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# High temperature oxidation behavior of ODS steels

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## Abstract

Oxide dispersion strengthened (ODS) steels are being developing for application as advanced fast reactor cladding and fusion blanket materials, in order to allow increased operation temperature. Oxidation testing of ODS steel was conducted under a controlled dry air atmosphere to evaluate the high temperature oxidation behavior. This showed that 9Cr-ODS martensitic steels and 12Cr-ODS ferritic steels have superior high temperature oxidation resistance compared to 11 mass% Cr PNC-FMS and 17 mass% Cr ferritic stainless steel. This high temperature resistance is attributed to earlier formation of the protective $\alpha$-$Cr_2O_3$ on the outer surface of ODS steels.

## 1. Introduction

Ferritic steels are well known to have excellent radiation resistant. However, they have inferior high temperature strength compared to conventional austenitic stainless steels, and their utilization is limited to around 600 °C. This disadvantage can be overcome by introducing thermally stable dispersoids in the ferritic matrix. The ODS ferritic steel is one of the most promising cladding materials for advanced liquid metal fast reactors [1–5] as well as being applicable as a low activated fusion reactor materials [6].

In addition to the neutron radiation resistance, the high temperature resistance to oxidation of the ODS ferritic steel is also required for its applicability. Although addition of Cr is effective in preventing high temperature oxidation, too much Cr leads to embrittlement due to the Cr-rich $\alpha'$ precipitate formation. In the ODS steel developed by the Japan Nuclear Cycle Development Institute (JNC), the Cr content is controlled in 9Cr-ODS martensitic steels and 12Cr-ODS ferritic steels. In this study, simple oxidation testing was conducted for evaluating the oxidation behavior of ODS steel claddings under relevant oxidation atmospheres at high temperature.

## 2. Experimental procedure

### 2.1. Material

The two types of ODS steel tubes were tested: 9Cr-ODS martensitic steel and 12Cr-ODS ferritc steel. The basic composition of these ODS steels is Fe–Cr–W–Ti–$Y_2O_3$. $Y_2O_3$ is thermally stable and the resulting improvement in creep rupture strength is excellent. The addition of Ti is an effective method of achieving uniformly distributed ultra-fine oxide particles, and the high temperature strength is significantly improved. In addition, W is introduced as a solution hardening element. The chemical composition of these ODS steels is listed in Table 1. For 12Cr-ODS ferritic steel tubes, both fine grain and large grain sizes are tested, where the large grains were developed by the recrystallization heat-treatment. The detail manufacturing process of these ODS tubes is cited in [7–9]. As a comparison, typical fast reactor cladding of austenitic stainless steel (PNC316)

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Table 1
The chemical composition of each materials

| Material | Chemical composition | | | | | | | | | | | | | | Remark |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | P | S | Ni | Cr | Mo | W | Ti | Nb | V | B | $Y_2O_3$ | |
| 9Cr-ODS | 0.13 | 0.05 | 0.044 | 0.002 | 0.002 | 0.022 | 9.01 | – | 1.95 | 0.21 | – | – | | 0.36 | |
| 12Cr-ODS | 0.024 | 0.05 | 0.046 | 0.002 | 0.003 | 0.034 | 11.95 | – | 2.01 | 0.30 | – | – | | 0.24 | Fine grain/ large grain |
| PNC316 | 0.054 | 0.78 | 1.72 | 0.028 | 0.003 | 13.45 | 16.22 | 2.35 | – | 0.08 | 0.080 | – | 0.004 | – | |
| PNC-FMS | 0.10 | 0.07 | 0.54 | 0.002 | 0.002 | 0.32 | 11.05 | 0.45 | 1.89 | – | 0.055 | 0.21 | – | – | |
| SUS430 | 0.03 | 0.7 | 0.3 | <0.03 | <0.03 | – | 17.0 | – | – | – | – | – | – | – | |

and ferritic-martensitic stainless steel (PNC-FMS) were also included in this test. The PNC316 is a class of type316 stainless steel containing 0.08 mass% Ti, 0.08 mass% Nb, 40 ppm B and 280 ppm P to improve the high temperature creep properties and the swelling residence. This material has been used as the cladding and ducts of the prototype fast breeder reactor MONJU. The PNC-FMS is 11 mass% Cr-ferritic-martensitic stainless steel that is V-Nb carbo-nitride precipitate strengthened and Mo–W solution hardened. The plate of SUS430 with higher Cr content of 17 mass% was also tested. The chemical composition of these materials is shown in Table 1.

### 2.2. Oxidation test

Oxidation testing was performed using pickled specimens in a controlled dry air atmosphere according to the Japanese Industrial Standard (JIS). The weight measurement for evaluating the amount of oxidation was performed at intervals of 50, 100, 400, 1000 and 2000 h at temperatures of 923, 1023 and 1123 K. Optical and SEM micrographs were taken for evaluating the thickness and state of the oxidized scale. Element distribution analysis was conducted by means of electron probe microanalysis (EPMA), and Raman spectroscopy measurements of the oxide scale were applied to identify the chemical form and compound.

## 3. Results

The weight gain due to oxidation vs. testing time at 1023 K is shown in Fig. 1. For 9Cr-ODS martensitic steel and 12Cr-ODS ferritic steel with fine grains, the weight gain due to oxidation is quite small and comparable to that of PNC316 containing 17 mass% Cr. Their

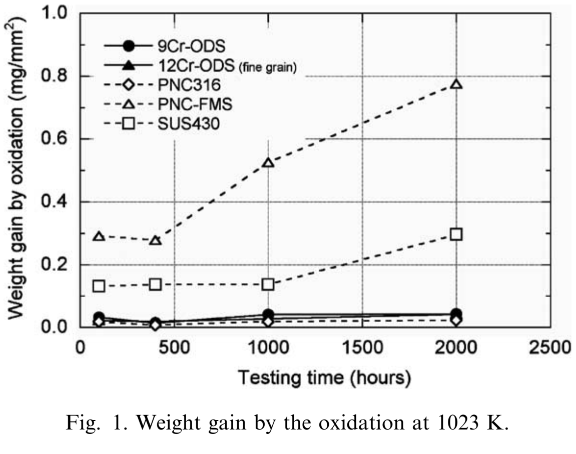

Fig. 1. Weight gain by the oxidation at 1023 K.

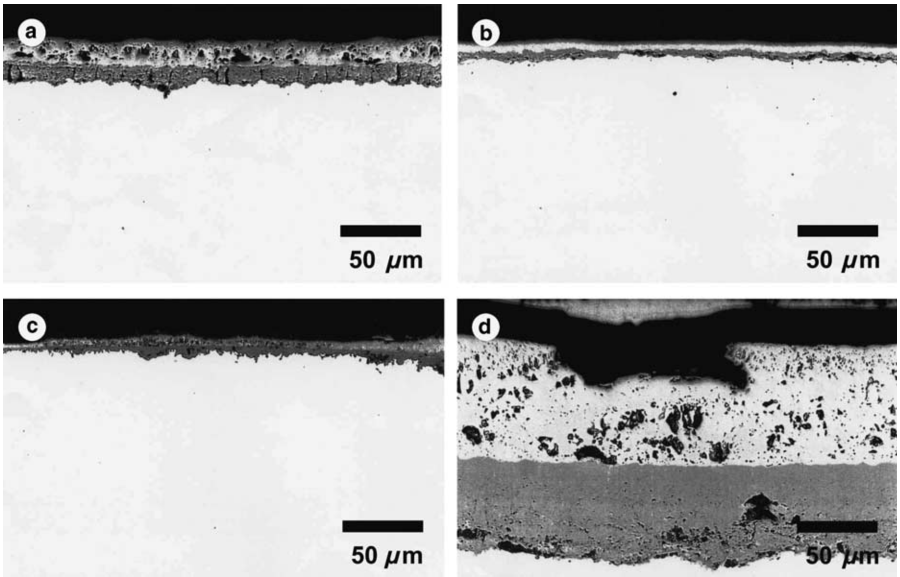

Fig. 2. Optical micrographs after the oxidization testing at 923 K for 2000 h. (a) 9Cr-ODS martensitic steel, (b) 12Cr-ODS ferritic steel, (c) PNC316, (d) PNC-FMS.

weight gain is limited to below 0.1 mg/mm$^2$, with almost no dependence on temperature and time. On the other hand, a quite large oxidation of 0.8 mg/mm$^2$ was observed in PNC-FMS. Comparing the oxidation behavior of 9Cr and 12Cr ODS steels with PNC-FMS, the ODS steels show superior resistance to oxidation, although Cr content in ODS steels and PNC-FMS is at almost the same level. The results of measurement on SUS430, which shows higher weight gain than that of ODS steels, shows that advanced oxidation resistance is attained with ODS steels, even compared to higher 17 mass% Cr containing stainless steel.

The optical micrographs after oxidation testing at 923 K for 2000 h are shown in Fig. 2. The thickness of the oxide scale of 9Cr-ODS martensitic steel (a) is about 20 μm, and that of 12Cr-ODS ferritic steel (b) and PNC316 (c) is about 10 μm with dense structure. Compared with these results, the oxide scale of PNC-FMS (d) is more than 100 μm with porous structure. The oxide scale is composed of a two layer structure: white color in outer and dark inner composites.

In order to identify the composites, the element distribution analysis by means of EPMA was conducted for 9Cr-ODS martensitic steel after the oxidization testing at 923 K for 2000 h, which is shown in Fig. 3. This result implies that scale consists of Fe-rich oxide in outer and Cr-rich oxide in inner layers. At the interface between ODS steel and oxide scale, further enriched Cr-oxide exists in the thin layer of a few micron meter. Y is slightly distributed in inner layer of oxidation and steel matrix.

From the Raman spectroscopy measurements, it was identified that outer Fe-rich and inner Cr-rich layers correspond to $\alpha$-$Fe_2O_3$ and spinel type $(Fe, Cr)_3O_4$, respectively. It also confirmed that $\alpha$-$Cr_2O_3$ is formed at matrix/scale interface.

## 4. Discussion

In oxidation tests, the Fe as a main constituent in steel tends to be easily oxidized at the early stage, but the further oxidation can be suppressed by formation of the protective $Cr_2O_3$ layer. This $Cr_2O_3$ formation is generally controlled by the supply rate of Cr to the reaction front. It is known that high Cr content in the steel as well as increasing diffusion flux through grain boundary, i.e., finer grains, accelerate the Cr-supply and accelerates the $Cr_2O_3$ formation.

In order to investigate the mechanism suppressing oxidation in ODS steels, short-term oxidation testing was carried out for 12Cr-ODS ferritic steel with fine grains and large grains as well as PNC-FMS at 923 K for 50 h. The results are summarized in Fig. 4.

In comparison of the optical micrographs, the difference of fine/large grain size in 12Cr-ODS is significant. The decrease of oxidation in the fine grain 12Cr-ODS ferritic steel can be attributed to the enhanced Cr-supplying rate throughout the accelerated grain

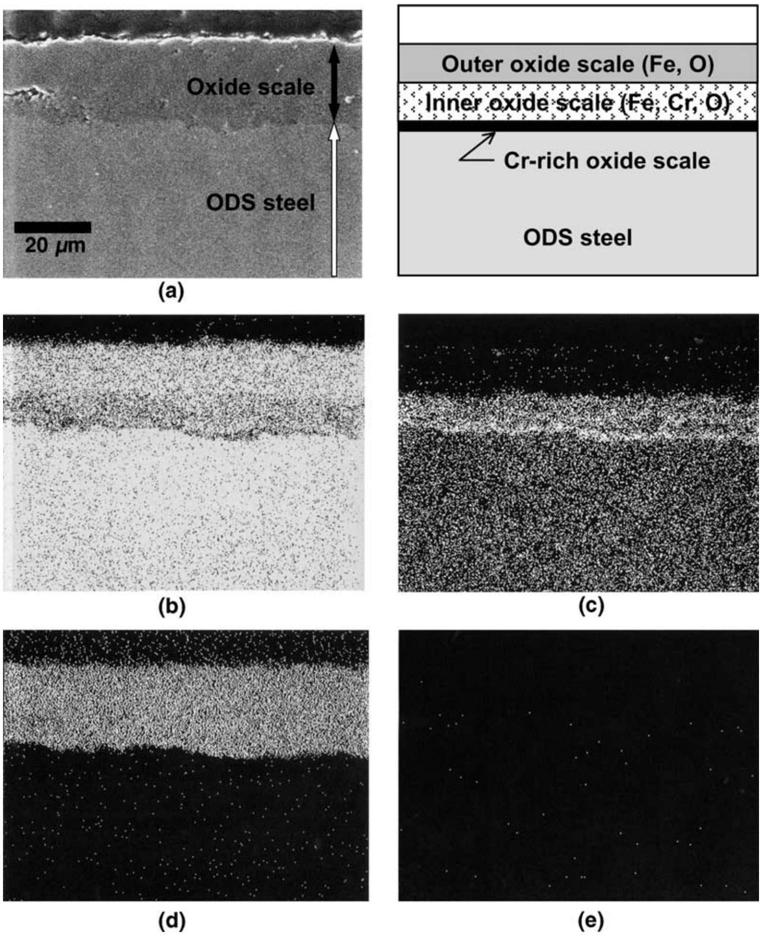

Fig. 3. Element distribution analysis by means of EPMA of 9Cr-ODS martensitic steel after the oxidation at 923 K for 2000 h. (a) SEM, (b) Fe, (c) Cr, (d) O, (e) Y.

boundary diffusion. In both cases, the Raman spectroscopy detected the protective α-$Cr_2O_3$ at the interface between matrix and scale.

Comparing 12Cr-ODS large grain and PNC-FMS, the Cr content is similar and grain size is rather smaller in PNC-FMS. Nevertheless, the protective α-$Cr_2O_3$ can not be detected by the Raman spectroscopy and oxidation is enhanced in PNC-FMS. Thus, the suppression of oxidation in 12Cr-ODS with large grains could be due to the effects of $Y_2O_3$ oxide particle itself.

It is known that addition of rare earth elements, i.e., Y, La, Ce, suppresses the oxidation of steels. This phenomenon is ascribed to the following interpretation. The internal oxide of rare earth elements, that are the most thermodynamically stable, may adhere to the protective α-$Cr_2O_3$. This is called keying-on effect [10–12]. The other interpretation is that void formation may be prevented by the annihilation of vacancies at the interface between internal oxide particles and steel matrix [13]. The $Y_2O_3$ particle dispersed finely in the steel matrix could play an important role in providing superior oxidation resistance through the above mechanism in the ODS steel.

## 5. Conclusion

The following results were obtained in the oxidation tests in a controlled dry air atmosphere:

(1) 9Cr-ODS martensitic steels and 12Cr-ODS ferritic steels have superior high temperature oxidation resistance compared to 11 mass% Cr PNC-FMS and even 17 mass% ferritic steel.
(2) The superior oxidation resistance of ODS steel is attributed to early formation of the protective α-$Cr_2O_3$ at the matrix and scale interface, which may be stabilized by finely dispersed $Y_2O_3$ particles.

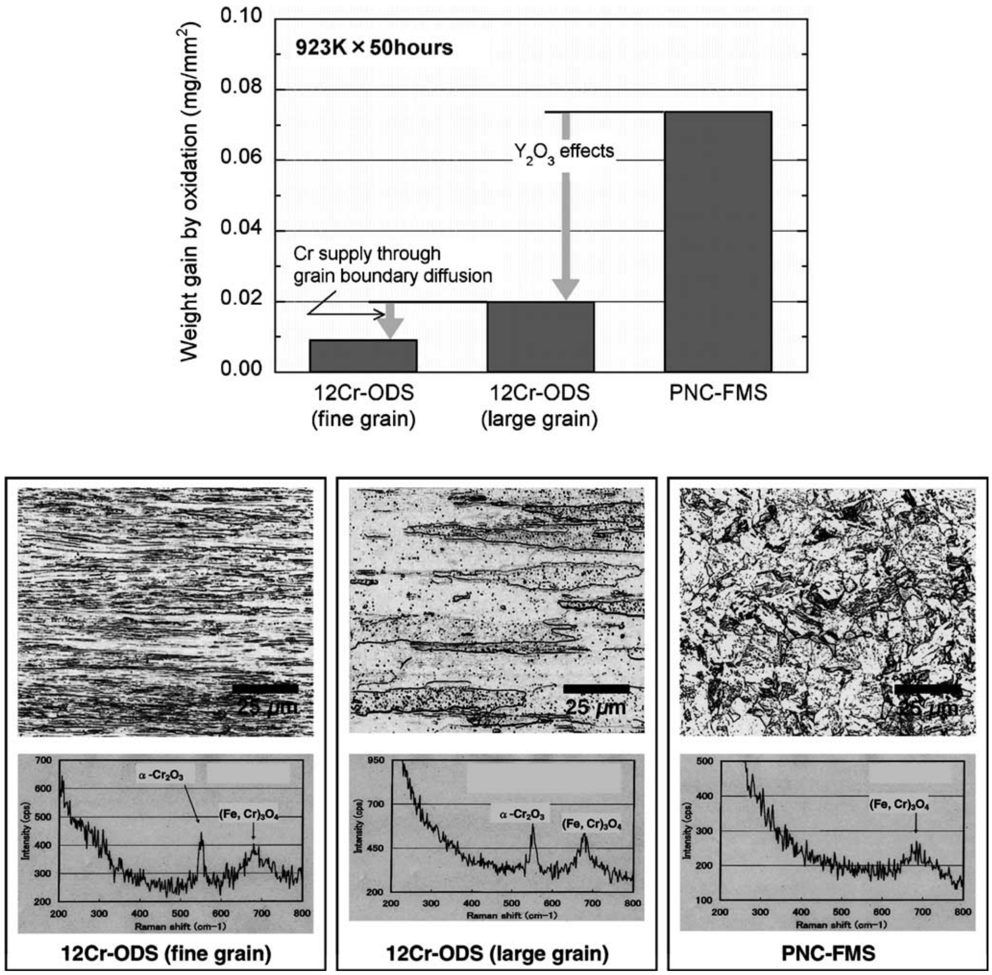

Fig. 4. Weight gain, Raman spectroscopy and micrographs for 12Cr-ODS steel and PNC-FMS oxidized at 923 K for 50 h.

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