Improvement of Corrosion Resistance of Vanadium Alloys in High-Temperature Pressurized Water

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Corrosion tests in pressurized and vaporized water were conducted for V-based high Cr and Ti alloys and V-4Cr-4Ti type alloys containing minor elements such as Si, Al and Y. Weight losses were observed for every alloy after corrosion tests in pressurized water. It was apparent that addition of Cr effectively reduced the weight change in pressurized water. The weight loss of V-4Cr-4Ti type alloys in corrosion tests in vaporized water was also reduced as Cr content increased. The V-20Cr-4Ti alloy had a slight weight gain, almost same as that of SUS316, which had the best corrosion properties in the tested alloys. The elongation of alloys with in excess of 10% Cr was reduced as Cr content increased. The elongations of the V-12Cr-4Ti and the V-15Cr-4Ti alloys were significantly reduced by corrosion and cleavage fracture was observed reflecting hydrogen embrittlement. The reduced elongations of the alloys were recovered to the same level of as annealed conditions after hydrogen degassing. After corrosion, the V-15Cr-4Ti-0.5Y alloy still kept enough elongation, suggesting that the addition of Y is effective to reduce the hydrogen embrittlement.

(Received September 21, 2004; Accepted January 24, 2005)

Keywords: corrosion, low activation materials, mechanical properties, fusion reactor materials, vanadium alloys

1. Introduction

Vanadium-based alloys nominally containing 4 mass% Cr and 4 mass% Ti have been considered to be a candidate structural material for fusion reactor applications,^{1,2)} since they have a low long-term activation, low irradiation after-heat, low thermal stress factor, good creep resistance,³⁻⁵⁾ compatibility with coolants such as liquid lithium,^{6,7)} and good mechanical formability. V-Cr-Ti-Si type alloys doped with Al and Y have been also studied, with the results showing a good combination of low swelling behavior and sufficient tensile ductility after irradiation.⁸⁻¹⁰⁾ These vanadium alloys have been developed for self-cooled lithium/vanadium blanket concept that is the use of liquid lithium as the breeding medium of tritium, where the lithium also self-cools the blanket.

Otherwise, blanket cooling by means of circulating pressurized water is being considered as a possible fusion reactor configuration, where stainless steels and ferritic steels are candidate structural materials. A water coolant offers excellent heat transfer characteristics, and it enjoys a well-developed technology from commercial fission reactor experience.

The vanadium-based alloys are non-magnetic materials, and they have good mechanical properties at elevated temperature. However, one of the main drawbacks to using vanadium-based alloys at elevated temperatures is their high affinity with gaseous elements, *i.e.*, H, N, and O.¹¹⁻¹³⁾ From a practical point of view, it is necessary to improve the oxidation and corrosion resistance of vanadium-based alloys, to expand their use in various different environments, such as pressurized water, helium gas and also vacuum leak condition.¹⁴⁻¹⁷⁾ Additions of Cr and Ti were expected to improve the corrosion properties of the alloys,^{18,19)} and additions of Al and Y were expected to contribute to the formation of a protective oxide layer.¹⁴⁻¹⁷⁾ However, the effects of increasing Cr and Ti or addition of Si, Al and Y on

corrosion properties in pressurized and vaporized water have not yet been clarified.

The objectives of this study are to evaluate the influence of Cr and Ti concentration and addition of minor elements such as Si, Al and Y on the corrosion properties of V-Cr-Ti type alloys in pressurized and vaporized water environments as well as the mechanical properties after corrosion tests.

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 V-based high Ti alloys, such as V-4Cr-10Ti and V-4Cr-15Ti (in mass%) alloys. In order to investigate the effect of doping of minor elements, such as Si, Al and Y, the alloys V-4Cr-4Ti-0.5Si, V-4Cr-4Ti-0.5Al, V-4Cr-4Ti-0.5Y and V-15Cr-4Ti-0.5Y were prepared. These were melted and fabricated at the Research Institute for Metals, Tohoku University. To reduce interstitial impurities such as C, O, and N, the raw V and Ti metals were electron beam refined, and arc-melted with a contamination reducer. A V-4Cr-4Ti alloy with less interstitial impurities, which were 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 alloy buttons were cold-rolled to sheets 1 mm in thickness. Coupon samples 10 mm × 15 mm × 1 mm for measurement of mass change were cut from each alloy sheet. These samples weighed about 850 mg. Small tensile test specimens were punched out from the 0.25 mm-thick sheet obtained by cold rolling of the 1 mm-thick sheet. The size of the gauge section was 5 mm × 1.2 mm. Each specimen was annealed at 1000~1200°C for 1 or 2 hours in a vacuum of 1×10^{-3} Pa to obtain recrystallized microstructures with a mean grain size of about 17 μ m.

Corrosion tests using a refreshed autoclave system were

Table 1 Chemical compositions of the vanadium alloys examined.

	(mass%)						(mass ppm)			
	V	Cr	Ti	Si	Al	Y	C	O	N	H
V-4Cr-4Ti	Bal.	4.28	4.25	—	—	—	93	235	171	5
V-7Cr-4Ti	Bal.	7.17	3.65	—	—	—	71	213	174	9
V-10Cr-4Ti	Bal.	10.55	4.15	—	—	—	118	276	249	11
V-12Cr-4Ti	Bal.	12.25	4.10	—	—	—	186	304	485	15
V-15Cr-4Ti	Bal.	14.46	3.95	—	—	—	240	273	382	12
V-20Cr-4Ti	Bal.	20.10	4.12	—	—	—	165	233	220	5
V-4Cr-10Ti	Bal.	4.22	9.76	—	—	—	214	275	314	4
V-4Cr-15Ti	Bal.	4.04	14.40	—	—	—	227	323	282	5
V-4Cr-4Ti-0.5Si	Bal.	3.84	3.85	0.52	—	—	222	120	625	7
V-4Cr-4Ti-0.5Al	Bal.	3.81	3.83	—	0.50	—	236	121	612	10
V-4Cr-4Ti-0.5Y	Bal.	4.01	4.03	—	—	0.50	278	89	604	10
V-15Cr-4Ti-0.5Y	Bal.	14.15	3.88	—	—	0.50	261	344	618	37
NIFS HEAT-1	Bal.	4.1	4.4	—	—	—	66	181	88	18

carried out in pressurized water (288°C , 8.6×10^6 Pa) containing 400 ppb dissolved oxygen for 300 hours. The oxygen levels in the inlet and outlet water were checked continuously and adjusted to the equilibrium state. Other corrosion tests in vaporized water (400°C , 10.6×10^6 Pa) were also conducted for 72 hours. After exposure, the weight change of each alloy was measured. Tensile tests before and after the corrosion tests were conducted at room temperature at a strain rate of $6.7 \times 10^{-4} \text{ s}^{-1}$. The fracture surfaces of the tested samples were observed by scanning electron microscope (SEM) and the surface oxides of the specimens were analyzed by X-ray diffraction.

3. Results and Discussion

Figure 1 shows the weight change per unit surface area of each alloy after the corrosion test in high-temperature pressurized water for 300 hours. Weight losses were observed for every alloy at this condition. In the V-4Cr-4Ti types, weight loss of V-4Cr-4Ti-0.5Y alloy was slightly smaller than in the other alloys. A comparison of V-4Cr-4Ti with V-15Cr-4Ti type alloys clearly shows that addition of Cr was effective in reducing weight change during corrosion. Photographs of the specimens were taken and the surfaces were observed by SEM after the corrosion test. The results

Fig. 1 Mass change for each alloy by corrosion in pressurized water for 300 hours.

Fig. 2 Photographs and micrographs of the surface for V-4Cr-4Ti and V-15Cr-4Ti alloys after corrosion in pressurized water.

are shown in Fig. 2. The appearance of the V-4Cr-4Ti alloy was very dark and its surface was covered with an oxide film consisting of VO_2 and V_2O_5 , according to the X-ray diffraction analysis. On the other hand, the surface of V-15Cr-4Ti alloy kept a shiny metallic color. Both surfaces had holes (marked by arrows into the micrographs), the diameter of which were around $5 \mu\text{m}$, where the oxide particles had existed. It is assumed that the weight loss of each alloy can be partly attributed to these holes.

To investigate the effect of corrosion on the mechanical properties of each alloy, tensile tests were conducted at room temperature before and after the corrosion tests. The stress-strain curves of V-4Cr-4Ti and V-15Cr-4Ti alloys are shown in Fig. 3, and the fracture surfaces are shown in Fig. 4. The

Fig. 3 Tensile Properties of V-4Cr-4Ti and V-15Cr-4Ti alloys before and after corrosion in pressurized water.

V-4Cr-4Ti

V-15Cr-4Ti

Fig. 4 Scanning electron micrographs of fracture surface of V-4Cr-4Ti and V-15Cr-4Ti alloys before and after corrosion in pressurized water.

V-15Cr-4Ti alloy showed about double the yield stress as well as the ultimate tensile strength of the V-4Cr-4Ti alloy, but the elongation of the V-15Cr-4Ti alloy was slightly greater than that of the V-4Cr-4Ti alloy. The effects of corrosion on their tensile properties were minimal. The stress-strain curves for each alloy were almost the same before and after the corrosion test. The elongations were slightly reduced after corrosion. The fracture surfaces of both alloys showed a ductile mode before and after the corrosion test. The reduction in area decreased after corrosion test for each alloy.

Figure 5 shows the weight change per unit surface area of each alloy after the corrosion test in high-temperature vaporized water for 72 hours. Other industrial materials, such as SUS304, SUS316, Zircaloy 2 and Zircaloy 4 were included in the test as reference alloys. Every V-4Cr-4Ti type

Fig. 5 Mass change for each alloy by corrosion in vaporized water for 72 hours.

alloy showed weight loss after corrosion test except for the V-20Cr-4Ti alloys. Other alloys showed a small weight gain. The oxide film of the V-4Cr-4Ti alloy was so fragile that most of the film was peeled off the surface before weight measurement, resulting in a significantly greater weight loss than the other alloys. It is estimated that the real weight loss of the V-4Cr-4Ti alloy is about 60 g/m^2 , taking account of the peeling off the oxide. The weight loss of V-4Cr-4Ti type alloys was reduced as the Cr content increased. The V-20Cr-4Ti alloy showed a slight weight gain, almost same as that of SUS316 that had the best corrosion properties of the tested alloys. Increasing the Ti content and the addition of minor elements, such as Si, Al and Y were also effective in reducing weight change for V-4Cr-4Ti type alloys. However, comparing the V-15Cr-4Ti with V-15Cr-4Ti-0.5Y alloys, the effect of addition of Y on weight change was not very significant. The dependence of weight change on Cr content is summarized in Fig. 6, where the peeling-off of the oxide film is taken into account for the V-4Cr-4Ti alloy. The figure shows that increasing the Cr content up to 12% was very effective in reducing weight change. But this effect was saturated over 12%.

Tensile tests before and after corrosion tests were also conducted at room temperature to investigate the effect of corrosion on the mechanical property. Figure 7(a) shows the

Fig. 6 Dependence of weight change on the Cr content of the alloy corrosion-tested in vaporized water.

Fig. 7 Tensile Properties of V-4Cr-4Ti, V-10Cr-4Ti, V-15Cr-4Ti and V-20Cr-4Ti alloys, (a) before and (b) after corrosion in vaporized water.

stress-strain curves of V-4Cr-4Ti, V-10Cr-4Ti, V-15Cr-4Ti and V-20Cr-4Ti alloys before corrosion. The yield stress and the ultimate tensile strength depended on the Cr content. However, the tensile strain for each alloy was almost the same, ranging from 0.25 to 0.3. After exposure to vaporized water, the resultant stress-strain curves are shown in Fig. 7(b). The V-4Cr-4Ti and V-10Cr-4Ti alloy kept almost the same elongation before corrosion. However, the elongation of the alloys containing over 10% Cr reduced with increasing Cr content. The V-20Cr-4Ti alloy fractured in the elastic deformation region after the corrosion test.

Figure 8 shows the stress-strain curves for the V-12Cr-4Ti and the V-15Cr-4Ti alloys after exposure to vaporized water and hydrogen degassing after corrosion test. The elongations of the V-12Cr-4Ti and the V-15Cr-4Ti alloys after the corrosion test were significantly reduced and cleavage fracture was observed reflecting a hydrogen embrittlement. After the corrosion test, a heat treatment was conducted in a vacuum of 3×10^{-2} Pa at 500°C for 1 h to degas hydrogen. As shown by the arrows in figure, after the degassing, the elongation of the alloy recovered to the same level as that in the annealed condition. The effects of hydrogen degassing on recovery of elongation depended on the Cr content: the higher the Cr content of the alloy, the greater the effect on the recovery.

Fig. 8 Effects of hydrogen-degassing on tensile properties of V-12Cr-4Ti and V-15Cr-4Ti alloys after corrosion in vaporized water.

Fig. 9 Tensile Properties of V-15Cr-4Ti-0.5Y alloys before and after corrosion in vaporized water.

Figure 9 shows the stress-strain curves of the V-15Cr-4Ti-0.5Y alloy before and after corrosion treatment. After the treatment, the elongation of the alloy was slightly reduced. However, the strain remained at around 0.25, and the reduction of elongation was much less than that of the V-15Cr-4Ti alloy. It is assumed that the addition of Y reduces hydrogen embrittlement, since the yttrium oxides on the surface prevent hydrogen from being absorbed into the matrix. Alternatively, the yttrium included in the matrix has a higher affinity with hydrogen than all of the other elements in the alloy. The yttrium then may form hydride, keeping the hydrogen content in the matrix low enough to preserve the high elongation of the alloy.

4. Summary

Corrosion tests were conducted in pressurized and vaporized water to investigate the effect of Cr and Ti, and small addition of minor elements, such as Si, Al and Y, on the corrosion resistance of V-Cr-Ti type alloys.

(1) Weight losses were observed for every alloy after corrosion test in pressurized water. It was clearly shown that addition of Cr was effective in reducing the weight change by corrosion in pressurized water.

(2) The effects of corrosion on their tensile properties were minimal. The stress-strain curves for each alloy were almost the same before and after corrosion in pressurized water.

(3) After the corrosion test in vaporized water, the weight loss of V-4Cr-4Ti type alloys was reduced as the Cr content was increased. The V-20Cr-4Ti alloy showed a slight weight gain almost identical to that of SUS316, that had the best corrosion properties of the tested alloys.

(4) The V-4Cr-4Ti and the V-10Cr-4Ti alloy kept almost the same elongation before corrosion in vaporized water. However, the elongations of alloys containing over 10% Cr decreased with increasing Cr content. The V-20Cr-4Ti alloy fractured in the elastic deformation region after the corrosion in vaporized water.

(5) The elongations of the V-12Cr-4Ti and the V-15Cr-4Ti alloys were significantly reduced by corrosion in vaporized water, and cleavage fracture was observed reflecting hydrogen embrittlement. After hydrogen degassing, the reduced elongations of alloys recovered to the same level as that before corrosion.

(6) After corrosion in vaporized water, the V-15Cr-4Ti-0.5Y alloy still maintained sufficient elongation. It is possible that the addition of Y is effective in reducing hydrogen embrittlement.

Acknowledgments

The authors gratefully acknowledge the contributions of Dr. T. Shishido, Institute for Materials Research, Tohoku University, to the preparation of the samples.

This work was partly supported by the JUPITER-II program (Japan-USA Program of Irradiation/Integration Test for Fusion Research) and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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