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Influence of Cr, Ti concentrations on oxidation and corrosion resistance of V–Cr–Ti type alloys

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Abstract

V–4Cr–4Ti alloys have been identified as the reference material for fusion reactor applications. One of the main issues of using them at elevated temperatures is their high affinity with gaseous elements. It is necessary to improve their oxidation and corrosion resistance, in order to use them in the various environments, such as vacuum leak and reaction with water. In this paper, V-based high Cr and Ti alloys were prepared and exposure tests in air and pressurized water were conducted to study the influence of Cr, Ti concentration on their oxidation and corrosion properties. After the oxidations in air, the weight gain was reduced as Cr concentration increased. The results of the tests in water showed weights of each alloy were reduced as corrosion time. The weight losses were significantly reduced as Cr concentration increased. It is concluded that addition of Cr is effective to reduce the weight change after corrosion particularly in water.

1. Introduction

Vanadium-based alloys nominally containing 4 wt% Cr and 4 wt% Ti have been identified as the reference material for fusion reactor applications [1,2] because they have lower long-term activation, lower irradiation afterheat, lower thermal stress factor, better creep resistance [3–5], compatibility with coolants such as liquid lithium [6,7], and better mechanical formability than other structural alloys. One of the main issues of using V-based alloys at elevated temperatures is their high affinity with gaseous elements, i.e., H, N, O [8–10]. From a practical point of view, it is necessary to improve oxidation and corrosion resistance of V-based alloys, in order to use them in the condition of various environments, such as vacuum leak [11–14] and reaction with water [15]. Additions of Cr and Ti were expected to improve the oxidation and corrosion properties of the alloys [7,16,17]. However, the effects of additions of Cr and Ti respectively on corrosion properties in air and pressurized water have not been clarified yet. The objectives of this study are to evaluate the influence of Cr and Ti concentration on corrosion properties of V–Cr–Ti type alloys including weight change and mechanical properties after exposure tests in air and corrosion tests in pressurized water.

2. Experimental procedures

The alloys examined in this study include V-based high Cr alloys, such as V–4Cr–4Ti, V–7Cr–4Ti, V–10Cr–4Ti, V–12Cr–4Ti, V–15Cr–4Ti and V–20Cr–4Ti and also include V-based high Ti alloys, such as V–4Cr–10Ti and V–4Cr–15Ti (in wt%) alloys. These alloys were prepared at Institute for Materials Research, Tohoku University. In order to reduce the contamination of the interstitial impurity element such as C, O, N, a high-purity V and Ti were used after electron beam refining

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Table 1
Chemical compositions of the vanadium alloys examined (in wt%)

	(wt%)			(wppm)			
	V	Cr	Ti	C	O	N	H
PUREV	Bal.	–	–	37	249	221	6
V–4Cr–4Ti	Bal.	4.275	4.250	93	235	171	5
V–7Cr–4Ti	Bal.	7.170	3.650	71	213	174	9
V–10Cr–4Ti	Bal.	10.55	4.145	118	276	249	11
V–12Cr–4Ti	Bal.	12.25	4.095	186	304	485	15
V–15Cr–4Ti	Bal.	14.46	3.950	240	273	382	12
V–20Cr–4Ti	Bal.	20.10	4.120	165	233	220	5
V–4Cr–10Ti	Bal.	4.215	9.755	214	275	314	4
V–4Cr–15Ti	Bal.	4.040	14.40	227	323	282	5
NIFS HEAT-1	Bal.	4.1	4.4	66	181	88	18

and an arc-melting furnace with a contamination reducer was adopted for alloying. A high-purity V–4Cr–4Ti alloy that was developed at the National Institute for Fusion Science (NIFS) and called NIFS-HEAT-1 was also examined. The chemical compositions of these alloys are shown in Table 1. The arc-melted buttons of the alloys were cold-rolled to 1 mm in thickness. 10×15×1 mm coupon samples for measurement of mass change were cut from each alloy. These samples weighed about 850 mg. Small size tensile test specimens were punched out from the 0.25 mm-thick-sheet obtained by cold rolling using the sheet of 1 mm thick, and the size of the gauge section was 5×1.2 mm. Each specimen was annealed at 1000–1200 °C for 1 or 2 h in a vacuum of 1×10^{-3} Pa to obtain recrystallized microstructures with mean grain size of about 17 μm.

Exposure tests were carried out at 500, 600, 700, 750, 800 and 900 °C for 1 h in air. The weight change of each alloy was measured after exposure. Corrosion tests by using a refreshed autoclave system were carried out in pressurized water (288 °C, 85 atm) containing 400 ppb dissolved oxygen for 300 h. The oxygen levels in the inlet and outlet water were checked continuously and adjusted to the state of equilibrium. The tests were interrupted after 24, 72 and 200 h, and the weight change of each alloy were measured to estimate the time dependence of the corrosion rate. Tensile tests after oxidation and corrosion were conducted at room temperature at a strain rate of 6.7×10^{-4} s^{-1}. The fracture surfaces of the tested samples were observed by scanning electron microscope (SEM). And characterizations of surface oxide layer were conducted by X-ray diffraction (XRD) analysis for each alloy.

3. Result and discussion

Fig. 1 shows the weight increase per surface area of each alloy after oxidation in air for 1 h. No significant weight gain was shown up to 600 °C. At over 700 °C exposure, weights of each alloy increased remarkably. As for the V-based high Cr alloys, the weight gain of alloys was reduced as Cr concentration increased at each temperature, but the rate of weight gain for each alloy was almost the same in every condition except for the V–4Cr–4Ti alloy. The error bars shown on the data of V–4Cr–4Ti alloy at 800 and 900 °C were estimations of the total weight including the oxide that came off from the surface. Increasing the Ti concentration showed no effect on protection of weight gain. At 800 and 900 °C exposure, similar tests could not be conducted on the V–4Cr–10Ti and V–4Cr–15Ti alloys due to melting of the surface oxide.

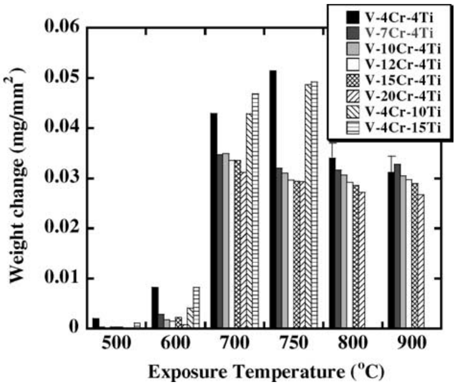

Fig. 1. Weight gain for each alloy after oxidation in air for 1 h.

The results of the fracture surface observations after tensile test by using SEM are shown in Fig. 2. The fracture surface of the V–4Cr–4Ti alloy was clearly discriminated between oxide layer, cleavage fracture zone and ductile rupture zone from the surface of the specimens. But, that of the V–20Cr–4Ti alloy was distinguished by two zones, cleavage crack zone and surface oxide layer. These two regions were related to the

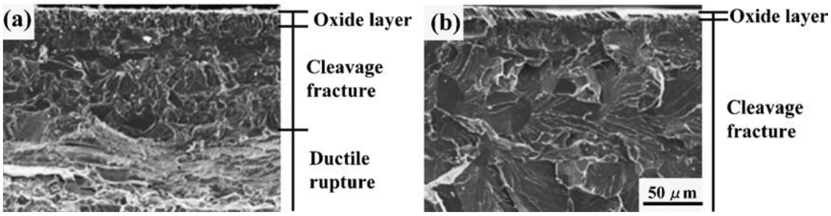

Fig. 2. Scanning electron micrographs of fracture surfaces after tensile test: (a) V–4Cr–4Ti and (b) V–20Cr–4Ti alloy after oxidation at 700 °C.

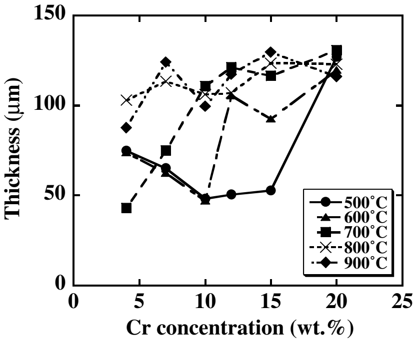

Fig. 3. Dependence of Cr concentration on the cleavage fracture zone of each alloys oxidized at several temperatures.

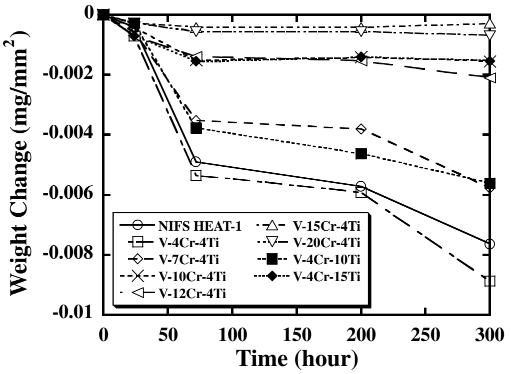

Fig. 4. Thickness of oxide layer for each alloy oxidized in air for 1 h.

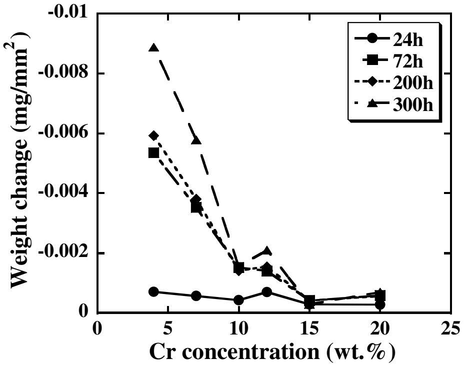

Fig. 5. Dependence of Cr concentration on the weight change of each alloy corroded in pressurized water for several times.

embrittlement of the alloy and corresponded to the depth of diffusion of oxygen into the alloys during exposure in air. Fig. 3 shows the Cr-concentration dependence on the thickness of cleavage fracture zone after exposure in air. Cleavage crack region was increased as exposure temperature increased. The weight gain of V-based high Cr alloys was reduced as Cr concentration increased. However, the cleavage fracture zones in their rupture plates were increased by the diffusion of oxygen into matrix even at 500 °C exposure. The oxide layer of each alloy was reduced as the Cr content level increased up to 600 °C exposure. But, over 700 °C exposure there was little effect of Cr-concentration on the growth of oxide layer. Main oxides in these oxide layers identified by XRD analysis were VO_2 and V_2O_5. According to the V-based high Ti alloys, the tensile properties of them were better than any other alloys at over 700 °C exposures, the weight gain of them was as much as that of V–4Cr–4Ti alloys. Main oxides in these oxide layers were VO_2 and V_2O_5. And a weak possibility of a small amount of TiO_2 was indicated.

Fig. 4 shows the weight change for each alloy corroded in pressurized water at 288 °C as a function of exposure time. Weight losses were observed in all cases. The result showed that weights of each alloy were reduced as corrosion time had passed. In Fig. 5, the dependences of Cr concentration on the weight change of V-based high Cr alloys are summarized for each temperature. After 24 h exposure, the effect of addition of Cr on weight losses was not so significant. But, weight losses of these alloys were reduced as Cr concentration increased after exposure for 72 h or more. As the results of the V-based high Ti alloys, the weight losses were reduced as Ti concentration increased as same as in the case of V-based high Cr alloys. But, the effect of reduction of weight loss by addition of Ti was less than that by addition of Cr. V_2O_3 and VO_2 were tentatively

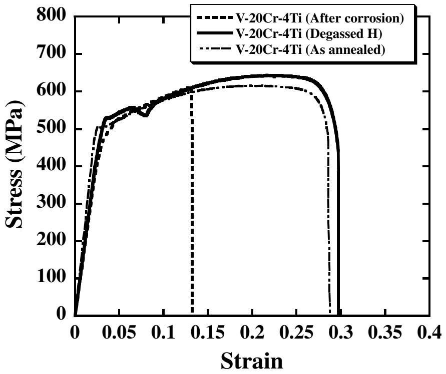

Fig. 6. Stress–strain curves for V–20Cr–4Ti alloy, after corroded in pressurized water for 300 h hydrogen-degassed after corrosion and as annealed.

identified by XRD analysis for main oxides of each alloy in surface oxide layer.

The tensile properties of each alloy after exposure in pressurized water for 300 h were almost the same as those of the as-annealed alloys except for V–20Cr–4Ti alloy. Fig. 6 shows the stress–strain curves for V–20Cr–4Ti alloys after exposure in pressurized water, hydrogen-degassed after corrosion and as-annealed condition. The elongation of V–20Cr–4Ti alloy after corrosion was significantly reduced and the cleavage fracture zone were increased considering to the invasion of hydrogen into matrix. After corrosion test, the heat treatment for degassing of hydrogen was conducted in a vacuum of 3×10^{-2} Pa at 500 °C for 1 h to observe the effect of hydrogen intrusion into the matrix on the embrittlement of the alloy and tensile properties were tested again. The elongation of the alloy was recovered to the same level of the as-annealed condition after treatment of degassing.

4. Summary

To evaluate the influence of Cr and Ti concentration on the corrosion properties of V–Cr–Ti type alloys, exposure tests in air and corrosion tests in pressurized water were conducted.

As consequences of exposure tests in air, weights of each alloy increased significantly at over 700 °C exposure and tensile properties of them were reduced as exposure temperature increased. The weight gain of V-based high Cr alloys was reduced as Cr concentration increased. However, tensile properties of them were reduced and cleavage fracture zones in their rupture plates were increased by the diffusion of oxygen into the matrix even at 500 °C exposure. The main oxides in these oxide layers were VO_2 and V_2O_5. Though the weight gain of V-based high Ti alloys was as much as that of V–4Cr–4Ti alloys, the tensile properties of them were better and the cleavage fracture zones were less than any other alloys at over 700 °C exposures.

The result of corrosion tests in pressurized water showed that weights of each alloy were reduced as corrosion time had passed. Weight losses of V-based high Cr alloys and V-based high Ti alloys by corrosion were reduced as Cr or Ti concentration increased. The tensile property of V–20Cr–4Ti alloy was significantly reduced and the cleavage fracture zones were significantly increased by the invasion of hydrogen in matrix.

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