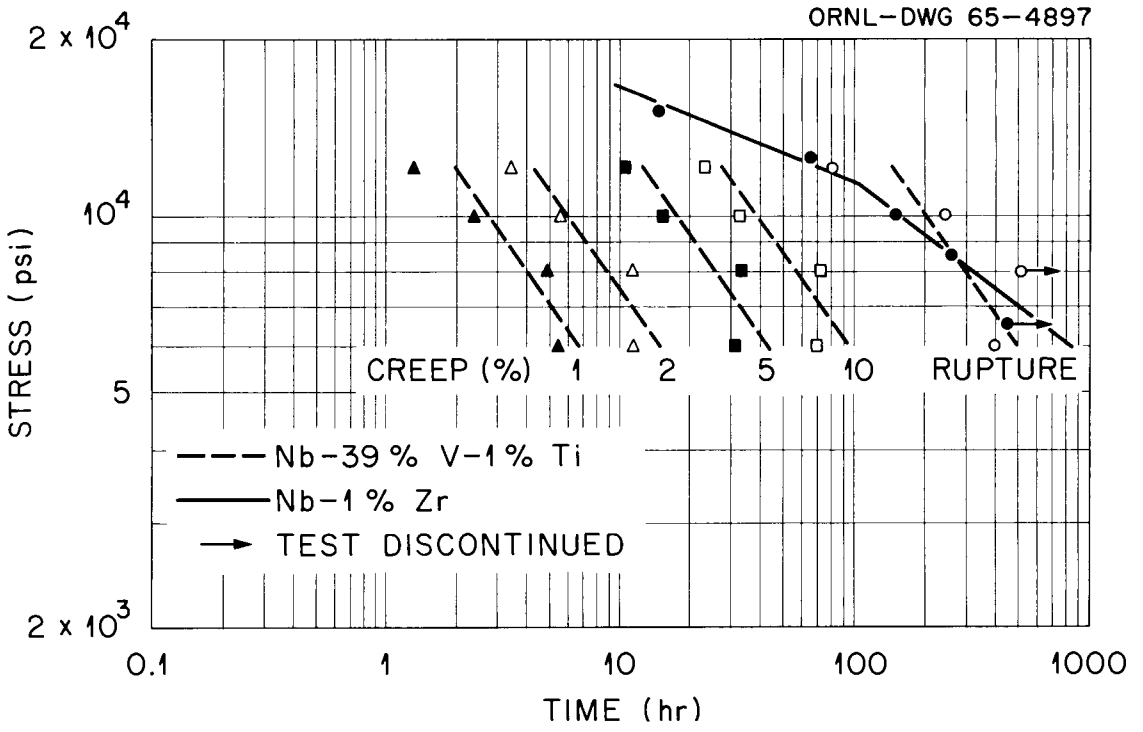

Fig. 8. Creep-Rupture Properties of Nb–39% V–1% Ti at 870°C (1600°F) and Rupture Properties of Nb–1% Zr at 980°C (1800°F).

WELDING

R. G. Gilliland and G. M. Slaughter

Welding tests were carried out by Armour on the composition Nb–40% V with good results. Annealed specimens of the alloy were butt welded by gas tungsten-arc techniques. Room temperature and 1100°C (2000°F) tensile and yield strengths of the weldments with no post-welding heat treatment were only slightly reduced over base-metal properties. Room temperature elongation (20%) of the welded specimen was good, whereas the 1100°C (2000°F) elongation (9%) was somewhat reduced from the elongation (31%) of the unwelded material at this temperature.

Armour found it possible for an annealed and gas tungsten-arc welded specimen of their Nb–39% V–1% Ti alloy to withstand a minimum bend of < 0.5 T. The same results were obtained on an annealed and unwelded specimen.

Welds in two ORNL alloys, Nb–30% V and Nb–50% V, were evaluated in room-temperature bend tests with the bend axis transverse to the welding direction. The alloys were first cold rolled to a thickness of about 0.040 in. and vacuum annealed for 2 hr at 1200°C (2200°F). A 2-in.-long, full-penetration, fusion weld was then made on specimens of each alloy. The Nb–50% V alloy welded satisfactorily, but the Nb–30% V alloy exhibited weld-metal cracking the full thickness of the specimen and for a distance of approximately one-half of the 2-in. length. (Work was terminated before the reason for the poor weldability of the Nb–30% V alloy was determined.)

Welds of these two niobium-vanadium alloys, including the sound portion of the cracked weld, were bend tested, and both specimens showed ductile behavior. Metallographic examination of the welds in the as-welded and the as-deformed conditions revealed the weld-metal structures shown in Fig. 9. The highly twinned structure for the as-deformed specimens is consistent with the findings made during the fabrication studies discussed earlier.

AGING

T. K. Roche

The aging effects observed for Nb–1% Zr which include increased tensile and yield strengths, decreased ductility, and correlative changes in hardness and microstructure, are the result of precipitation of ZrO_2 due to the restriction of the oxygen solubility in the presence of zirconium.[15] Thus, the tendency of a particular heat of the alloy to age was found to be predictable on the basis of the oxygen content and the annealing temperature.

Because of the above considerations, aging studies were performed on Nb–40% V and Nb–40% V–1% Zr alloys containing 350 and 380 ppm O, respectively, following solution heat treatment at 1600°C (2910°F). Specimens were aged for times up to 500 hr at 925°C (1700°F). Hardness

[15]D. O. Hobson, Aging Phenomena in Columbium-Base Alloys, ORNL-3245 (March 1962).

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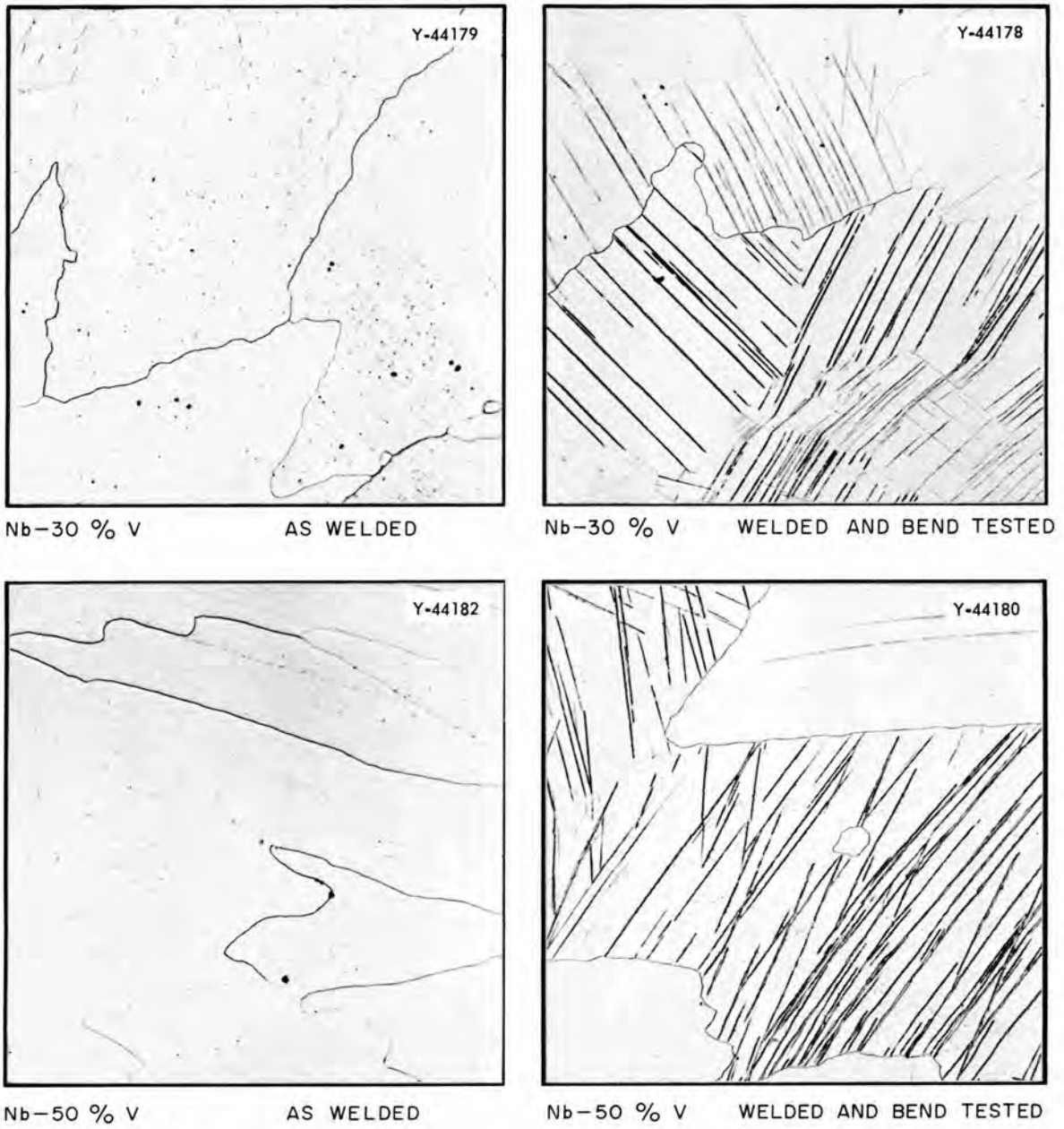

Fig. 9. Microstructure of Welds in Niobium-Vanadium Binary Alloys. Etchant: 10 p HNO_3 10 p H_2SO_4 25 p HF 50 p H_2O. 200×

and metallographic results are shown in Figs. 10 through 12. No indication of aging was noted for the binary alloy either metallographically or by hardness measurements. The Nb–40% V–1% Zr composition showed the precipitation of a pepper-like phase, presumed to be ZrO_2, which increased in amount with time. However, hardness evaluation of this alloy indicated not a strong aging response, but instead, rapid overaging.

These studies indicate that zirconium behaves similarly in niobium-vanadium alloys and niobium as far as restricting oxygen solubility. Additional work would be required to better establish the consequences of such an aging reaction in this alloy system.

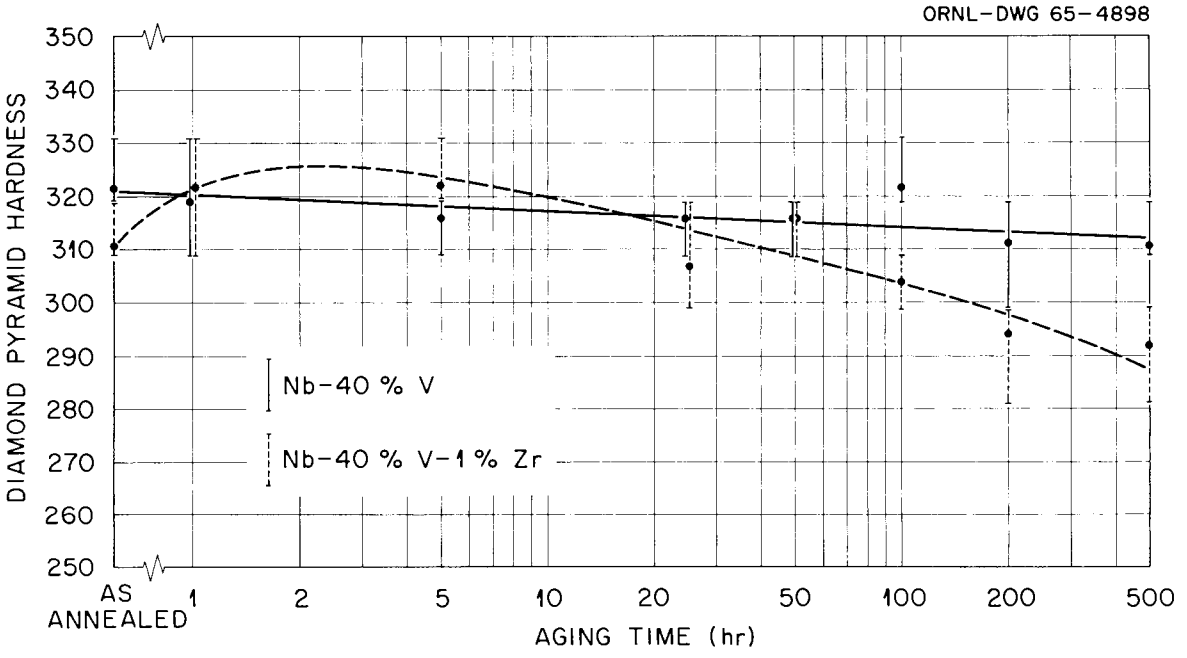

Fig. 10. Diamond Pyramid Hardness of Nb–40% V and Nb–40% V–1% Zr After Solution Annealing 2 hr at 1600°C (2910°F) and Aging at 925°C (1700°F).

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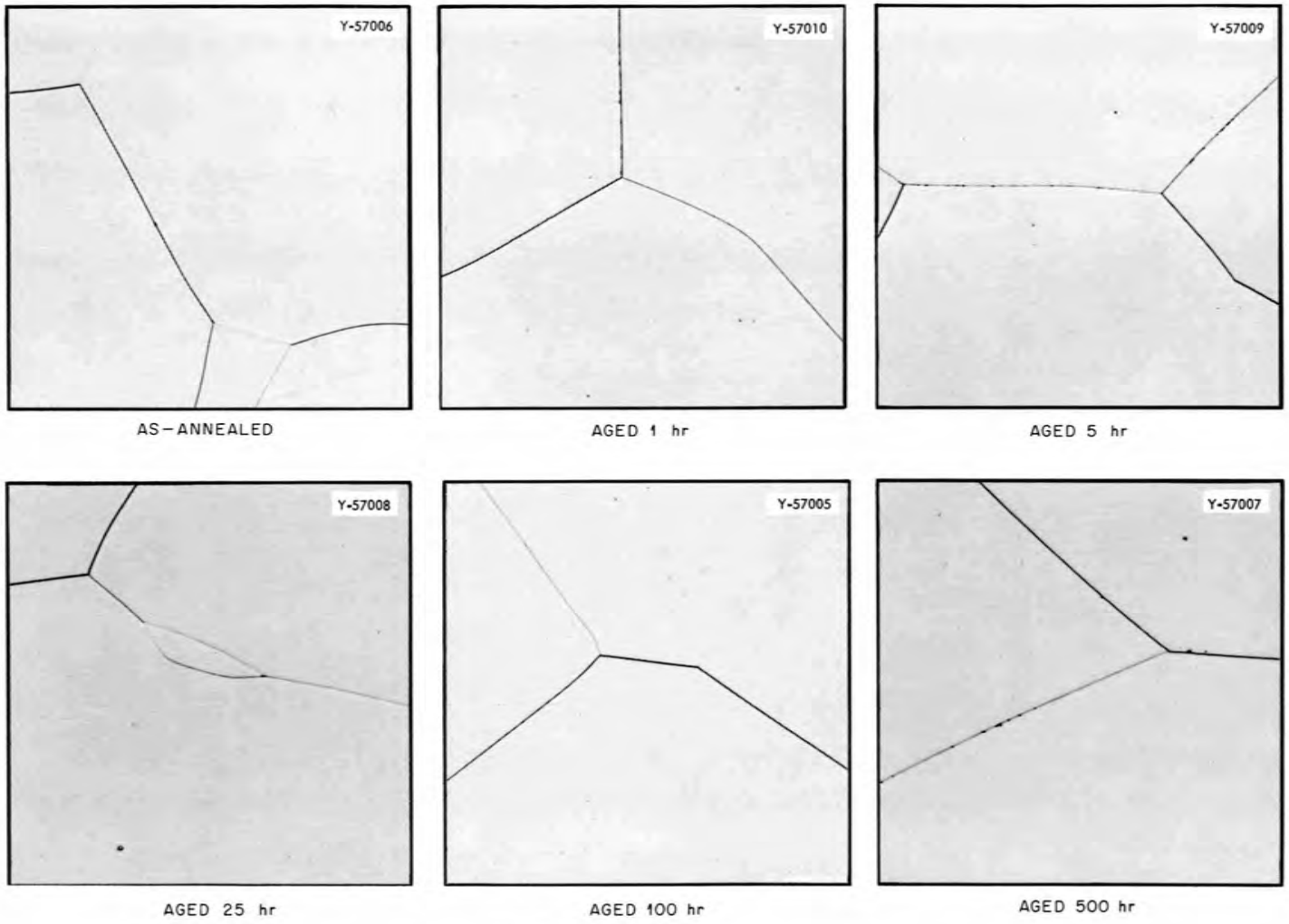

Fig. 11. Microstructures of Nb-40% V after Solution Annealing 2 hr at 1600°C (2910°F) and Aging at 925°C (1700°F). Etchant: 10 p HNO_3 10 p H_2SO_4 25 p HF 50 p H_2O.

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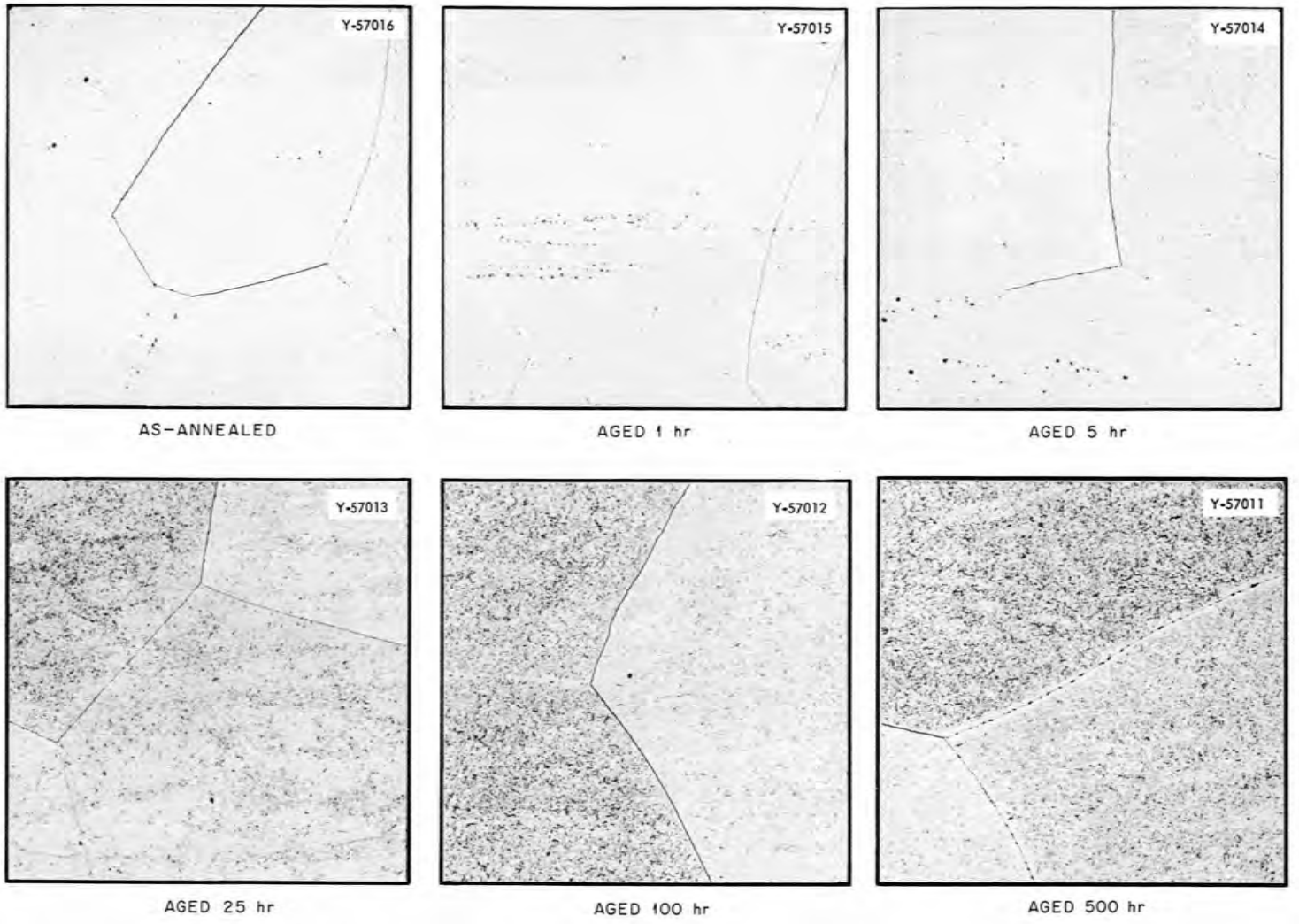

Fig. 12. Microstructures of Nb–40% V–1% Zr after Solution Annealing 2 hr at 1600°C (2910°F) and Aging at 925°C (1700°F). Etchant: 10 p HNO_3 10 p H_2SO_4 25 p HF 50 p H_2O.

EVAPORATION

D. T. Bourgette

The use of a material at elevated temperatures in the environs of space raises questions about the stability of such a material with respect to evaporation. Because niobium-vanadium alloys were under consideration for space application, the Armour alloy, Nb–39% V–1% Ti, was subjected to evaporation studies. Tests were carried out with cylindrical specimens (cut from the tube shown in Fig. 3) enclosed in water-cooled glass capsules which were continuously evacuated. The capsules, in turn, were suspended in an induction coil for heating the specimens. Two tests were performed at 1100°C (2000°F) for 672 hr at pressures of 5×10^{-7} and 2×10^{-9} torr.

The evaporation tests resulted in the formation of a deposit on the capsule walls with the deposit formed at the lower pressure being greater. Weight change measurements together with chemical analyses are presented in Table 9. The deposits were found to be essentially vanadium and titanium. In the case of the test at 10^{-9} torr good agreement was found between the deposit weight and the weight loss of the specimen. There was no appreciable change in interstitial content of this specimen except for a decrease in hydrogen content. At 10^{-7} torr there was a net increase in the weight of the specimen even though evaporation was observed. This was caused by an increase in oxygen and carbon contents of the specimen. However, an unexplained discrepancy in the materials balance was apparent in that the net increase in weight of the specimen was not equivalent to the increase in weight of interstitials less the weight of deposit.

These studies point out a potential problem area in the use of materials for long times at high temperatures in high vacuums. Losses through evaporation would undoubtedly be reflected to a certain degree in property changes.

Table 9. Results of Evaporation Tests on Nb–39% V–1% Ti for 672 hr at 1100°C (2000°F)[a]

Test Pressure (torr)	Specimen Area (cm^2)	Specimen Weight			Posttest Analyses					
		Initial (g)	Final (g)	Change (mg)	Deposit (mg)		Specimen (ppm)			
					V	Ti	C	O	H	N
2.8×10^{-9}	20.67	8.38680	8.38398	−2.82	1.88	0.63	440	810	3	130
4.6×10^{-7}	20.11	8.17690	8.17729	+0.39	0.18	0.095	490	1100	3	130

[a]Pretest analysis of specimens (ppm): C 440, O 810, H 21, N 120

SUMMARY AND CONCLUSIONS

In this investigation several niobium-vanadium alloys were evaluated for properties related to their potential use in advanced reactor systems. Properties such as fabricability, corrosion behavior in lithium, strength, weldability, aging response, and stability in high vacuums were of interest. The alloys included niobium-vanadium binary compositions within the range of 1 to 60% V together with alloys in the 30 to 50% V range containing small additions of titanium and zirconium. The purpose of these latter two elements was for a specific effect each was to contribute to properties: titanium, slight strengthening; and zirconium, stabilizing oxygen and thereby improving corrosion resistance in lithium(but restricting oxygen solubility and thereby promoting an aging reaction).

Of the alloys fabricated, the compositions containing 30 to 60% V displayed a high degree of fabricability by cold rolling, attributed to the propensity of these compositions to deform by twinning. Difficulty was experienced during an attempt to process seamless tubing of an alloy Nb–39% V–1% Ti. This failure was probably caused by contamination during processing and/or an incorrect reduction and annealing schedule.

From the results obtained on the alloy Nb–40% V, it appears that the binary alloys behave similarly to pure niobium when considering the effect of oxygen on corrosion resistance in lithium. With increasing oxygen content within the range of 500 to 4000 ppm, the corrosion

resistance of Nb–40% V decreased when tested at 815°C (1500°F). Zirconium additions would be expected to enhance corrosion resistance.

Zirconium seems to restrict the solubility of oxygen in niobium-vanadium alloys, as it does in pure niobium. This can result in an aging reaction through the precipitation of ZrO_2. Although comparative metallographic studies on two alloys, Nb–40% V and Nb–40% V–1% Zr, after solution annealing at 1600°C (2900°F) and aging at 925°C (1700°F) showed precipitation in the zirconium-bearing alloy, hardness measurements indicated rapid overaging of this alloy for the given heat-treating conditions. To establish the consequences of aging in the niobium-vanadium-zirconium system, more data would be required.

Good postweld bend ductility at room temperature was displayed by gas tungsten-arc fusion welds in the alloys Nb–30% V and Nb–50% V, even though weld-metal cracking occurred in the Nb–30% V alloy during the welding operation. The observed cracking is not believed to constitute a problem in view of the good welding history of similar alloys as reported by other investigators.

The tensile properties of niobium-vanadium binary alloys at 1100°C (2000°F) peak within the composition range of 25 to 40% V, and these properties are competitive with those of other second-generation niobium alloys strengthened with tungsten, zirconium, and carbide dispersions. Hot-hardness measurements on binary alloys containing up to 60% V corroborated the strenghtening influence of vanadium additions to niobium as well as the expected peak in strength as a function of composition.

Stress-rupture and creep-rupture properties of niobium-vanadium base alloys have proved disappointing. The alloys Nb–40% V and Nb–40% V–1% Zr showed a lack of creep resistance at 1200°C (2200°F) in a cantilever-beam slow-bend test. Conventional creep-rupture testing of the alloy Nb–39% V–1% Ti at 870°C (1600°F) showed the rupture data to be approximately equivalent to rupture data on the alloy Nb–1% Zr at 982°C (1800°F) and that the time to a given strain was very short.

Vanadium and titanium losses were experienced by the alloy Nb–39% V–1% Ti when subjected to evaporation tests in high vacuums at 1100°C (2000°F). These studies pointed out a potential problem area in the use of niobium-vanadium alloys for long times at high temperatures in space environments.

Thus, niobium-vanadium base alloys represent compositions with many attractive properties for short-time applications at elevated temperatures. The major deterrent to the use of these alloys for long-time application appears to be a lack of creep strength. As a result, these alloys would be less satisfactory than other presently available niobium alloys.

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