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Corrosion properties of oxide dispersion strengthened steels in super-critical water environment

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Abstract

The effects of alloying elements on corrosion resistance in super critical pressurized water (SCPW) have been investigated to develop corrosion resistant oxide dispersion strengthened (ODS) steels. Corrosion tests were performed in a SCPW (783 K, 25 MPa) environment. Weight gain was measured after exposure to the SCPW. For the improvement of corrosion-resistance, the effects of chromium, aluminum, and yttrium on the corrosion behavior were investigated. The 9–12 wt%Cr ODS steels showed almost similar corrosion behavior with the ordinary ferritic/martensitic steel in the SCPW. However, the addition of high chromium (>13 wt%) and aluminum (4.5 wt%) are very effective to suppress the corrosion in the SCPW. Anodic polarization experiments revealed that the passive current of the ODS steels are lower than the ordinary ferritic/martensitic steels. Addition of aluminum improves the Charpy impact property of the ODS steels.

1. Introduction

Oxide dispersion strengthened (ODS) ferritic/martensitic steels have been developed for the application to fuel cladding material for fast breeder reactor (FBR) [1–4]. Because of the dispersion of the oxide particles, the ODS steels showed high strength at high temperature [5]. As for irradiation effects on the mechanical properties, recent irradiation experimental works clearly showed that the ODS steels were highly resistant to irradiation embrittlement at temperatures between 573 and 773 K up to 15 dpa [6,7].

The ODS steels developed for FBR fuel cladding material contain chromium at most 12%. It is well known that the corrosion resistance in high-temperature water reduces significantly with decreasing chromium concentration below 13% [8]. Thus, for ODS ferritic/martensitic steels, the most critical issue for the application to the water-cooling solid breeder fusion blanket is to improve their corrosion resistance in SCPW environment. The ODS ferritic/martensitic steels also have been considered to be effective to increase the thermal efficiency of a water-coolant solid blanket of a fusion reactor by increasing the operation temperature. Furthermore, the ODS steels can be easily applied to the fuel cladding materials for SCPW reactor, and also cladding material for high burn-up operation of a light water reactor as a cross-cutting material for different nuclear systems.

The goal of this study is to develop ODS ferritic/martensitic steels, which are resistant to corrosion in SCPW with high resistance to neutron irradiation embrittlement, and high temperature strength by means of alloy design. In this work, SCPW corrosion behavior of the 9Cr and 12Cr ODS steels was evaluated, and the effect of Cr and Al additions on the corrosion resistance was investigated.

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2. Experimental

2.1. Materials

The materials used were low-activation ODS ferritic/martensitic steels [1–4], and they were divided into two groups. The chemical compositions are shown in Table 1. The details of the fabrication process of the ODS steels were given in the previous papers [1–4]. The first generation of ODS steels were developed by JNC for the application to fuel claddings of a fast breeder reactor. Two different ODS steels were investigated: a 12Cr-ODS steel and a 9Cr-ODS steel. For comparison, an ordinary ferritic/martensitic 10Cr steel and SUS316L, as shown in Table 1(a)), were also investigated. The second generation of ODS steels were developed to investigate the effect of Cr and Al on the corrosion resistance. The Cr concentration was changed from 14% to 22%. Most of the steels contained 4.5% Al.

2.2. Corrosion rate measurement in SCPW

Corrosion tests were performed in the closed system of SCPW (783 K, 25 MPa). The elapsed times of the tests were 200, 400 and 600 h. After the corrosion test, the weight changes of the specimens were measured, and microstructures were observed by optical microscopy. The autoclave system for the corrosion tests is shown in Fig. 1.

2.3. Anodic polarization measurement

In order to compare the formation behavior of passive oxide films in each material, anodic polarization measurements were carried out in 1 mol H_2SO_4 solution at 303 K at a scanning speed of 20 mV/min in the range from −0.4 to 1.1 V.

2.4. Charpy impact test

In order to evaluate the mechanical property and the effect of thermal embrittlement as the σ-embrittlement, a miniaturized Charpy V notch (MCVN) test was performed before and after aging at 1073 K for 1 h. MCVN specimens were machined with the dimensions of 1.5 mm × 1.5 mm × 20 mm and the notch geometry of 0.3 mm in notch depth, 0.08 mm in notch root radius and 30° in notch angle with the longitudinal direction parallel to the extruding direction [9].

3. Results and discussion

3.1. Corrosion test in SCPW

Fig. 2 shows the dependence of weight gains on corrosion test period of the ODS steels. The weight gain

Table 1
Chemical compositions of materials used in this work

Materials	C	Si	Mn	Ni	Cr	Fe	Mo	W	V	Nb	Ti	Cu	N	Y	Y_2O_3
(a) Materials used in first corrosion test															
12Cr-ODS	0.02	0.05	0.046	0.035	11.97	Bal.	–	2.02	–	–	0.30	–	0.010	0.19	0.24
9Cr-ODS(1)	0.13	0.05	0.044	0.021	9.00	Bal.	–	1.95	–	–	0.20	–	0.013	0.29	0.37
9Cr-ODS(2)	0.13	0.006	0.01	0.02	9.11	Bal.	–	1.95	–	–	0.18	–	0.017	–	–
9Cr-ODS(3)	0.13	0.005	0.01	0.02	8.84	Bal.	–	1.91	–	–	0.29	–	0.010	0.35	0.44
F/M Steel	0.15	0.039	0.80	0.50	10.52	Bal.	0.40	1.81	0.20	0.049		–	0.072	–	–
SUS 316	0.05	0.72	1.01	10.21	17.23	Bal.	2.18	–	–	–	–	–	–	–	–
Inconel	0.02	0.18	0.17	61.51	21.65	3.64	9.0	–	–	3.45	0.23	–	–	–	–
Hasteloy G-30	0.01	0.5	1.1	Bal.	29.1	15.4	5.0	2.7	–	0.81	–	1.8	–	–	–

Materials	C	Si	Mn	P	S	Cr	W	Al	Ti	N	Y	Y_2O_3
(b) Materials used in second corrosion test												
19Cr(K1)	0.05	0.041	0.06	<0.005	0.002	18.37	0.29	<0.01	0.28	0.014	0.29	0.368
13Cr-4Al(K2)	0.04	0.033	0.06	<0.005	0.002	13.64	1.65	4.12	0.28	0.009	0.30	0.381
19Cr-4Al(K3)	0.08	0.033	0.06	<0.005	0.002	16.00	1.82	4.59	0.28	0.006	0.29	0.368
16Cr-4Al(K4)	0.09	0.039	0.06	<0.005	0.002	18.85	1.83	4.61	0.28	0.005	0.29	0.368
22Cr-4Al(K5)	0.10	0.039	0.07	<0.005	0.002	22.05	1.80	4.55	0.27	0.005	0.28	0.356
29Cr-4Al-1.8Si(K6)	0.10	1.75	0.06	<0.005	0.002	19.02	1.85	4.69	0.28	0.005	0.29	0.368

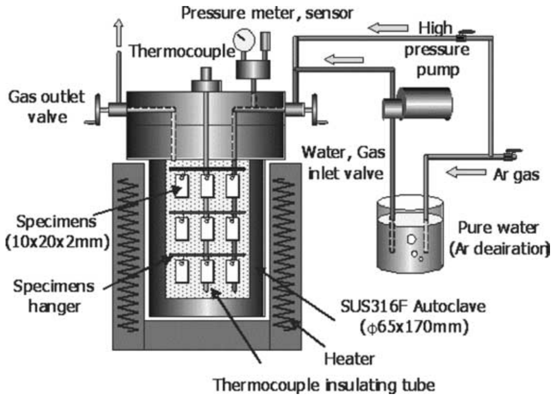

Fig. 1. The autoclave system for corrosion tests in supercritical pressurized water.

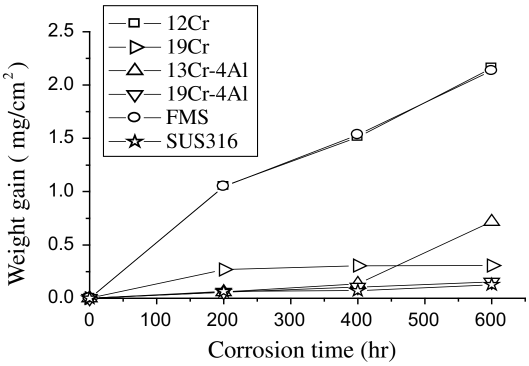

Fig. 2. The effect of Cr and Al on the corrosion properties of ODS ferritic/martensitic steel in SCPW (783 K, 25 MPa).

of the 12Cr-ODS steels of the first generation of ODS steels is almost the same as that of a ferritic/martensitic steel, and about 1 order of magnitude larger than for SUS316. These results indicated that high-chromium steels showed high corrosion resistance. The addition of yttrium is sometimes effective to increase the corrosion resistance in dry air. However in this work, the effect of yttrium from 0.24 to 0.44 wt% was not very large. As compared with 12Cr-ODS steels of first generation of ODS steels, when increasing the chromium concentration to 19 wt%, corrosion rate was greatly decreased, and addition of aluminum caused a reduction of corrosion. Furthermore, an increase of chromium and an addition of aluminum at the same time resulted in the suppression of corrosion. It shows that addition of chromium over 13 wt% and aluminum (4.5 wt%) are very effective in suppressing corrosion in SCPW.

3.2. Surface oxidation behaviour

The cross sectional view of the microstructure near the specimen surface after corrosion tests in SCPW (783

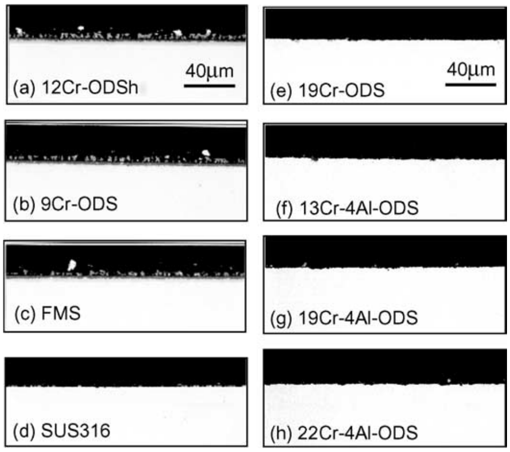

Fig. 3. The cross-sectional view of the microstructure near the specimen surface after corrosion tests in SCPW (783 K, 25 MPa) in (a) 12Cr-ODS, (b) 9Cr-ODS, (c) FMS, (d) SUS316, (e) 19Cr-ODS, (f) 13Cr–4Al-ODS, (g) 19Cr–4Al-ODS and (h) 22Cr–4Al-ODS.

K, 25 MPa) is shown in Fig. 3. It is clear that the oxidation layers of the first generation ODS steels (Fig. 3(a) and (b)) consist of multi-layer films and are similar to that of ferritic/martensitic steel and thicker than that of SUS316, as expected from the weight gain test results. However the oxidation layers of the second generation of ODS steels (Fig. 3(e)–(h)) are too small to distinguish the multi-layer oxide film with the optical microscope, as shown in Fig. 3.

3.3. Effect of chromium concentration

It is known that the corrosion rate of metallic materials in water decreases with increasing chromium concentration. Fig. 4 shows the effect of chromium concentration on the corrosion properties of ODS steel in super critical water. When there was no addition of aluminum, 12Cr-ODS steel shows similar corrosion property to 9Cr-ODS steel. But 19Cr-ODS steel shows good corrosion property. When aluminum was added in ODS steels, weight gain also decreased with increasing chromium concentration. This is considered to be due to the formation of Al_2O_3 or slowing the rate of the formation of Cr_2O_3 [10,11]. Fig. 4 suggests that a saturation point occurs around 15 wt% Cr.

3.4. Anodic polarization curve

In order to investigate the corrosion behaviour of the steels, anodic polarization curves were obtained for SUS304, ferritic steel (JLF-1: 9Cr–2W–0.1C martensitic steel) and two sorts of 9Cr-ODS steels (MD20, ME22) of which the chemical compositions were similar to that of 9Cr-ODS(1), and shown in Fig. 5. Although the an-

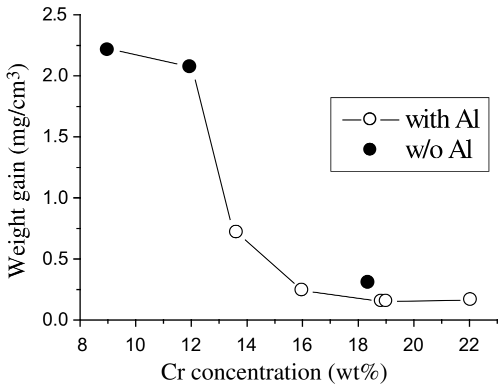

Fig. 4. The effect of Cr concentration on the corrosion properties of ODS steel in SCPW (783 K, 25 MPa, 600 h).

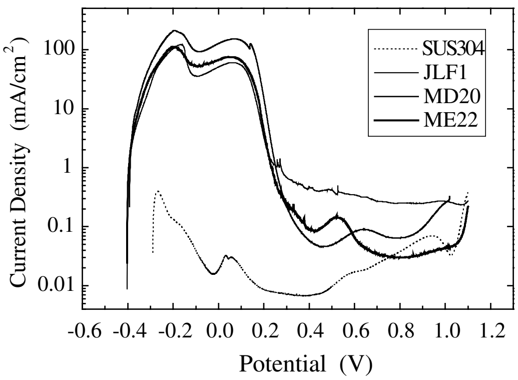

Fig. 5. Anodic polarization curves obtained for SUS304, ferritic steel (JLF-1: 9Cr–2W–0.1C ferritic steel) and two sorts of 9Cr-ODS steels (MD20, ME22).

odic current densities of the ODS steels were almost the same as that of 9Cr ferritic steel (JLF-1), and more than two order higher in the active region than that of SUS304 austenitic steel, the passive current densities of the ODS steels were about one order lower than that of JLF-1 steel and almost similar to that of SUS304.

3.5. Charpy impact property

Fig. 6 shows the test temperature dependence of the total absorbed energy of the ODS steels before and after aging. Ductile-to-brittle transition temperature (DBTT) of 19Cr–4Al-ODS steel is lower than that of 19Cr-ODS steel by about 30 K. The DBTT shift occurred in both ODS steels after aging at 1073 K for 1 h. The ΔDBTT of the 19Cr-ODS steel and the decrease of upper shelf energy, are larger than those of 19Cr–4Al-ODS steel. It shows that the addition of aluminum is also effective in improving the impact property. The improvement of Charpy properties by addition of Al is considered to be due to diminishing anisotropy in the tensile properties at

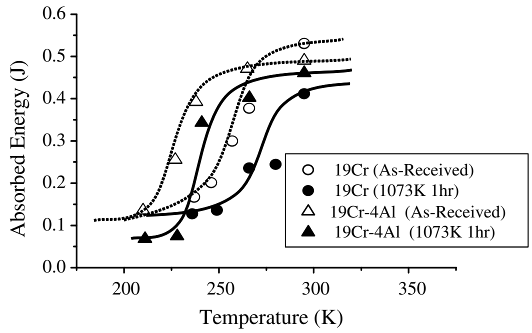

Fig. 6. Test temperature dependence oftotal absorbed energy for 1.5 mm miniaturized Charpy specimen of ODS steels before and after the aging at 1073 K for 1 h.

room temperature, which showed almost similar ductility in both the axial and radial direction of extruded bar. In any case the DBTT of all aged specimens of the ODS steel is still below room temperature.

4. Conclusions

1. ODS steels (9–12wt% Cr) showed almost similar corrosion behavior with ferritic/martensitic steel in the SCPW (25 MPa, 793 K). No significant beneficial effect of yttrium (0.24–0.44 wt%) was observed in the corrosion behavior in 9 and 12Cr-ODS steels. Addition of Cr over 13 wt% and Al (4.5 wt%) are very effective in suppressing the corrosion in the SCPW.
2. Passive current density of the ODS steel is one order of magnitude lower than that of ferritic steel at room temperature.
3. Addition of aluminum also brings better Charpy impact properties of the ODS steels; it decreases the DBTT and reduces the thermal embrittlement.

Acknowledgements

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