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Abstract

Corrosion data are presented for several vanadium alloys exposed to flowing lithium at 427, 482, and 538°C. The corrosion behavior is evaluated by weight change measurements. Metallographic results and data on the non-metallic element transfer in lithium-exposed specimens are also presented. The influence of alloy composition and exposure conditions on the corrosion behavior of vanadium alloys is discussed.

1. Introduction

Vanadium-base alloys offer several advantages over other candidate structural alloys for fusion reactor first wall/blanket systems. The relatively high thermal conductivity and low thermal expansion coefficient result in lower thermal stresses compared to other structural materials, such as austenitic stainless steels and low-alloy ferritic steels. Several vanadium alloys exhibit greater resistance to radiation damage and to corrosion/mass transfer in liquid lithium or Pb-17Li environments and also have low long-term activation. A major concern regarding the use of vanadium alloys for such applications is their reactivity with nonmetallic elements, such as oxygen, nitrogen, and carbon. This paper presents data on the nonmetallic element transfer and dissolution behavior of several vanadium alloys in a flowing lithium environment.

2. Experimental procedure

Corrosion tests were conducted in a forced-circulation lithium loop equipped with cold- and hot-trapping purification capabilities to control the concentration of nonmetallic elements. A detailed description of the loops and the test procedure has been presented earlier [1-2]. Three corrosion test runs of 1500 to 2500-h duration were conducted at temperatures between 538 and 371°C. For each run, thin foils of various vanadium alloys and some ferritic steels were exposed in two separate isothermal test vessels maintained at different temperatures. All specimens were mechanically polished before exposure. Lithium was circulated at ~1 L/min from the high temperature to the low-temperature test vessel. For all tests, the concentrations of C and H were ~10 and 120 wppm, respectively, and the nitrogen content varied between 100 and 20 wppm for the different tests.

The corrosion behavior was evaluated by weight change measurements. Several specimens were analyzed chemically to determine the changes in nonmetallic elements after exposure to lithium. Microhardness measurements were also performed to determine the depth of these compositional changes.

3. Results

3.1 Dissolution behavior

The weight losses of several vanadium alloys exposed to flowing lithium at 482 and 427°C (run 8) are shown in Fig. 1. At both temperatures, the weight losses of all alloys increase linearly with time after an incubation period ranging up to 700 h. The incubation period increases with an increase in the Ti content of the alloy. Alloys containing 15 or 20% Ti, in fact, show a weight gain during the initial 700-h exposure to lithium. The weight loss of vanadium alloys with time is somewhat different than for the ferritic or

austenitic steels [2], which show rapid dissolution during the initial transient period. It will be shown in the next section that the weight change for vanadium alloys represents two competing processes, viz., weight loss due to dissolution of alloy elements and weight gain from pickup of nonmetallic elements, particularly nitrogen, from lithium. The latter dominates during the initial period of lithium exposure.

The weight losses for the V-15Cr-5Ti alloy exposed to lithium at 538, 482, 427, and 371°C are shown in Fig. 2. At all temperatures, a steady-state dissolution rate is achieved after a short incubation period. The dissolution rates increase with an increase in temperature, although the rates at 482 and 538°C are approximately the same.

The steady-state dissolution rates for the various vanadium alloys exposed to lithium during test runs 5, 6, and 8 are given in Table 1. During exposure, the concentration of N in lithium was ~100, 50, and 20 wppm for runs 5, 6, and 8, respectively. Pure vanadium shows the highest dissolution rates and the alloys with 15 or 20% Ti have the lowest rates. At 482°C, the dissolution rates decrease in the following order: pure V, V-3Ti-1Si, V-5Ti-(10 to 15Cr), V-12 to 15Cr-(3Fe-1Zr), and V-15 to 20Ti-(7.5Cr). A similar trend is also seen at 427°C; however, all alloys that contain Ti show low dissolution rates.

The data also indicate that for the present lithium exposure conditions, the dissolution rates of all vanadium alloys are greater than those for the ferritic steels. For example, steady-state dissolution rates for ferritic HT-9 and Fe-9Cr-1Mo steel at 482 and 427°C, and similar lithium conditions, are ~0.2 mg/m²·h and 0.07 mg/m²·h, respectively.

Micrographs of the surfaces of the various vanadium alloys exposed to lithium at 482°C are shown in Figs. 3 and 4. The surface features of these

alloys may be classified into three general categories based on the Ti content in the alloy, viz., alloys containing no Ti, 5% Ti, and >15% Ti. The pure vanadium specimen has an etched appearance with heavily corroded regions; however, it is relatively free of reaction products. The V-10Cr-3Fe-1Zr and V-15Cr alloys also have an etched appearance, but the surfaces contain some reaction products. The surfaces of the alloys containing 5% Ti show patches of reaction products. The patches are diffuse and ill-defined in the Cr-containing alloys. The alloys containing 15 or 20% Ti develop a uniform scale of reaction products (Fig. 4). The appearance of the surface scale is not significantly different for alloys with and without Cr. Electron microprobe X-ray analyses of the V-5Ti-(12 to 15Cr) and V-15 to 20Ti-(7.5Cr) alloy surfaces showed that nitrogen was present and that the concentrations of Cr and Ti were not significantly different from those in the bulk alloy.

Metallographic examination of cross sections of the various lithium-exposed specimens revealed a similar behavior. Alloys containing >15% Ti develop a uniform reaction scale after exposure to lithium. Micrographs of the cross sections of V-20Ti and V-15Cr-5Ti specimens exposed to lithium are shown in Fig. 5. The V-20Ti specimens develop a uniform surface scale during the initial ~700 h of exposure and the thickness of the scale increases with an increase in temperature, e.g., ~1.5, 2.5, and 6.0 μm at 427, 482, and 538°C, respectively. However, the scale thickness does not change significantly with time, i.e., the rate of movement of the alloy/scale interface is approximately the same as recession of the specimen surface. The formation of the reaction scale accounts for the weight gain for the V-20Ti specimens during the initial ~700-h exposure. The V-15Cr-5Ti specimens show patches of surface layer (~2 μm thick), which appear to be breaking off from the specimen, Fig. 5. The spalling of reaction scale from the specimen

surface may account for the large weight loss for V-15Cr-5Ti alloy. A similar behavior was observed for pure vanadium and the various vanadium alloys containing $\leq 5\text{Ti}$.

All the Cr-containing alloys, with the exception of V-7.5Cr-15Ti, were very brittle after exposure to lithium. The V-10Cr-3Fe-1Zr alloy, in particular, cracked very easily during handling.

3.2 Nonmetallic element transfer

Several corrosion specimens were analyzed chemically to determine the changes in nonmetallic elements after exposure to lithium. The concentrations of nitrogen, oxygen, and carbon in pure V, V-10Cr-3Fe-1Zr, V-20Ti, and two heats of V-15Cr-5Ti specimens exposed to lithium at 427, 482, and 538°C are given in Table 2. All alloys show significant increase in the nitrogen content. The gain in nitrogen increases with exposure time and temperature. Analyses of the specimens with and without the surface reaction scale indicate that the increase in nitrogen content is associated with the surface reaction scale as well as the bulk material. The solubility of nitrogen in vanadium is ~3600 and 4700 wppm at 482 and 538°C, respectively [3].

The V-10Cr-3Fe-1Zr and V-15Cr-5Ti alloys also show an increase in carbon while pure vanadium shows little or no change in carbon content. The solubility of carbon in vanadium is 366 and 265 wppm at 482 and 427°C, respectively [3]. Consequently, the C content measured in the pure V specimens represent the saturation value. The vanadium alloys have carburized and should contain carbides of Ti, Cr, or Zr. For the present conditions of lithium exposure (i.e., ~10 wppm C), all vanadium alloys, including pure V, should carburize. It is likely that the V_2C , which forms on pure V specimens, is not adherent and spalls during lithium exposure.

The oxygen content of pure V and V-15Cr-5Ti alloy decreased after exposure to lithium and the V-10Cr-3Fe-1Zr and V-20Ti alloys show only minor changes in oxygen. For cold-trap temperature between 200 and 220°C, the concentration of oxygen in lithium is estimated to be between 35 and 50 wppm. Under these conditions, the equilibrium concentration of oxygen in vanadium will be extremely low (<1 ppb). The results indicate that the loss of oxygen from vanadium alloys is very slow.

The depth of the changes in nonmetallic elements in the lithium-exposed specimens was determined by microhardness measurements. The results for V-15Cr-5Ti and V-10Cr-3Fe-1Zr alloys are shown in Figs. 6 and 7, respectively. Both alloys show an increase in hardness after lithium exposure; however, the hardness profiles for the two alloys are distinctly different. The V-15Cr-5Ti alloy shows a sharp increase in hardness of the surface region (10 to 20- μ m deep) of the specimen, while the V-10Cr-3Fe-1Zr alloy exhibits a more uniform increase in hardness. The results indicate that the increase in hardness is caused primarily by the increase in the nitrogen content of the alloys; the microhardness results agree very well with changes in the concentration of nitrogen. For example, the difference in the nitrogen content of Cam and ANL heats of V-15Cr-5Ti alloy (2361 and 2808 wppm N, respectively) is reflected in their hardness profiles, shown as closed and open triangles in Fig. 6. Also, the V-10Cr-3Fe-1Zr alloy exposed for 687 h at 482°C shows a hardness increase to a depth of >30 μ m and contains 4570 wppm N while the two heats of V-15Cr-5Ti exposed for 1600 to 2000 h at 482°C show an ~10- μ m hardened region and contain 2400 to 2800 wppm N.

The difference in the hardness profiles for V-10Cr-3Fe-1Zr and V-15Cr-5Ti alloys can be attributed to the precipitation of TiN in the latter. The formation of TiN in V-15Cr-5Ti alloy will decrease the diffusion of N into the

alloy and hence, a thinner hardened layer relative to V-10Cr-3Fe-1Zr alloy which shows a flat hardness profile. The microhardness of three alloys with 5Ti and different amounts of Cr, exposed to lithium at 482°C, is shown in Fig. 8. All alloys have an identical hardness profile.

The effect of carbon on the hardness profiles of vanadium alloys cannot be estimated from the present results. Additional data are needed to evaluate the carburization behavior of vanadium alloys in lithium.

4. Discussion

The temperature dependence of the equilibrium values of nitrogen and carbon concentrations in lithium for which metal nitrides and carbides are stable [3,4] is shown in Fig. 9. The equilibrium nitrogen concentration in lithium for the formation of Li_9CrN_5 [5] are also plotted. The results indicate that for the exposure conditions during runs 5, 6, and 8, the carbides of Ti, V, and Cr, ternary nitride of Cr, and nitrides of V and Ti are expected to be stable (the nitrogen content during run 8 is slightly lower than the equilibrium value required for the formation of V_2N ; however, the difference is insignificant). Consequently, the chemical interactions to form these compounds will have a dominant role in the corrosion behavior of vanadium alloys in lithium.

Metallographic results indicate that the low dissolution rates of the alloys containing $\geq 15\text{Ti}$, e.g., V-20Ti and V-7.5Cr-15Ti, are due to the formation of a protective surface scale. Chemical analyses of the specimens indicate that the scale is primarily composed of mixed nitrides. The composition of metallic elements in the scale is approximately the same as that in the bulk alloy. This nitride scale, however, is quite brittle and can spall when exposed to thermal stresses. Alloys containing 5Ti or less do not

develop a uniform surface scale. The reaction products easily break off from the alloy surfaces, resulting in high dissolution rates. The dissolution rates for V-15Cr-1Ti in lithium at 482 and 538°C (viz., 3 to 5 mg/m²·h) agree fairly well with the rate (~3 mg/m²·h) obtained at 550°C in flowing lithium containing ~10 wppm nitrogen [6]. The scales on these alloys are also primarily nitrides. However, the contribution of carbide formation on the dissolution behavior of the alloys cannot be evaluated from the existing data. A similar behavior is observed for pure V, i.e., high dissolution rates due to chemical interactions between V and nonmetallic elements such as N and/or C.

The addition of Cr to vanadium seems to influence the chemical interactions and reduce dissolution rates. However, the Cr-containing alloys embrittle after exposure to lithium. The cause of embrittlement is not known. It can arise from the pickup of hydrogen from lithium, but a significant change in hydrogen content is not observed in the lithium-exposed specimens. The V-15Cr-5Ti and V-10Cr-3Fe-1Zr alloys show significant carburization, which may cause embrittlement. The influence of carburization on the tensile properties of vanadium alloys needs investigation.

5. Conclusions

The corrosion data for several vanadium alloys indicate that for the present tests, the concentrations of N and possibly C in lithium are above acceptable limits, and chemical interactions between alloy elements and N and/or C in lithium play an important role in the corrosion behavior of these alloys. When exposed at 482°C to lithium containing 20 to 50 wppm N and 8 to 12 wppm C, the dissolution rates of the various vanadium alloys decrease in

the following order: pure V, V-3Ti-1Si, V-5Ti-(12 to 15Cr), V-10 to 15Cr-(3Fe-1Zr), and V-15 to 20Ti-(7.5Cr). The alloys containing 15 to 20Ti develop a protective nitride scale. For the present exposure conditions, all vanadium alloys pick up nitrogen and carbon from lithium and lose oxygen. The Cr-containing alloys embrittle after exposure to lithium.

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Table 1. Dissolution rates for vanadium alloys exposed to flowing lithium

	Dissolution rate (mg/m ² ·h) ^a					
	Run 6 (~50 wppm N) ^b		Run 8 (~20 wppm N) ^b		Run 5 (~100 wppm N) ^b	
	538°C	482°C	482°C	427°C	427°C	372°C
Pure V	-	-	c	2.76	-	-
V-10Cr-3Fe-1Zr	-	-	0.86	0.73	-	-
V-15Cr	-	-	1.38	0.47	-	-
V-5Ti	-	-	6.34	-	-	-
V-12Cr-5Ti	-	-	4.64	0.17	-	-
V-15Cr-5Ti	2.66	2.95	4.97	0.27	0.54	0.036
V-20Ti	-	0.22	0.72	0.24	-	-
V-7.5Cr-15Ti	-	-	0.48	d	-	-
V-3Ti-1Si	-	-	7.15 ^e	0.75	-	-

^aDissolution rates based on net weight loss. The values are not corrected for weight change due to nonmetallic element transfer.

^bRepresents the average nitrogen content in lithium during the different test runs.

^cDissolution rates change with time, i.e., the rates are ~13 mg/m²·h during the initial 500-h exposure and decrease to ~2 mg/m²·h for longer times.

^dThe specimen showed weight gain for times up to ~800 h.

^eCalculated from a single exposure time.

Table 2. Composition of Nonmetallic Elements in Several Vanadium Alloys Exposed to Lithium

Alloy	Specimen ID	Test Run	Exposure Condition		Composition ^a (wppm)		
			Temp. (°C)	Time (h)	N	O	C
Pure V	-	-	Unexposed		161 ± 41	1,101 ± 73	360
	V-70	8	427	1405	565 ± 71	889 ± 107	320
	V-84	8	482	484	681 ± 65	986 ± 97	340 [330]
	V-64	8	482	1508	3,404 ± 187	737 ± 122	270 [-]
V-10Cr-3Fe-1Zr	-	-	Unexposed		271 ± 66	607 ± 100	890
	V-52	6	482	687	4,570 ± 250	724 ± 157	990
	V-57	6	482	619	-	-	1270
	V-66	8	482	1080	-	-	1070
	V-51	6	538	590	12,418 ± 621	524 ± 140	-
	V-55	6	538	794	-	-	1190
V-15Cr-5Ti(Cam)	-	-	Unexposed		527 ± 109	1,291 ± 168	390
	V-71	8	427	1405	607 ± 84	422 ± 119	500 [610]
	V-65	8	482	1992	2,361 ± 114	505 ± 119	570 [-]
	V-59	6	482	619	-	-	530
V-15Cr-5Ti(ANL)	-	-	Unexposed		299 ± 68	1,384 ± 112	390
	V-53	6	482	1618	2,808 ± 177	537 ± 163	700
	V-50	6	538	1384	-	-	-
					[10,022 ± 505]	[562 ± 98]	[670]
V-20Ti	-	-	Unexposed		566 ± 168	1,163 ± 254	-
	V-49	6	538	1384	-	-	-
					[5,735 ± 295]	[1,416 ± 124]	[-]

^aValues within brackets represent concentrations for specimens which were mechanically polished to remove the surface reaction scale. The concentration of H ranged between 3 and 8 wppm for the various specimens with or without lithium exposure.

Fig. 1. Weight Loss Versus Exposure Time for Vanadium Alloys Exposed to Flowing Lithium at (a) 482°C and (b) 427°C. Each symbol type represents weight loss for a single specimen after various exposure times.

Fig. 2. Weight Loss Versus Exposure Time for V-15Cr-5Ti Alloy Exposed to Flowing Lithium at Various Temperatures. Each symbol type represents weight loss for a single specimen after various exposure times.

VANADIUM ALLOYS EXPOSED AT 482°C

Fig. 3. Micrographs of the Surfaces of Vanadium Alloys Exposed to Lithium at 482°C for Various Times.

VANADIUM ALLOYS EXPOSED AT 482°C

Fig. 4. Micrographs of the Surfaces to Vanadium Alloys Containing >15% Ti Exposed to Lithium at 482°C for Various Times.

V-15Cr-5Ti 538°C 1384 H

(a)

RUN 6 482°C 687 H

(b)

Fig. 5. Micrographs of the Cross Sections of (a) V-15Cr-5Ti and (b) V-20Ti Specimens Exposed to Lithium.

Fig. 6. Microhardness of the Surface Region of V-15Cr-5Ti Alloy Exposed to Lithium.

Fig. 7. Microhardness of the Surface Region of V-10Cr-3Fe-1Zr Alloy Exposed to Lithium.

Fig. 8. Microhardness of Vanadium Alloys Containing 5Ti and Different Amounts of Cr Exposed to Lithium.

Fig. 9. Temperature Dependence of the Nitrogen and Carbon Concentrations in Lithium at which Selected Structural Metal Nitrides and Carbides are Stable.