

CORROSION OF V AND V-BASE ALLOYS IN HIGH-TEMPERATURE WATER*

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SUMMARY

Corrosion tests of nonalloyed V, V-5Cr-5Ti, and V-15Cr-5Ti were conducted in high-purity deoxygenated water at 230°C for up to ≈4500 h. The effects of Cr concentration in the alloy and temperature on the corrosion behavior were determined from weight-change measurements and microstructural observations. An expression was obtained for the kinetics of corrosion as a function of Cr content of the alloy and temperature.

INTRODUCTION

Vanadium-base alloys are being considered for the first-wall/blanket structure in fusion reactors that employ a liquid-metal cooling system. Because reference alloys that contain 4–5% Cr and Ti exhibit excellent mechanical properties after neutron irradiation,¹ their use in reactor designs with an aqueous coolant is also of interest. For this application, the alloy should resist corrosion and possible embrittlement by uptake of corrosion-product H. In this study, corrosion tests were conducted on pure V, V-5Cr-5Ti, and V-15Cr-5Ti in high-purity deoxygenated water at 230°C.

EXPERIMENTAL PROCEDURE

Details of the experimental procedures are described in Ref. 2. Tabular specimens were cut from thin sheets of material whose compositions are given in Table 1. Approximate dimensions of the pure V, V-5Cr-5Ti, and V-15Cr-5Ti specimens (in mm) are 28 x 15 x 0.6, 20 x 8 x 1, and 10 x 10 x 1.5, respectively. Specimens were annealed in vacuo at 1055°C for 1 h. Vickers microhardness values (25-g load) before and after annealing were 186 vs. 121, 237 vs. 195, and 254 vs. 195, for pure V and the 5Cr and 15Cr alloys, respectively. V-15Cr-5Ti specimens are from the same heat used in a previous corrosion investigation at 288°C.³ Corrosion tests were conducted on duplicate specimens of each alloy, i.e., two sets of six specimens were prepared for each alloy so that one set (two specimens) could be removed from the autoclave for metallographic evaluation and H analysis at ≈1-month intervals over an ≈6-month period. During each time interval, all specimens were removed from the autoclave and weighed. Consequently, six measurements were obtained for each alloy and its duplicate after ≈1 month of exposure, five measurements after 2 months of exposure, etc. Corrosion tests on pure V were conducted for up to ≈3 months. The surface area of each specimen was measured by an image analysis technique. Tests were conducted in a refreshed Hastelloy C276 (62%Ni-16%Cr-16%Mo) autoclave system at 230°C (±2°C) with ≈100 psi overpressure (above saturation) to maintain liquid-phase water. Dissolved-oxygen concentration of inlet water was maintained at <12 ppb. Weight changes of the specimens were determined to ±1 μg.

Table 1. Composition of V and V-base alloys

Alloy	Heat ID	Composition (wt.%)							Impurity Concentration (wt. ppm)							
		Cr	Ti	O	N	C	H	Si	Al	Fe	Mo	Nb	Cu	S	P	Ca
V	820630	<0.01	<0.005	200	62	75	3	780	100	230	410	<50	<50	10	<30	–
5Cr-5Ti	T87	4.9	5.3	460	18	210	9	300	200	600	400	<100	<100	90	10	50
15Cr-5Ti	L-1	12.8	5.0	830	50	370	4	300	100	800	200	<100	100	40	<10	80

RESULTS

Weight loss versus time of exposure for pure V and the two alloys is shown in Fig. 1. The data were fitted to the expression $W = A \cdot t^n$, where W is the weight loss in $g \cdot m^{-2}$, t is the exposure time in hours, and A and n are empirical fitting parameters. The values of n in the power-law expression range from ≈1.0 for

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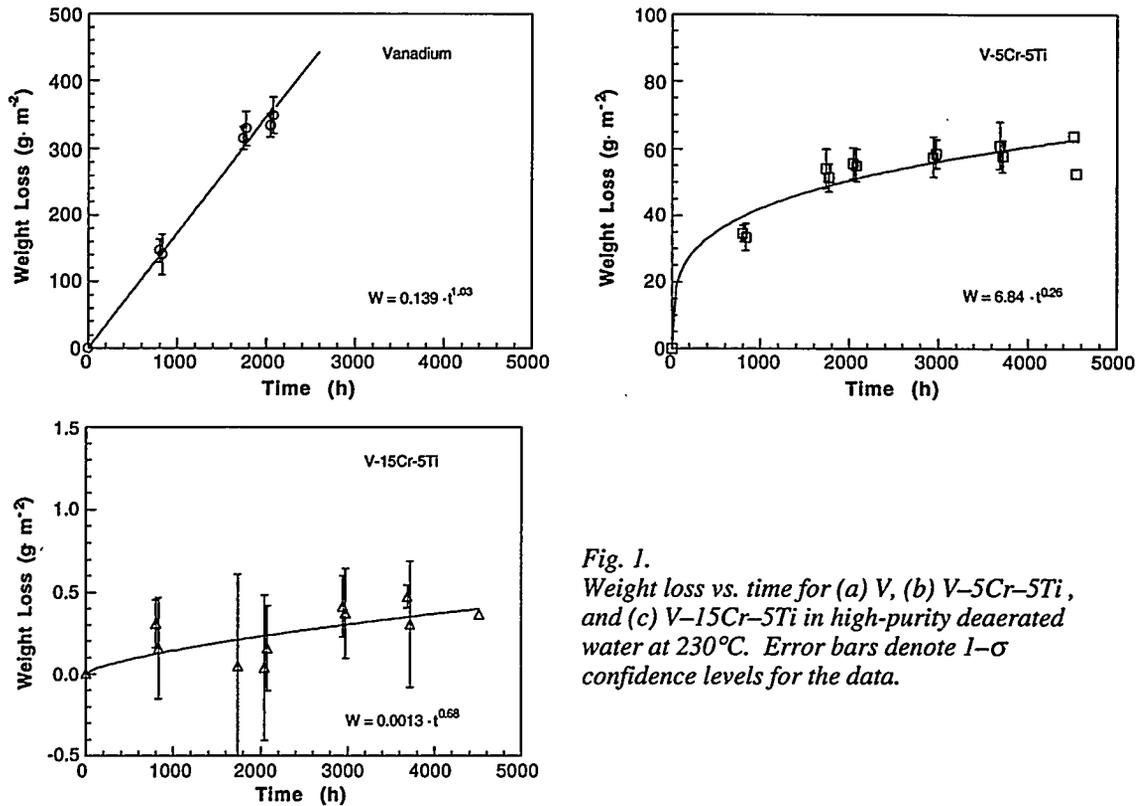


Fig. 1. Weight loss vs. time for (a) V, (b) V-5Cr-5Ti, and (c) V-15Cr-5Ti in high-purity deaerated water at 230°C. Error bars denote 1- σ confidence levels for the data.

pure V to ≈ 0.3 for the V-5Cr-5Ti alloy. Exposure time in the figures was adjusted slightly to delineate data from the two sets of specimens. Measured weight loss for V-15Cr-5Ti was very small when compared with pure V and V-5Cr-5Ti, as indicated by the different ordinate scales on the figures. The effect of Cr concentration on weight loss at ≈ 2046 h is shown in Fig. 2. Corrosion decreases according to an exponential dependence on Cr concentration in the alloys.

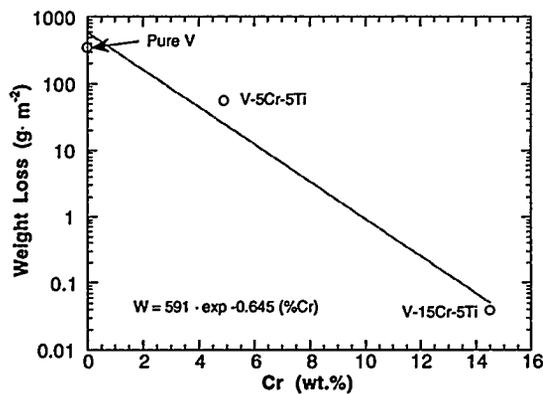


Fig. 2. Effect of Cr concentration on weight loss of V-Cr-5Ti at 2046 h in high-purity deaerated water at 230°C

The effect of temperature on the corrosion rate of V-15Cr-5Ti at ≈ 2000 h is shown in Fig. 3, based on results from this work at 230°C and a previous investigation at 288°C.³ Loss in thickness in $\mu\text{m}/\text{yr}$ is also denoted on the figure. The results indicate that the corrosion rate of this alloy decreases rapidly with temperature, i.e., the activation energy is ≈ 40 kcal/mol.

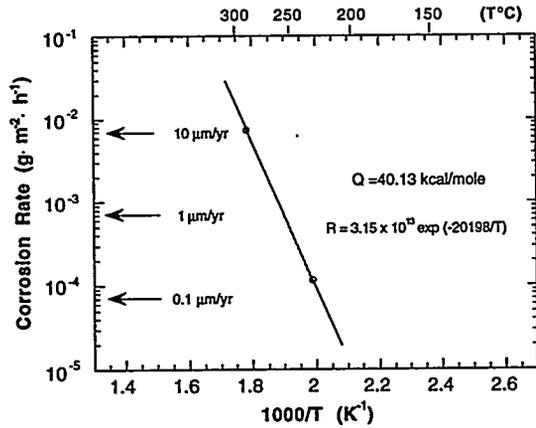


Fig. 3.
Effect of temperature on corrosion rate of
V-15Cr-5Ti in high-purity deaerated water
at ≈ 2000 h

Parameters for corrosion weight loss of the materials at 230°C are given in Table 2 along with calculated loss in weight at 2000 h and loss in thickness at 1 yr (8760 h), based on these parameters and an average alloy density of ≈ 6.16 g·cm $^{-3}$. The table also includes results for V-15Cr-5Ti in water that contained ≈ 30 , 190, and 4000 ppb dissolved oxygen at 288°C, from Ref. 3.

Table 2. Best-fit parameters in relationship $W = A \cdot t^n$ for V and V-base alloys, and calculated loss in weight (W) and thickness (L) at 2000 and 8760 h (1 yr), respectively, in high-purity deaerated water

Material	Temp. (°C)	Oxygen (ppb)	A (g·m $^{-2}$)	n	W at 2000 h (g·m $^{-2}$)	L at 1 yr (μ m)
V	230	12	0.139	1.03	349.0	259.0
V-5Cr-5Ti	230	12	6.835	0.26	49.3	11.8
V-15Cr-5Ti	230	12	1.31×10^{-3}	0.68	0.23	0.10
V-15Cr-5Ti ^a	288	30	3.41×10^{-3}	1.10	14.6	12.0
V-15Cr-5Ti ^a	288	190	2.84×10^{-2}	0.67	4.62	2.0
V-15Cr-5Ti ^a	288	4000	6.19×10^{-3}	0.91	6.25	24.0

^aData from Ref. 3.

Figure 4 shows the dependence of calculated loss in thickness at 1 yr on Cr concentration, based on the parameters in Table 2 and the relationships in Fig. 1. Loss in thickness at one year also exhibits an exponential dependence on Cr concentration in V-Cr-5Ti alloys, and is consistent with experimental data for ≈ 2000 h, shown in Fig. 2. If the temperature dependence of the corrosion of V-Cr-5Ti alloys is the same as that of V-15Cr-5Ti in Fig. 3, the results in Figs. 2 and 3 can be used to develop an expression for loss in thickness L of V-Cr-5Ti alloys as a function of temperature in high-purity deoxygenated water at any time, e.g., 1 yr, as follows:

$$d \ln L = \frac{\partial \ln L}{\partial T} \Big|_{\text{Cr}} dT + \frac{\partial \ln L}{\partial X_{\text{Cr}}} \Big|_T dX_{\text{Cr}}, \quad (1)$$

where the partial derivatives were evaluated from results in Figs. 3 and 4 and are given by

$$\frac{\partial \ln L}{\partial T} \Big|_{\text{Cr}} = -\frac{20196}{T^2} \quad (2)$$

$$\frac{\partial \ln L}{\partial X_{\text{Cr}}} \Big|_T = -0.534. \quad (3)$$

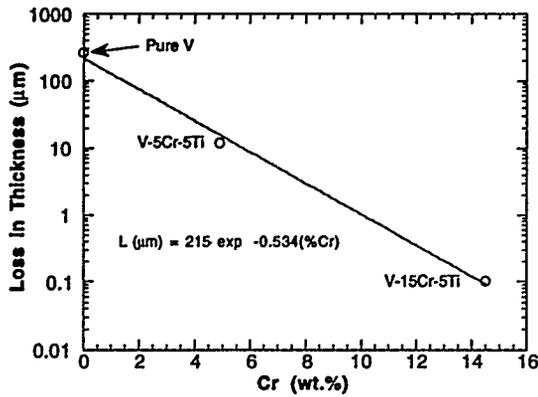


Fig. 4.
Effect of Cr concentration on loss of thickness of V-Cr-5Ti alloys in high-purity, deaerated water at 230°C for 8760 h (1 yr), based on parameters in Table 2

When Eqs. 2 and 3 are inserted into Eq. 1, the expression (Eq. 4) can be integrated between the limits

$$\int_{0.1}^L d \ln L = - \int_{503}^T \frac{20196}{T^2} dT - \int_{15}^X 0.534 dX \quad (4)$$

to yield the loss in thickness (μm) at 1 yr (Eq. 5).

$$\ln L = 45.814 - \frac{20196}{T} - 0.534 (X_{\text{Cr}}). \quad (5)$$

Because corrosion of each material follows a different rate law, i.e., a linear law for pure V and a ≈ 0.3 power dependence on time for V-5Cr-5Ti, Eq. 5 is only valid for the time that was selected, viz., 1 yr. Nevertheless, this expression enables one to assess the effects of temperature and Cr concentration on corrosion in the context of alloy selection and operating temperature. A corrosion allowance of $\approx 20 \mu\text{m}/\text{yr}$ may be acceptable for the first-wall of a fusion reactor.⁴ In Fig. 5, the estimates of the corrosion of V-Cr-5Ti alloys at 1 yr from Eq. 5 are presented with values obtained from Table 2 for the three materials at 230 and 288°C. Equation 5 provides a reasonable representation of corrosion behavior; however, experimental data at other temperatures and for other alloy compositions are not available to assess the validity of the expression.

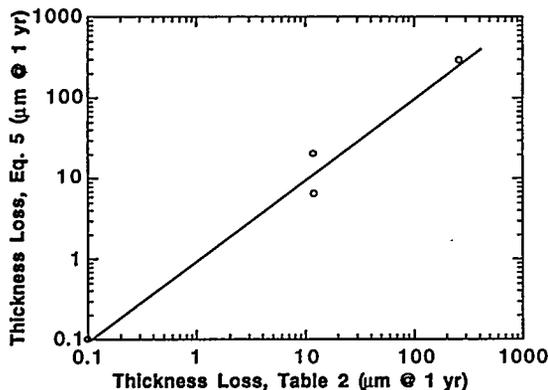


Fig. 5.
Loss of thickness of V-Cr-5Ti alloys in high-purity deaerated water at 1 yr, from Eq. 5 and parameters in Table 2

Specimens were analyzed to determine uptake of corrosion-product H by the materials during long-term exposure to high-temperature water. Table 3 shows that H pickup by V and the alloys was minimal in these experiments, which suggests that H embrittlement from this source of H should not be a concern.

Table 3. Hydrogen (ppm) in V, V-5Cr-5Ti, and V-15Cr-5Ti after exposure to water at 230°C

Material	Exposure Time (h)			
	0	799	2046	4508
V	3	37.5	56.5	—
V-5Cr-5Ti	9	—	14.6	22.5
V-15Cr-5Ti	4	—	2.9	3.0

Metallographic sections of the specimens were prepared and examined by scanning electron microscopy (SEM). The photomicrographs indicate an adherent $\approx 30\text{-}\mu\text{m}$ -thick corrosion-product film on V specimens for exposure times ≥ 1700 h. Films on V-5Cr-5Ti were $\approx 8\text{ }\mu\text{m}$ thick for all of the exposure times; those on V-15Cr-5Ti were much thinner ($< 1\text{ }\mu\text{m}$). Figure 6 shows the corrosion-product layer on V-5Cr-5Ti specimens after ≈ 3 and 6 months of exposure to water at 230°C. Although film thickness did not increase with exposure time, slight intergranular oxidation is evident after ≈ 3 and 6 months. Detachment of the film from the metal in Fig. 6 occurred during specimen preparation. Because film thicknesses were small, characterization by X-ray diffraction was not attempted. However, X-ray diffraction powder patterns in a previous study³ indicated that the corrosion product on V-15Cr-5Ti contained V, Cr, and Ti. X-ray peaks were consistent with tetragonal and/or orthorhombic forms of $\text{Cr}_{0.1}\text{V}_{0.9}\text{O}_2$. TiO_2 and TiV_2O_6 were also identified.

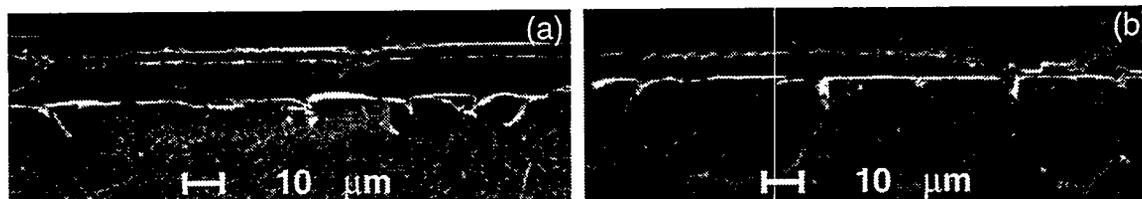


Fig. 6. SEM photomicrographs of oxide/metal interface of V-5Cr-5Ti specimens after exposure to high-purity deaerated water at 230°C for (a) 2046 and (b) 4508 h

CONCLUSIONS

Vanadium and V-Cr-Ti alloys that contained Cr and Ti undergo weight loss and thinning during exposure to high-purity deoxygenated water at temperatures $\leq 288^\circ\text{C}$. Corrosion resistance of V-Cr-5Ti alloys increases with Cr concentration in the alloy. Pickup of H liberated by the corrosion reaction was minimal during the ≈ 6 -month corrosion test; which suggests that H embrittlement due to corrosion should not be a concern. An expression was developed for loss of thickness as a function of temperature and Cr content of the alloy. If V-base alloys are considered for structural applications in a fusion reactor with an aqueous coolant, the influence of water velocity on corrosion behavior should be investigated.

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