HIGH TEMPERATURE OXIDATION AND CORROSION BEHAVIOR OF SEVERAL OXIDE DISPERSION STRENGTHENED FERRITIC ALLOYS

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Abstract

The high temperature oxidation and Electrochemical corrosion behaviour of several ODS ferritic alloys with different Cr content (12~18 %) were investigated. The oxidation tests were conducted at temperature between 600 ℃ to 1100 ℃ in air exposed for up to 500 h. Weight gain was measured after long time exposure to high temperature in air. Electrochemical corrosion behaviour was measured to compare the basic corrosion resistance of different ODS alloys. XRD, SEM-EDS and EPMA were used to characterize the structure, morphology, and composition of the oxide and corrosion scales.

1. Introduction

Oxide Dispersion Strengthened (ODS) ferritic steels are an emerging class of nanostructured alloys, which contain Y-Ti-O enriched dispersion strengthened nano particles (or even clusters) with very high number density. These complex nano oxide particles are stable at high temperature (even close to the melting point of the steel) or under irradiation up to 800 °C [1-4], which make ODS ferritic steels excellent high temperature mechanical properties and neutron irradation resistance ability [5, 6]. Recent studies indicate that the ODS ferritic steels also show excellent corrosion-resistance properties [7, 8]. ODS ferritic steels have been considered as one of the most promising cladding candidate material for supercritical water-cooled reactors (SCWR). Sufficient general corrosion resistance to maintain the strength of the cladding, and the high-temperature oxidation resistance of this ODS steel are very important required properties.

In this study, different Cr content (12-18%) ODS ferritic alloys were investigated by exposing samples at high temperature in air. Electrochemical corrosion behaviour was also tested to compare the basic corrosion resistance of different ODS alloys.

2. Materials and experiment

The three kinds of ODS steels used in this investigation were produced precisely according to their chemical composition for a special work. The chemical compositions of these materials are given in Table 1. The mixtures of nitrogen atomized powders and 30 nm Y_2O_3 powders were mechanically alloyed via a planetary ball mill and then HIPing at 1150℃ for 2 h.

Table 1 Nominal chemical composition of the ODS steels used in this investigation (wt %)

Materials	C	Si	Mn	Cr	V	W	Ta	Ti	Al	Y_2O_3
12-ODS	0.13	0.15	0.5	12	0.18	2	0.08	0.5	-	0.35
14Cr-ODS	0.06	0.2	-	14	-	2	-	0.5	-	0.35
18Cr-ODS	0.02	0.15	-	18	-	2	-	0.5	4	0.35

The test samples were cut from the above-mentioned steels in rectangular shape with a dimension of 10 mm×10 mm×2 mm. These samples were polished using 1200-grid abrasive paper to obtain a good surface preparation. Then, cleaned ultrasonically in acetone and dried. The oxidation tests were investigated at 600 ℃, 700 ℃, 850 ℃ respectively up to 500 h and 1100 ℃ up to 20 h in a muffle in air.

The electrochemical behaviour of different ODS steels was studied by recording anodic and cathodic potentiodynamic polarization curves. The tests were performed at 303±1 K in a three electrode assembly. A saturated calomel electrode was used as the reference; a platinum foil was used as counter electrode. All potentials are reported vs. SCE. The experiments were measured after 10 min of immersion in the testing solution (no deaeration, no stirring). The working electrode was prepared from a square sheet of ODS steels such that the area exposed to solution was 1 cm^2. Measurements were performed in the 1 M HSO_4 solution equilibrium with the atmosphere by changing the electrode potential automatically from - 0.4 to 1.1 V vs. corrosion potential at a scan rate of 20 $mVmin^{-1}$.

SEM with back-scatter mode and EDS was used for the analysis of the oxide layers on surface and cross section of the specimens. The elemental distribution was measured by means of electron probe microanalysis (EPMA). In order to analyze the structural change of the corroded surfaces of the specimens, X-ray diffraction (XRD) analysis was performed.

3. Results and discussion

3.1 High temperature oxidation behavior

Fig.1 shows the morphologies of the oxide scales formed on different ODS steels after exposure at 600℃ and 700℃ for up to 500 h respectively. When exposuring at 600℃, almost no oxidation occurred on all samples. But surface analysis via EDS indicated that some Mn enrichment occurred for the sample of 12 Cr ODS steel, as shown in Fig. 1(a) indicated by the arrows. When the exposring temperature increased to 700 ℃, only slight oxidation occurred on the sample of 12 Cr ODS and 14 Cr ODS steel, while no oxidation occurred on the sample of 18 Cr ODS steel. From the cross section morphology, as shown in Fig. 1(b) and (c), we can see that the thickness of oxidation layer for the sample of 12 Cr ODS steel is only ~ 0.5 μm after exposure at 700℃ for 100 h, and the thickness increased to ~ 1.5 μm after exposure for 500 h. Fig. 1 (c) shows that this very thin oxide scale actually included two layers, namely the outer oxide layer and inner oxide layer. This was also demonstrated by the EPMA analysis. EPMA images in linescan mode reveals that the outer layer contained more Cr, while Mn and O existed in the layer close to the matrix. Fig. 1 (d) shows that the whole surface of the sample of 12 Cr ODS steel was covered with regular particles with the grain size about 1 μm after exposure at 700 ℃ for 500 h. XRD results revealed that these particles are spinel oxides with a composition of $MnFe_2O_4$, as well as a phase of $Cr_{1.3}Fe_{0.703}$ were found on the surface. Also from Fig. 1(d) we can see that cracks occurred on the oxidation layer, which indicate a tendency to spall of the oxidation layer. For the sample of 14 Cr ODS steel, only part of the surface were covered with spinel oxides contained Fe and Cr, while for the sample of 18 Cr ODS steel, almost no oxide was found on the surface, but some Al riched phase were found, as shown in Fig. 1(a) indicated by the arrows.

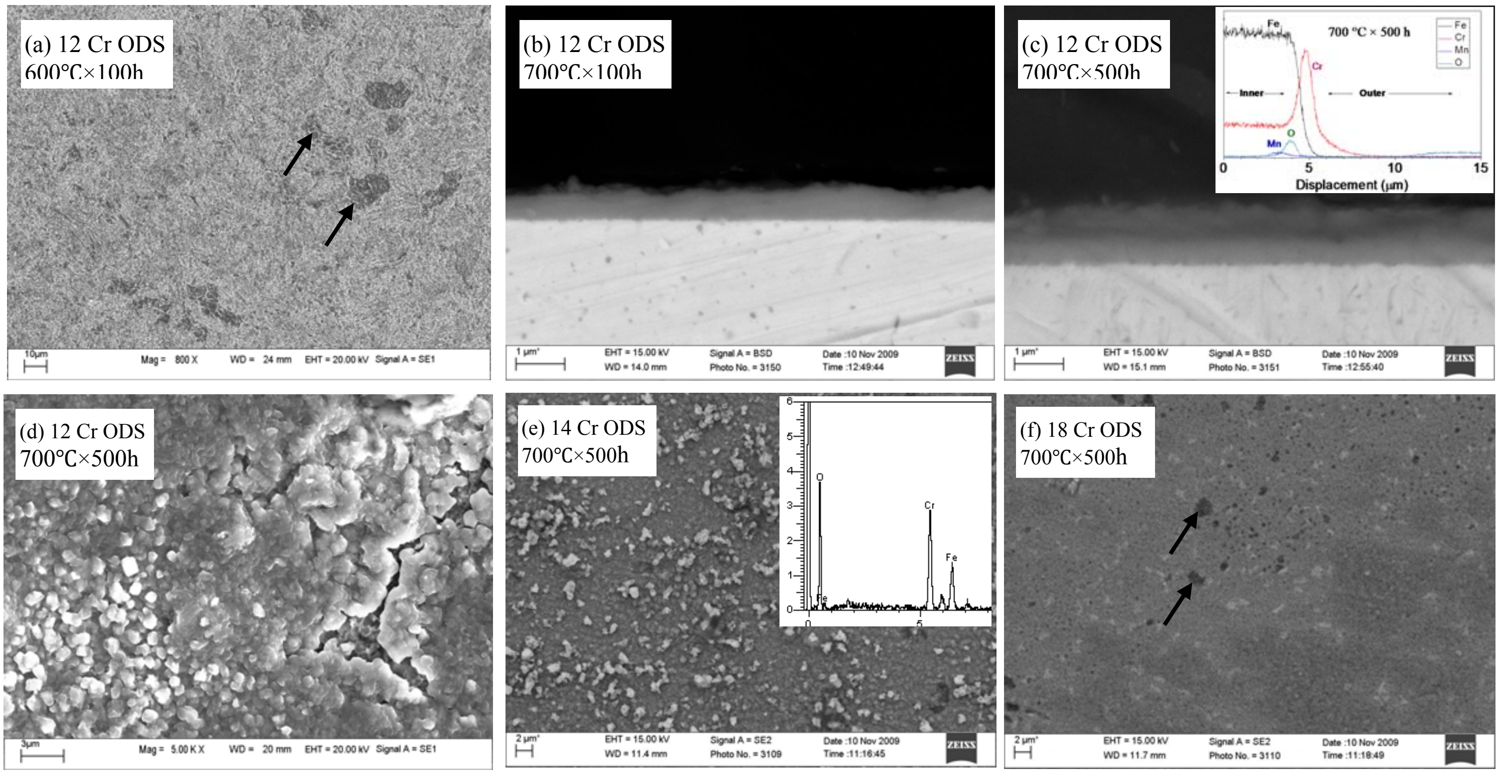

Fig. 1 Surface and cross section morphology of ODS steels after oxidation tests at 600℃ and 700℃

Fig. 2 shows the morphologies of the oxide scales formed on the ODS steels samples after exposure at 850℃ for 50 h and 500 h respectively. For the sample of 12 Cr ODS steel, almost the whole oxidation surface was covered with regular spinel type oxides and the grain size was ~3 μm after exposure for 50 h. When the exposure time increased to 500 h, the surface morphology demonstrate that the oxide layer has a tendency to spall. For the sample of 14 Cr ODS steel, dense fine spinel type oxides were covered on the whole surface after exposure for 50 h, also a tendency to spall of the oxide layer was found after exposure for 500 h. Still almost no oxidation was found for the sample of 18 Cr ODS steel after exposure at 850℃ for 500 h.

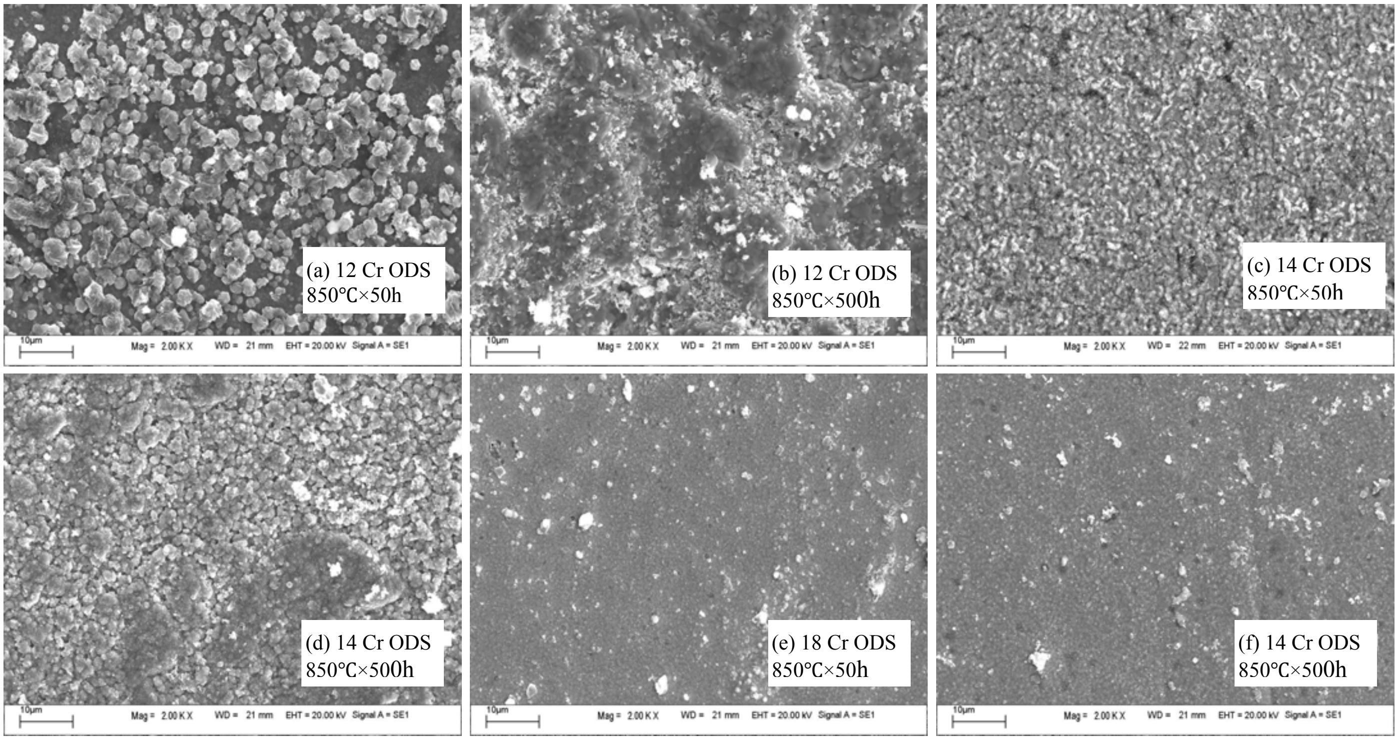

Fig. 2 Surface morphology of ODS steels after exposure at 850°C for different time

When the oxidation temperatue increased to 1100 ℃, heavy oxidation occurred for the sample of 12 Cr ODS and 14 Cr ODS steel after exposure for 20 h. The size of oxide particles formed on the surface are more than 20 µm. Obivous cracks can be found between oxide particles. For the sample of 18 Cr ODS steel, obvious oxidation also can be found, but the oxide layer are rather dense and absence of cracks. The weight changes as a function of test duration are presented in Fig. 3(d), which is quite accordance with the morphology observation. The weight gain of 12 Cr ODS and 14 Cr ODS steel are much higher than that of 18 Cr ODS steel. The weight gains of the samples of 12 Cr and 14 Cr ODS after exposure for 20 h are much smaller than that of after exposure for 4 h should be due to the spalling of the oxidation layer. This result also demonstrates much stronger tendency of oxide layer spall of 12 Cr and 14 Cr ODS steel than that of 18 Cr ODS steel.

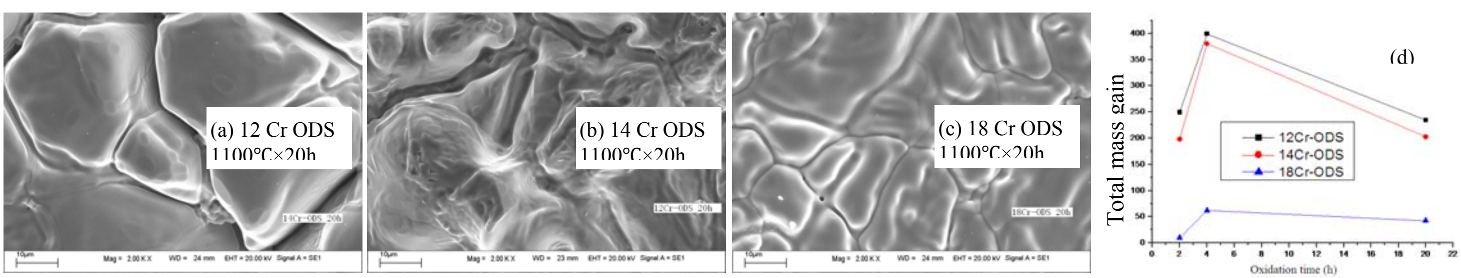

Fig. 3. the surface morphology of ODS steels after exposure at 1100℃ for 20 h (a) to (c), and weight gain curve (d)

3.2 Electron chemical corrosion behavior

The corrosion resistance of the ODS steels samples can be characterised by the polarization curves measurements, as shown in Fig. 4 (a). It is obvious that the higher the Cr content of the ODS steels, the lower the corrosion current density will be. For the sample fo 18Cr ODS, a passivation region can be found in the curve, which demonstrates that a protect passive film formed on this material. That is why a dense surface was found for the sample of 18 Cr ODS steel after testing, as shown in Fig. 4(d). While the surface morphology of corrosion products shows that large corrosion pits can be found for the sample of 12Cr-ODS, And heavy corrosion occurred on the grain boundary area for the sample of 12 Cr and 14Cr-ODS steel, as seen in Fig. 4 (b) and (c).

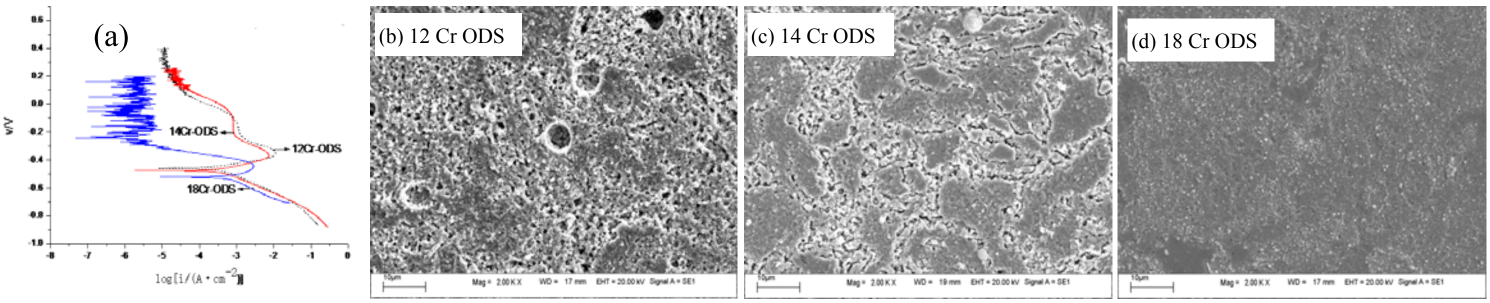

Fig. 4. The polarization curves (a) and surface morphology of ODS steels after testing in 1 mol/L HSO_4 solutions

4. Conclusions

Three ODS ferritic steels were tested by heating in air for various times at different temperatures and electronchemical corrosion. At 600 °C in air, no obvious oxidation occurred for all materials. A thin oxide scale with a thickness of ~ 1.5 μm formed for the sample of 12 Cr ODS steel after exposure at 700 °C for 500 h. This thin oxide scale include two layers, $Cr_{1.3}Fe_{0.703}$ in the outer layer and $MnFe_2O_6$ near the matrix. At 850°C in air, obvious oxidation occurred on both 12 Cr ODS steel and 14 Cr ODS steel. The oxide layer has a strong tendency to spall. At 1100°C in air, slight oxidation occurred for the sample of 18 Cr ODS steel, while strong oxidation occurred for the samples of 12 Cr ODS steel and 14 Cr ODS steel. The formed oxide particles are larger than 20 μm after exposure for 20 h, and obvious cracks can be found between oxide particles.

Electrochemical corrosion behaviour testing in 1 mol/L HSO_4 solutions shows that passive film formed for the sample of 18 Cr ODS steel. The surface of 18 Cr ODS steel is rather dense and homogenous, while large corrosion pits and heavy corrosion around the grain boundary were found for the surface of 12 Cr ODS steel and 14 Cr ODS steel.

5. Acknowledgements

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