Journal of Nuclear Materials 398 (2010) 132–138

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Corrosion resistance of Al-alloying high Cr–ODS steels in stagnant lead–bismuth

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ABSTRACT

Corrosion resistances of oxide dispersion strengthened ferritic steels containing 3.5 wt% Al and 14–17 wt% Cr were examined. Experiments were performed in stagnant lead–bismuth eutectic (LBE) containing 10^{-6} and 10^{-8} wt% oxygen at 550 and 650 °C. The maximum exposure duration was 5000 h. Observations of the cross-sections of exposed samples obtained by scanning electron microscopy and Auger electron spectroscopy suggested that a very thin Al oxide layer was formed continuously. The materials containing 3.5 wt% Al exhibited good corrosion resistance despite being exposed to 5000 h of LBE containing 10^{-6} wt% at 650 °C. Furthermore, a favourable influence of adding minor amount of Zr was detected after 5000 h exposure to LBE containing 10^{-8} wt% oxygen at 650 °C.

1. Introduction

Oxide dispersion strengthened (ODS) ferritic steels show good creep strength [1] and neutron irradiation tolerance [2]. Therefore, these materials are considered for cladding tube application in fast reactors. The lead-bismuth eutectic (LBE) cooled system is one of fast reactor concepts in the Generation IV International Forum. However, LBE is known to be corrosive. We reported that 9Cr–ODS martensitic steel showed a dissolution attack after 2000 h in stagnant LBE containing 10^{-6} wt% oxygen at 600 and 650 °C [3,4]. The compatibility with LBE should be improved for application in this harsh environment.

Some groups indicated the effectiveness of Al addition for improvement of corrosion resistance in LBE with an oxygen content of 10^{-6} wt% at 420–600 °C [5–7]. For example, Müller et al. proposed that the minimum Al content needed for the formation of protective Al oxide layer was about 8 wt% [5], and Hosemann et al. proposed it was 5.5 wt% [7]. Moreover, it has been reported that increasing the Cr content promotes formation of a protective Al oxide scale [8]. However, Al addition coarsens ODS particles and decreases its high-temperature strength [9]. A significantly higher Cr concentration also causes thermal aging embrittlement. Kimura et al. recommended that the Cr content should be lower than 16 wt% in order to reduce the susceptibility to thermal aging embrittlement [10]. On the other hand, adding W and reactive elements such as Zr can probably improve the high-temperature strength by solid solution strengthening and suppressing the coarsening of ODS particles due to Al addition, respectively [11]. We need to clarify the effects of these elements with respect to the formation of protective scales.

In our previous study [12], we conducted corrosion tests at temperatures of 550 and 650 °C for durations of up to 3000 h in stagnant LBE containing 10^{-6} and 10^{-8} wt% oxygen using ODS ferritic steels having 0–3.5 wt% Al and 14–17 wt% Cr. The study showed that protective Al oxide scales were formed on the surface of all the samples containing about 3.5 wt% Al and 14–17 wt% Cr in any of the cases. In this study, the cross-sections of samples after a 3000 h exposure to LBE containing 10^{-8} wt% oxygen at 650 °C were examined in detail using a scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectrometer (EDS) and an Auger electron spectroscopy (AES). In addition, longer corrosion tests for up to 5000 h were conducted under the same conditions for some ODS steels containing about 3.5 wt% Al mentioned above and some new ODS steels containing W and Zr in addition to 3.5 wt% Al. After exposure, the specimens were examined using SEM/EDS.

2. Experimental

Seven types of ferritic ODS steels having varying concentrations of Al, Cr, W, and Zr were used. Table 1 lists their nominal chemical compositions. They were manufactured by hot extrusion of mechanically alloyed powders at 1150 °C, and the consolidated

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doi:10.1016/j.jnucmat.2009.10.023

Table 1
Chemical compositions of the ODS steels in wt%.

ID	Cr	Al	C	Ti	Y	O	W	Zr	Fe
ODS1	16.1	3.4	0.02	0.09	0.27	0.14	–	–	Bal.
ODS2	13.7	3.4	0.04	0.07	0.28	0.14	–	–	Bal.
ODS3	17.3	3.5	0.05	0.09	0.27	0.14	–	–	Bal.
ODS6	16.1	3.4	0.03	0.09	0.27	0.13	1.61	–	Bal.
ODS9	15.4	3.8	0.03	0.10	0.28	0.16	1.85	–	Bal.
ODS14	14.9	3.7	0.05	0.09	0.27	0.17	1.84	0.63	Bal.

bars were annealed by a 60 min heat treatment carried out at 1150 °C followed by air-cooling. Specimens with 27 × 8 × 2 mm dimensions were cut from the bars for performing the corrosion test, and the surface finish was achieved by grinding with a 50 grain corundum disk.

The specimens were mounted in alumina crucibles filled with molten LBE and were placed in the COSTA device having controlled temperatures and oxygen concentrations [13]. The oxygen concentration in the COSTA device is controlled via the gas phase that is kept in equilibrium with the molten LBE. Table 2 enlists the test conditions. After exposure, the specimens were washed in oil at 180 °C to remove the LBE residue, and their cross-sections were analysed using SEM (Hitachi S-800) with EDS (Thomson WIN EDS). AES analysis on ODS3 after 3000 h exposure in LBE containing 10^{-8} wt% oxygen at 650 °C was also conducted by ULVAC-PHI Model 680 because the thickness of Al scale was partially too thin to be detected by SEM/EDS analysis in some ODS steels. AES analysis enables to observe element distributions with higher spacial resolution than SEM/EDS analysis, but it depends heavily on the surface flatness of the samples. In addition, polishing in general manners introduces edge drop, which prevents cross-section observation of oxide scales. Therefore, a focused ion-bean technique was employed to pick up a sample from the surface of the ODS steel after surface coating with W.

3. Results

Table 3 shows the suitability of the ODS steels after 5000 h exposure. The details are explained for each condition. In this study, all EDS line scans were stopped after reaching the matrix. Therefore, elemental compositions were not measured along the entire line printed in the SEM images.

3.1. Corrosion behaviour of ODS steels in LBE containing 10^{-6} wt% oxygen at 550 °C

Fig. 1a shows a SEM image and EDS line analysis result on ODS3 after 5000 h exposure. Comparison with samples after 1000 and 3000 h exposure [12] shows no change. The surface does not show any dissolution attack. Although it is difficult to observe oxide scale in the SEM image, EDS line analysis indicated that the surface is protected by a very thin Al oxide layer having a thickness of less than 0.5 μm. ODS2 showed results similar to ODS3. The surfaces of ODS9 and 14 are also covered mainly by very thin Al oxide layers, but the magnetite on the surface and the composite oxide below the magnetite were detected partially as shown in Fig. 1b. Al concentration in such composite oxides tends to increase near the matrix boundary as depicted in Fig. 1b.

3.2. Corrosion behaviour of ODS steels in LBE containing 10^{-8} wt% oxygen at 550 °C

No dissolution attack was observed on any of the test samples after 5000 h exposure even at a low concentration of dissolved oxygen. The surfaces on all the test samples were protected by very thin layers of composite oxides mainly containing Al as shown in Fig. 2a. Small parts of ODS9 and 14 were covered by relatively thick Cr–Al composite oxide layers having a thickness of a few μm as shown in Fig. 2b. Al concentration in the Cr–Al

Table 2
Test conditions.

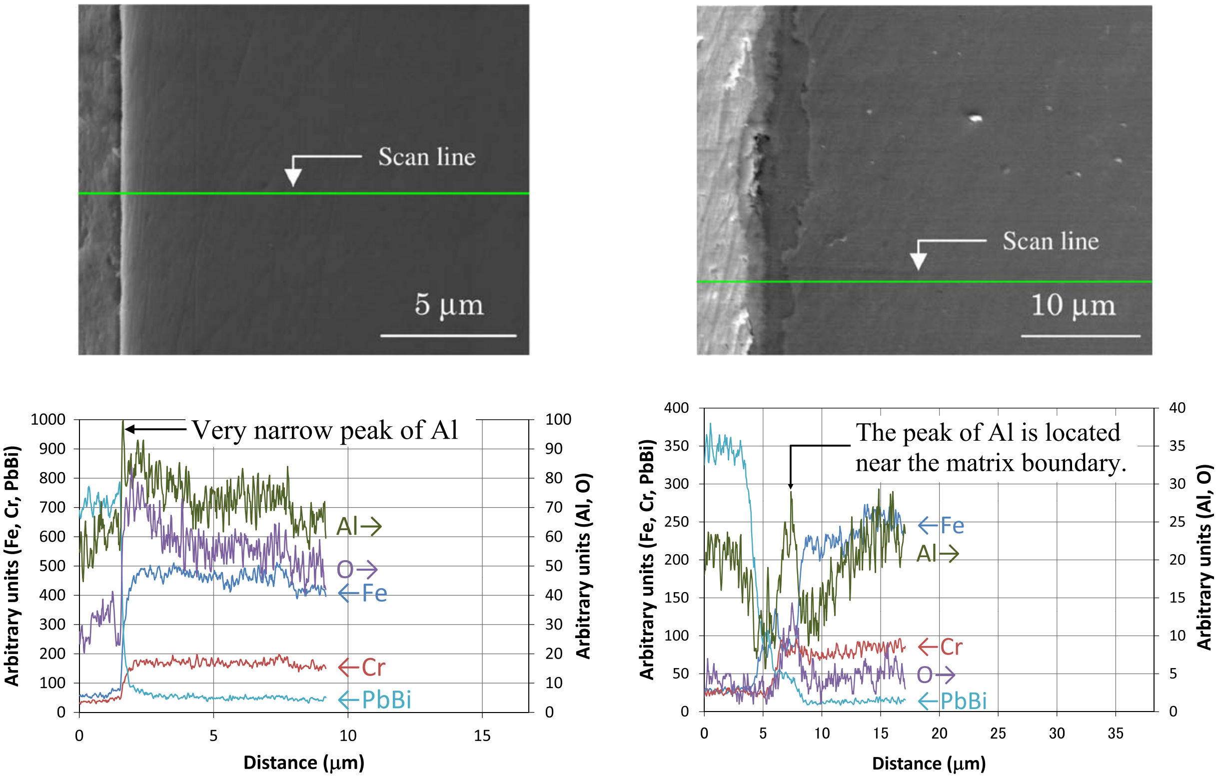
ID	Basic chemical compositions	Exposure time (h)			Temperature (°C)	Dissolved oxygen content in LBE (wt%)
		1000	3000	5000		
ODS1	16.1 Cr–3.4 Al	[12]	[12][b]	–	550, 650	10^{-8}, 10^{-6}
ODS2	13.7 Cr–3.4 Al	[12]	[12][b]	[a]		
ODS3	17.3 Cr–3.5 Al	[12]	[12][b]	[a]		
ODS6	16.1 Cr–3.4 Al–1.6 W	[12]	[12][b]	–		
ODS9	15.4 Cr–3.8 Al–1.9 W	–	–	[a]		
ODS14	14.9 Cr–3.7 Al–1.8 W–0.6 Zr	–	–	[a]		

[a] Corrosion test and post exposure examination were conducted.
[b] Detailed examination by using SEM/EDS and AES was conducted in this study.

Table 3
Suitability of ODS steels after 5000 h exposure.

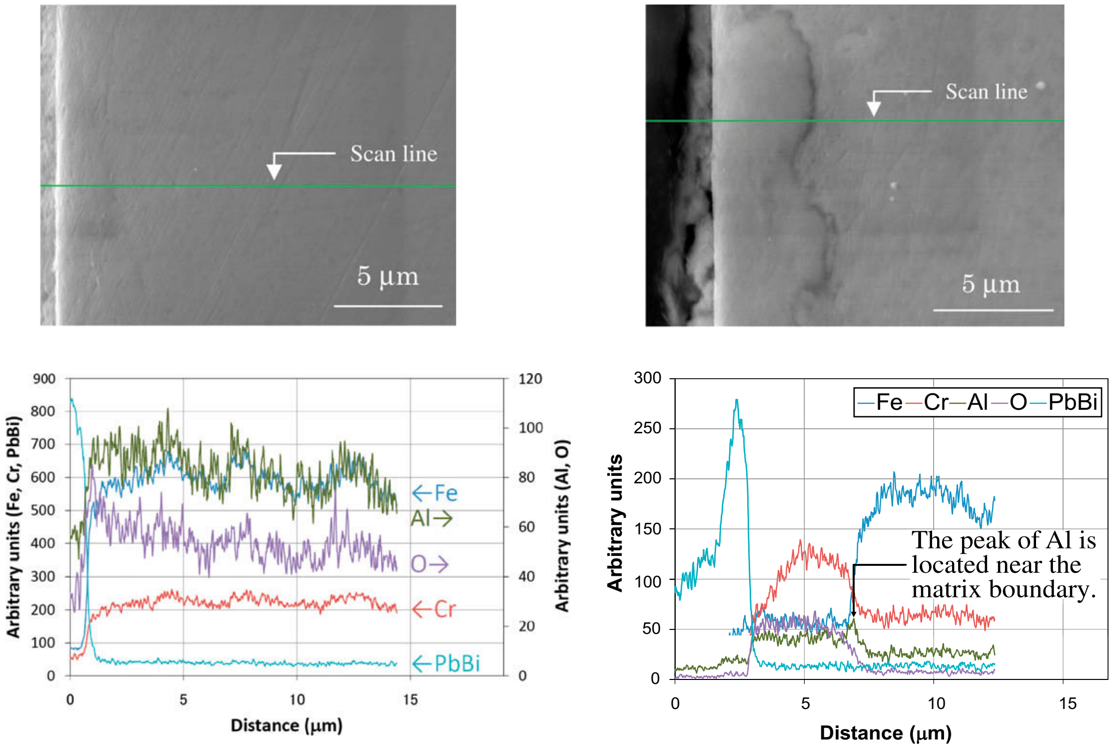
ID	Basic chemical compositions	Temperature (°C)	Dissolved oxygen content in LBE (wt%)	
			10^{-8}	10^{-6}
ODS-2	13.7 Cr–3.4 Al	550	[a]	[a]
		650	[b]	[a]
ODS-3	17.3 Cr–3.5 Al	550	[a]	[a]
		650	[b]	[a]
ODS-9	15.4 Cr–3.8 Al–1.9 W	550	[a]	[a]
		650	[b]	[a]
ODS-14	14.9 Cr–3.7 Al–1.8 W–0.6 Zr	550	[a]	[a]
		650	[a]	[a]

[a] LBE attack was not detected.
[b] LBE attack was detected.



(a) ODS3 (b) ODS14

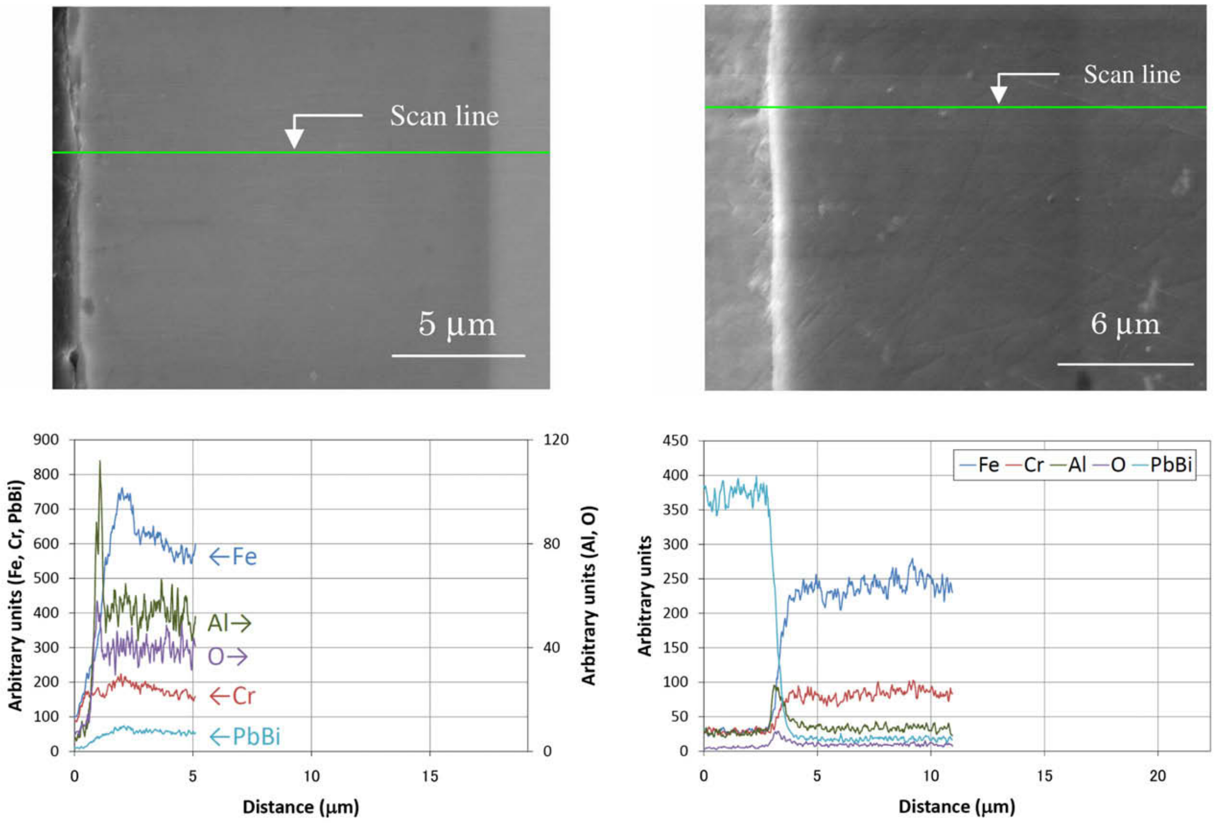
Fig. 1. SEM images and EDS line scan analysis results of ODS steels after 5000 h exposure to LBE containing 10^{-6} wt% oxygen at 550 °C.



(a) ODS3 (b) ODS9

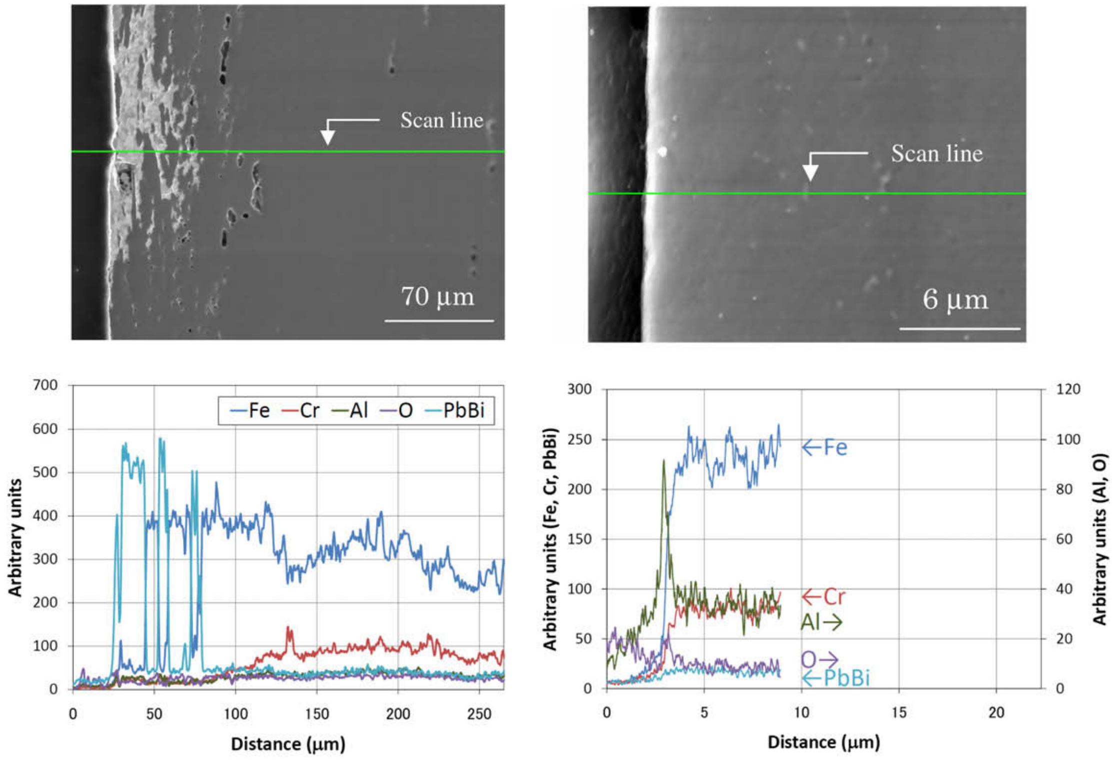
Fig. 2. SEM images and EDS line scan analysis results of ODS steels after 5000 h exposure to LBE containing 10^{-8} wt% oxygen at 550 °C.

composite oxides tends to increase near the matrix boundary. In Fig. 2b also, a local peak of Al concentration on the boundary between the composite oxide and the matrix proves this observation.



(a) ODS2 (b) ODS9

Fig. 3. SEM images and EDS line scan analysis results of ODS steels after 5000 h exposure to LBE containing 10^{-6} wt% oxygen at 650 °C.



(a) ODS2 (b) ODS14

Fig. 4. SEM images and EDS line scan analysis results of ODS steels after 5000 h exposure to LBE containing 10^{-8} wt% oxygen at 650 °C.

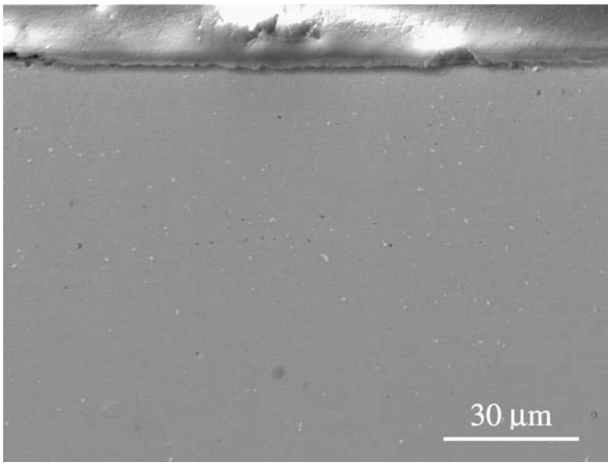


Fig. 5. SEM image of the cross-section of ODS6 after a 3000 h exposure to LBE containing 10^{-6} wt% oxygen at 650 °C.

3.3. Corrosion behaviour in LBE containing 10^{-6} wt% oxygen at 650 °C

SEM images and EDS line analysis results of ODS2 and ODS9 after 5000 h shown in Fig. 3 suggest that these materials maintain corrosion resistance. The other test materials showed good corrosion resistance, too. The oxide scales of these samples were similar to those obtained after a 5000 h exposure in LBE containing 10^{-8} wt% oxygen at 550 °C. We previously conducted corrosion tests on 9Cr–ODS steel and 12Cr steel under similar conditions, and reported that they lost corrosion resistance only after a 2000 h exposure [3,4]. Therefore, the addition of about 3.5 wt% Al is very effective in improving the compatibility with LBE.

3.4. Corrosion behaviour in LBE containing 10^{-8} wt% oxygen at 650 °C

Our previous paper reported that ODS steels containing about 3.5 wt% Al showed good corrosion resistance with a 3000 h exposure [12]. However, dissolution attacks on the surfaces of ODS2, 3 and 9 were observed partially after a 5000 h exposure, as shown in Fig. 4a, although the remaining surfaces were protected by

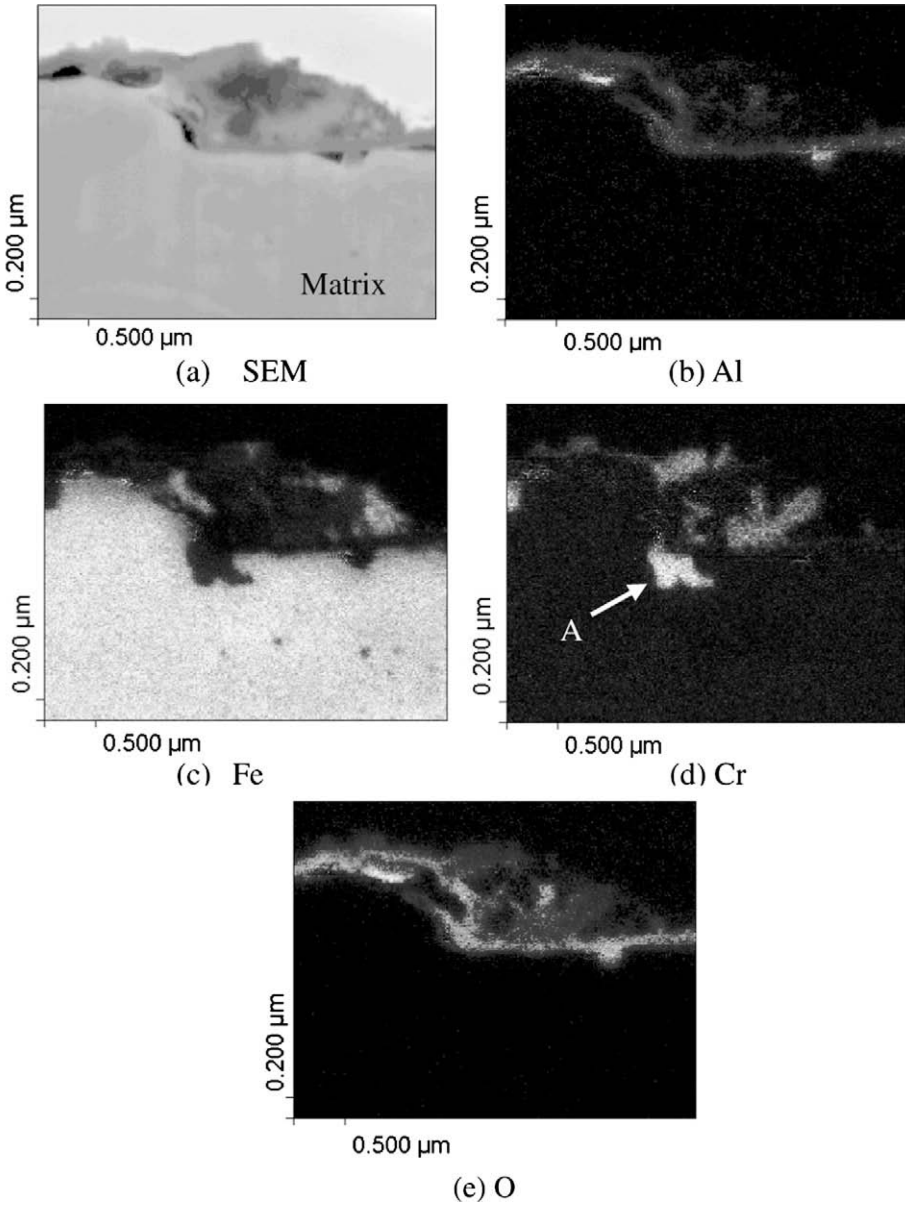


Fig. 6. AES images of ODS3 after 3000 h exposure in LBE containing 10^{-8} wt% oxygen at 650 °C.

composite oxide layers mainly containing Al. On the other hand, ODS14 containing about 0.6 wt% Zr indicated a good corrosion resistance even under this severe condition. A SEM image and an EDS line analysis result of ODS14 are presented in Fig. 4b. The surface of ODS14 is covered with a thin Al oxide layer.

4. Discussion

4.1. Effect of W

Fig. 5 shows an SEM image of ODS6, which contains about 1.6 wt% W and has chemical composition similar to ODS1 for the other elements, after a 3000 h exposure in LBE containing 10^{-6} wt% oxygen at 650 °C. ODS6 showed good corrosion resistance for exposure duration of up to 3000 h under any conditions, in a manner similar to ODS1 reported in the previous paper [12]. Moreover, there was no significant difference in the oxide layer formation between ODS1 and ODS6. The effect of W on the oxide layer formation and corrosion resistance is negligible.

4.2. Effect of Al

All ODS steels tested in this study, which containing about 3.5 wt% Al, showed good corrosion resistance even after a 5000 h exposure, except in LBE containing 10^{-8} wt% oxygen at 650 °C. On the other hand, 9Cr–ODS steel and 12Cr steel devoid of Al lost their corrosion resistances only after 2000 h in LBE containing 10^{-6} wt% oxygen at 600 and 650 °C [3,4]. In our earlier study, the ODS steel containing about 2 wt% Al suffered from dissolution attacks after a 3000 h exposure in LBE containing 10^{-8} wt% oxygen at 550 °C [12]. These results show that the addition of 3.5 wt% Al is very effective in improving the corrosion resistance.

The Al addition also contributes to the formation of a dense thin oxide layer. Fig. 6a–e present an SEM image of ODS3 after a 3000 h exposure to LBE containing 10^{-8} wt% oxygen at 650 °C and the distributions of Al, Fe, Cr and O obtained by AES analysis, respectively. The massive composite oxides shown in Fig. 6 were detected locally and mainly contained Fe, Cr or both. Cr concentration was often high near such massive composite oxides, as indicated by an arrow A in Fig. 6d. Thus, the formation of massive composite oxides could be related to the non-uniformity of chemical composition. SEM/EDS analysis indicated that Al concentration in these composite oxides tends to increase near the matrix boundary, as mentioned in the previous section, and Fig. 6b shows this phenomenon typically. Although a composite oxide appeared, the Al oxide layer was formed on the boundary with the matrix and suppressed further growth of the massive composite oxide.

4.3. Effect of Cr

ODS2, 3 and 9, which contain about 3.5 wt% Al, showed similar corrosion resistance on a 5000 h exposure with no dependence on Cr concentration. Maximum thicknesses of ODS1, 2, 3 and 6 containing about 3.5 wt% Al and about 13.5–17.5 wt% Cr after a 3000 h exposure to LBE containing 10^{-8} wt% oxygen at 650 °C were measured in 10 fields of view by SEM/EDS line analysis. The mean values are plotted in Fig. 7. Error bars indicate a single standard deviation. It should be noted that the mean thicknesses of the oxide layers are much thinner than these values. Although the mean maximum thickness of oxide layers decreases slightly around 17.5 wt%, the error bars are large and so there is no significant dependence on Cr concentration.

Cr concentration in the range of 13.5–17.5 wt% does not apparently affect the corrosion resistance of ODS steels containing about 3.5 wt% Al.

4.4. Effect of Zr

ODS14 doped with Zr showed almost the same or better corrosion resistance than ODS9, which had a similar chemical composition to ODS14, except that it lacked Zr. Moreover, it is noteworthy that ODS14 was free from dissolution attacks after a 5000 h exposure in LBE containing 10^{-8} wt% oxygen at 650 °C, in contrast to ODS9. Numerous studies have reported that a minor addition of reactive elements, such as Zr, Ce, Y and Hf, improves the high-temperature oxidation resistances of Al_2O_3 and Cr_2O_3 formers [14–18]. This phenomenon is usually called the reactive element effect (REE). Many mechanistic models to explain the various aspects of the REE have been proposed. One of them, for example, is change in oxide growth mechanism [14,15]. The addition of a reactive ele-

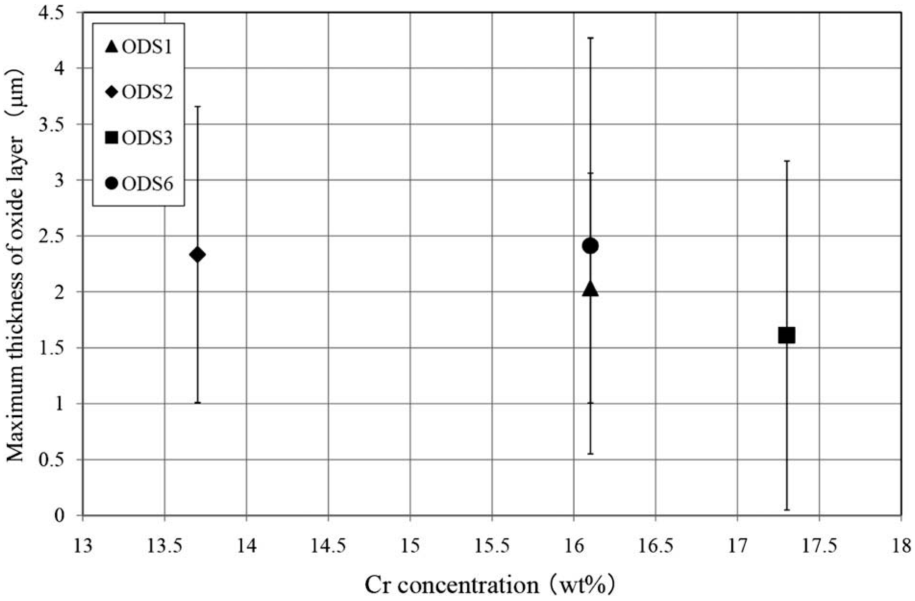


Fig. 7. The relationship between Cr concentration and mean maximum thickness of the oxide layer after a 3000 h exposure in LBE containing 10^{-8} wt% oxygen at 650 °C. (Al concentration: ~3.5 wt%).

ment inhibits a cationic external diffusion, decreases the oxidation rate and consequently improves the scale adherence. It was also reported that the addition of a reactive element developed the oxide scale consisted of small equiaxed grains, and allowed relaxation of growth or thermal stress without crack formation [16]. The formation of oxide pegs to the matrix may also contribute to improving scale adhesion [17]. Thus, most of proposed models are related to improvement of scale adherence. But spallation of scales was not observed for the ODS steels suffered from dissolution attacks after a 5000 h exposure in LBE containing 10^{-8} wt% oxygen at 650 °C. Therefore, these models cannot explain improvement of corrosion resistance by a minor addition of Zr in our case. The selective oxidation is also discussed as other benefit of the REE. In the case of Cr_2O_3-formers, a reactive element reduces the amount of chromium required in an alloy to form a protective scale. In the case of Al_2O_3-formers, however, there appears to be no effect on the amount of aluminium required to form an alumina scale [18].

In our study, the main purpose of Zr addition lies in preventing ODS particles from combining with Al and suppressing their coarsening using lower Gibbs free energy of Zr for oxide formation than Al. In fact, Ohnuki et al. conducted transmission electron microscopy observation of the ODS steels containing Al and Zr, and have shown that the minor addition of Zr is effective to achieve our purpose [19]. As a result, the Al content available for oxide scale formation on the surface would increase although it would be only 0.2–0.3 wt%. Sano et al. evaluated a partial potential diagram of Fe–Cr–4 wt% Al–O system at 600 and 700 °C by thermodynamic calculation, not considering the effect of ODS particles [20]. Based on their diagram, the critical Al content is about 4 wt% for the formation of protective scale on the surface of Fe–15 wt% Cr in LBE containing about 10^{-8} wt% oxygen in this temperature range. On the other hand, the Al content of ODS14 is 3.7 wt%, which is very close to the estimated critical Al content. In such a case, increase in Al content available for oxide scale formation will be effective even if it is only 0.2–0.3 wt%. This might be one of reasons for improving corrosion resistance by adding Zr. The Zr effects need to be investigated further.

5. Conclusion

Corrosion resistances of oxide dispersion strengthened ferritic steels containing 3.5 wt% Al and 14–17 wt% Cr were examined. The experiments were conducted at 550 and 650 °C in a stagnant LBE containing 10^{-6} and 10^{-8} wt% oxygen. All the ODS steels containing about 3.5 wt% Al showed good corrosion resistance, even after a 5000 h exposure, except in an LBE containing 10^{-8} wt% oxygen at 650 °C. In addition, it was proved that the Al oxide scale suppressed a massive composite oxides growth. The addition of about 3.5 wt% Al contributes to the formation of a dense oxide layer and is very effective for improving corrosion resistance in LBE. Furthermore, the favourable influence of adding a minor amount of Zr was detected after a 5000 h exposure to LBE containing 10^{-8} wt% oxygen at 650 °C. Although a detailed investigation is required, an increase in the Al content available for oxide scale formation may improve the corrosion resistance. On the other hand, Cr concentration in the range of about 13.5–17.5 wt% does not apparently affect the corrosion resistance of ODS steels containing about 3.5 wt% Al. The effect of W on the oxide layer formation and corrosion resistance was also negligible.

Acknowledgements

The authors thank Dr. G. Müller, Dr. A. Weisenburger, Dr. A. Heinzel and Dr. A. Jianu in Forschungszentrum Karlsruhe for conducting the corrosion tests and for fruitful discussions.

Present study is the result of “Super ODS Steel R&D towards Highly Efficient Nuclear Systems” entrusted to Kyoto University by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

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