

Corrosion resistance of high-Cr oxide dispersion strengthened ferritic steels in super-critical pressurized water

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Abstract

The effects of alloying elements, such as Cr and Al, 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, and then oxide layers were analyzed by low angle X-ray diffraction and SEM microscopy. The weight gains of all high-Cr ODS steels are smaller than an austenitic stainless steel (SUS316L). More uniform and thinner oxidation layers were observed on the ODS steels after corrosion compared to those on 9Cr martensitic steel and SUS316L.

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1. Introduction

Oxide-dispersion-strengthened (ODS) ferritic/martensitic steels have been developed for application as fuel cladding material for the sodium-cooled fast breeder reactor (SFR) [1,2]. Because of the dispersion of the oxide particles, the ODS steels show high strength at high temperatures [3]. As for irradiation effects on the mechanical properties, recent irradiation experimental work clearly showed that the ODS steels were highly resistant to irradiation embrittlement at temperatures between 573 and 773 K up to 15 dpa [4,5].

The application of ODS ferritic/martensitic steels to the fusion blanket is essential to increase the thermal efficiency of fusion reactors by increasing the operational temperature. The ODS steels developed for SFR fuel cladding material contain 12% chromium at most. It is well known that the corrosion resistance in high-temperature water reduces significantly with decreasing chromium concentration below 13% [6–12]. Thus, the most critical issue for the application of ODS steels to the water-cooling solid breeder fusion blanket is to improve their corrosion resistance in super critical pressurized water (SCPW) environment.

In our previous work [7–13], it was reported that the addition of chromium (>13 wt%) and aluminum (4.5 wt%) to the ODS steels were very effective in suppressing the corrosion in a SCPW (783 K, 25 MPa) environment. Addition of aluminum also improves the Charpy impact property of the high

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Cr ODS steels. However, there is a limitation to Cr concentration, because an increase in Cr concentration often resulted in the thermal aging embrittlement of the steels.

The goal of this study is to use alloy design to develop ODS ferritic/martensitic steels, those are resistant to corrosion in SCPW, have high resistance to neutron irradiation embrittlement, and display high temperature strength. This paper describes results on the effects of chromium concentration on the long term corrosion resistance in the SCPW for high-Cr ODS steels.

2. Experimental

2.1. Materials

The materials used were high Cr ODS ferritic steels [7–13]. The chemical compositions are shown in Table 1. The details of the fabrication process of the ODS steels are given in previous papers [1,2]. These ODS steels were developed to investigate the effect of Cr and Al on corrosion resistance as well as mechanical properties. The Cr concentration ranged from 14% to 22%. Most of the steels except

for K1 ODS steel, contained 4.5% Al. All of the ODS steels were finally heat treated at 1323 K for 1 h, then air-cooled.

2.2. Corrosion rate measurement in SCPW

Fig. 1 shows the autoclave system for the corrosion test. Specimens were cut with the dimensions of 10 mm × 18 mm × 2 mm, and mechanically polished to grit #800. The test was done in the closed system of SCPW at 783 K (± 10 K) with a pressure of 25 MPa. The weight changes of the specimens were measured after the corrosion test up to 2400 h.

2.3. Analysis of oxide layer after corrosion test

In order to analyze the structure of corroded surface of each material, X-ray analysis (Co K α radiation) was performed with an incidence beam angle of one degree. The estimated penetration depth of X-ray beam is about 1 μ m. A field-emission scanning electron microscope (FE-SEM) was used for the observation of oxide layers on surface and cross section of specimens. Before cutting the specimens for the observation of cross section, Ni-plating

Table 1
Chemical compositions of materials used in this work (wt%)

Materials	C	Si	Mn	P	S	Cr	W	Al	Ti	N	Y	Y ₂ O ₃
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
14Cr-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
16Cr-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
19Cr-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

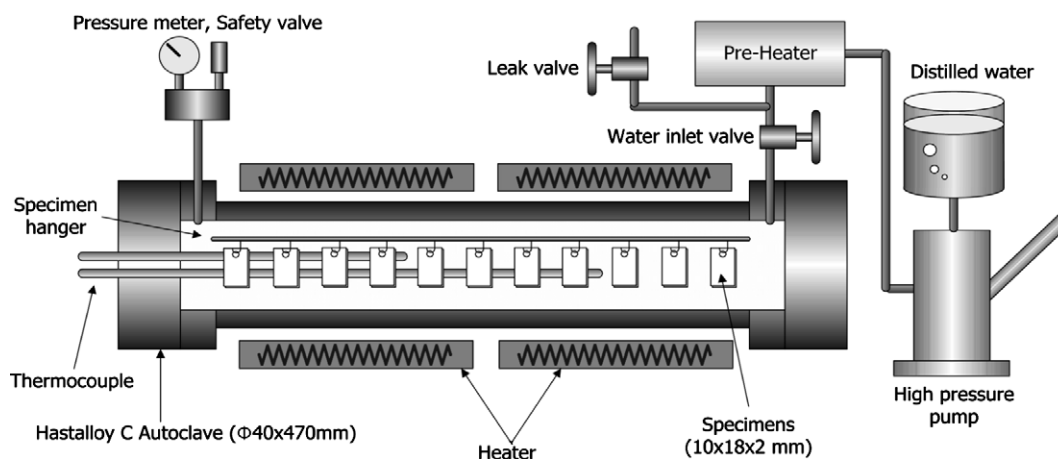


Fig. 1. Autoclave system for corrosion tests in supercritical pressurized water (783 K, 25 MPa).

was carried out in a bath of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$: 30 g, NH_4Cl : 3 g, H_2BO_3 : 3 g, distilled water: 200 ml at a current density of 0.5 A at 3 V.

3. Results and discussion

3.1. Weight change in SCPW

Fig. 2 shows the dependence of weight gains on time. This results indicate that the weight gains of all high-Cr ODS steels are smaller than an austenitic stainless steel (SUS316L). It is noticed that the ODS steel which contained even 14 wt% of Cr showed higher resistance to corrosion than SUS316L that contained 18 wt% of Cr and 10 wt% of Ni. The ODS steels with higher Cr concentration show better corrosion resistance. The weight gains of the 9Cr martensitic steel (JLF1), were much larger than that of the SUS316L.

3.2. XRD analysis

X-ray diffraction spectra obtained from the specimen surfaces of 9Cr martensitic steel (JLF1) and 22Cr-4Al ODS steel (K5) exposed to super critical pressurized water (783 K, 25 MPa) are shown in Fig. 3. The oxide layer on the 9Cr martensitic steel (JLF1) was identified as magnetite (Fe_3O_4), and its intensity is much stronger than that of base metal element, Fe. The spinel type oxide (Fe, Cr) $_3\text{O}_4$, as well as Fe_3O_4 was found on the surface for

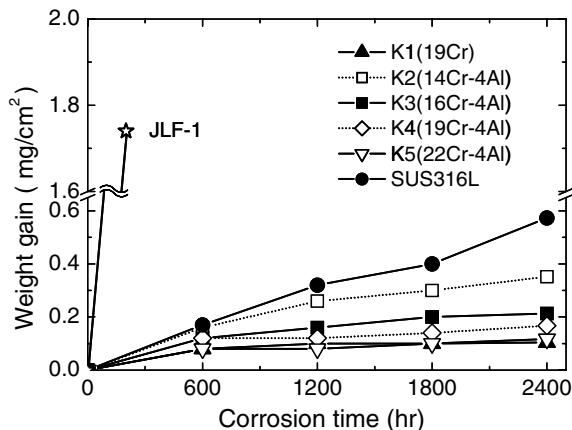


Fig. 2. Weight gains of the high-Cr ODS ferritic steels as well as those of a 9Cr martensitic steel (JLF1) and an austenitic stainless steel (SUS316L) in super critical pressurized water (783 K, 25 MPa).

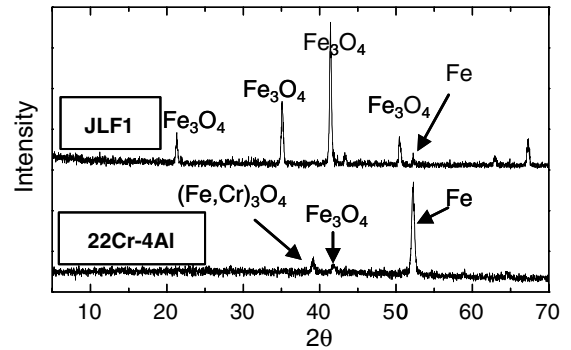


Fig. 3. X-ray diffraction patterns obtained from the 9Cr martensitic steel (JLF1) and 22Cr-4Al ODS steel (K5) exposed to super critical pressurized water (783 K, 25 MPa) for 2400 h.

SUS316L and ODS steels, and the intensity of spinel type oxide was much weaker than that of Fe, indicating that the corrosion depth is much shallower than JLF-1. The intensity ratio of Fe_3O_4 oxide to Fe in each material is plotted in Fig. 4. In spite of very short exposure period (200 h), 9Cr martensitic steel showed much larger relative intensity ratio of the Fe_3O_4 oxide than that of ODS steels. It is of note that the ratio of the 14Cr ODS steel was smaller than SUS316L, although Cr concentration was lower than that of this steel and the lowest in the

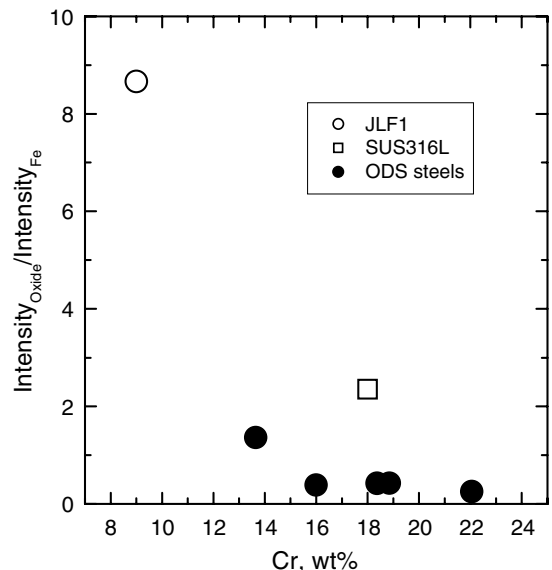


Fig. 4. Intensity ratios of oxide to Fe with Cr concentration obtained by means of low angle X-ray diffraction analysis after corrosion test in super critical pressurized water (783 K, 25 MPa) for 2400 h.

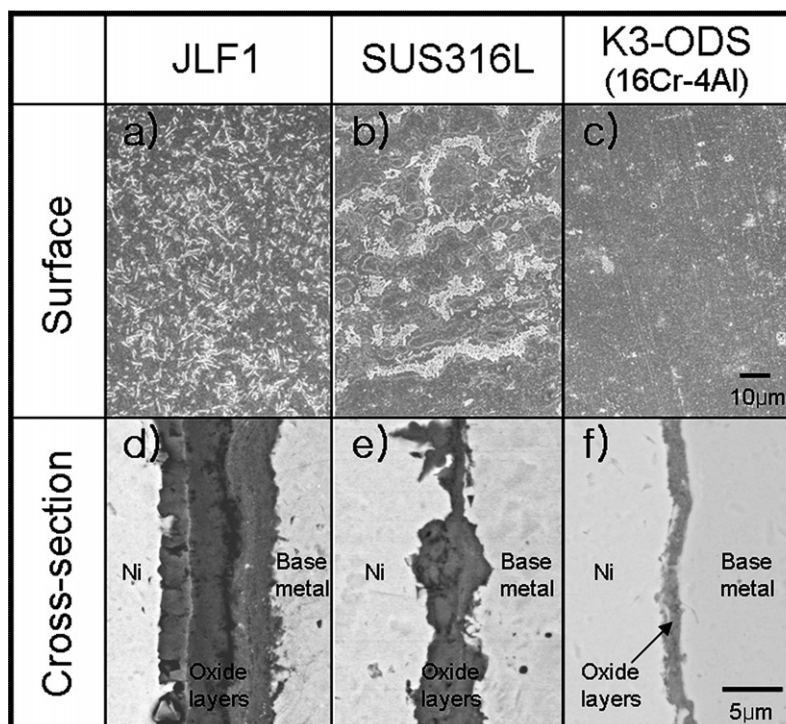


Fig. 5. SEM images taken from the surfaces and cross sections of oxide scales formed on JLF1, SUS316L, and 16Cr-4Al ODS steel (K3), after corrosion test in super critical pressurized water (783 K, 25 MPa) for 2400 h.

ODS steels tested. The ratio became smaller with increasing Cr concentration.

3.3. SEM microscopy

Fig. 5 shows the back scattered electron images of surfaces (top) and the cross sections (bottom) of JLF-1, (a) and (d), SUS316L, (b) and (e), and K3-ODS, (c) and (f), observed by FE-SEM after corrosion tests in SCPW (783 K, 25 MPa). The surface of the 16Cr-4Al ODS steel was covered by a very clean corrosion-protective oxide ($\text{Cr, Fe}_3\text{O}_4$), which are dark coloured areas. The light coloured area are considered to be so-called iron-rich nodules that was never observed in 19 or 22Cr ODS steels. The cross sections near the surface after corrosion tests are shown in Fig. 5(d)–(f). Left bright side, middle dark area and right bright side are Ni plate, oxide film and base metal, respectively. It is clear that the oxide film of 9Cr martensitic steel (Fig. 5(d)) consist of multi-layers and was thicker than that of SUS316L (Fig. 5(e)), as expected from the weight gain test results. However, the oxide film of the 16Cr-4Al ODS steel (Fig. 5(f)) is too thin to distinguish each oxide layer by means of SEM. The

oxidation film of SUS316L was very irregular, while that of the ODS steel was very uniform.

The mechanism of high resistance to corrosion of the ODS steels in the SCPW is not clearly known yet, though it is expected that the yttria particles play a role in producing a continuous fine protective oxide layers containing Cr on the surface of the specimen [14].

4. Conclusions

1. The ODS steel which contained only 14 wt% of Cr showed higher resistance to corrosion than SUS316L that contained 18 wt% of Cr and 10 wt% of Ni. The ODS steels with higher Cr concentrations showed better corrosion resistance.
2. The XRD peak height ratio of the 9Cr martensitic steel showed much larger relative intensity ratio of the Fe_3O_4 oxide than that of ODS steels. The ratio became smaller with increasing Cr concentration.
3. Among the micrographs of surface, the surface of the 16Cr-4Al ODS steel was covered by a protective oxide ($\text{Cr, Fe}_3\text{O}_4$). The oxide film of 9Cr

martensitic steel consisted of multi-layers and was thicker than that of SUS316L.

4. The mechanism of high resistance to corrosion of the ODS steels in the SCPW is not clear yet, though it is expected that the yttria particles play a role to produce a continuous fine protective oxide layers containing Cr on the surface of the specimen.

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