Journal of Nuclear Materials 386–388 (2009) 507–510

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

Corrosion behavior of Al-alloying high Cr-ODS steels in lead–bismuth eutectic

S. Takaya [a,*], T. Furukawa [a], K. Aoto [a], G. Müller [b], A. Weisenburger [b], A. Heinzel [b], M. Inoue [a], T. Okuda [c], F. Abe [d], S. Ohnuki [e], T. Fujisawa [f], A. Kimura [g]

[a] Advanced Nuclear System R&D Directorate, Japan Atomic Energy Agency, 4002 Narita, O-Arai, Ibaraki 311-1393, Japan
[b] Institute for Pulsed Power and Microwave Technology, Forschungszentrum Karlsruhe GmbH, P.O. Box 3640, D-76021 Karlsruhe, Germany
[c] Kobelco Research Institute, 1-5-5 Takatsukadai, Nishi-ku, Kobe, Hyogo 651-2271, Japan
[d] Structural Metals Center, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
[e] Graduate School of Engineering, Hokkaido University, N13, W8, Kita-ku, Sapporo 060-8628, Japan
[f] Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan
[g] Institute of Advanced Energy, Kyoto University, 1 Gokasho, Uji, Kyoto 611-0011, Japan

ARTICLE INFO

PACS:
81.65.Kn

ABSTRACT

The corrosion resistances of ODS steels with 0–3.5 wt% Al and 13.7–17.3 wt% Cr, and a 12Cr steel were examined. The experiments were conducted at 550 and 650 °C for up to 3000 h in stagnant LBE containing 10^{-6} and 10^{-8} wt% oxygen for the ODS steels, and at 550 °C for up to 5000 h in that containing 10^{-8} wt% oxygen for the 12Cr steel. Protective Al oxide scales were formed on the surfaces of the ODS steels with approximately 3.5 wt% Al and 13.7–17.3 wt% Cr. Addition of Al is very effective in improving the corrosion resistance of ODS steels. The ODS steel with 16 wt% Cr and no Al did not show any corrosion resistance except in LBE with 10^{-6} wt% oxygen at 550 °C. The corrosion resistance may not be improved by solely increasing Cr concentration.

1. Introduction

The development of high-corrosion-resistance materials is very important for enhancing the efficiency of lead–bismuth eutectic (LBE) cooled fusion reactors and fast breeder reactors. Austenitic steels, for example, suffer from severe dissolution attack at over 500 °C [1–3]. Ferritic and martensitic steels, on the other hand, form thick oxide scales in similar conditions, restricting them to lower-temperature applications [2,4,5]. Studies have also shown that Al has a beneficial influence on the compatibility of materials in LBE. Alloys containing 8–15 wt% Al have a very good corrosion resistance at 420–600 °C due to their alumina scale [2]. With regards to oxide-dispersion-strengthened (ODS) steel, one of the most promising candidates, we have reported that high Cr-ODS steels with more than 4 wt% Al have much higher corrosion resistance than a 9Cr-ODS steel without Al [6]. Addition of Al, however, may cause coarsening of ODS particles and a decrease in high-temperature strength. A significantly higher Cr concentration results in aging embrittlement. Therefore, we need to clarify the effect of Al and Cr on the formation of protective scales, and to find the optimal amount of these elements to balance corrosion resistance with high-temperature strength. In this study, we examined ODS steels with various Al and Cr concentrations, using a 12Cr steel for comparison.

2. Experimental

Five types of ferritic ODS steels, with various Al and Cr concentrations, and one 12Cr steel were tested. Their chemical compositions are listed in Table 1. The ODS steels were manufactured by hot extrusion of mechanically alloyed powders at 1150 °C, and consolidated bars were annealed by 60 min of heat treatment at 1150 °C, followed by air cooling. The 12Cr steel was cast, hot rolled, normalised by 100 min of heat treatment at 1070 °C and then tempered for 440 min at 770 °C. Each heat treatment was followed by air cooling. The dimensions of the ODS specimens were 27 × 8 × 2 mm, and those of the 12Cr steel were 27 × 6 × 2 mm. Their surfaces were finished by grinding.

The specimens were mounted in alumina crucibles filled with molten LBE and placed in the COSTA device with controlled temperatures and oxygen concentrations [4]. The test conditions are listed in Table 2. After exposure, the specimens were washed in oil at 180 °C to remove LBE residues, and their cross-sections were analyzed using a scanning electron microscope (SEM) with an energy-dispersive X-ray analyzer (EDX).

---

[*] Corresponding author. Tel.: +81 (0)29 267 4141; fax: +81 (0)29 267 3761.
E-mail address: takaya.shigeru@jaea.go.jp (S. Takaya).

0022-3115/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2008.12.155

Table 1
Chemical compositions of the ODS steels and the 12Cr steel (wt%).

ID	C	Si	Mn	P	S	Cr	Al	Ti	N	Y_2O_3	Ni	Mo	W	Cu	V	Nb
ODS1	0.02	0.02	0.03	<0.005	0.002	16.1	3.4	0.09	0.002	0.34	–	–	–	–	–	–
ODS2	0.04	0.01	0.02	<0.005	0.002	13.7	3.4	0.07	0.016	0.36	–	–	–	–	–	–
ODS3	0.05	0.02	0.04	<0.005	0.003	17.3	3.5	0.09	0.006	0.34	–	–	–	–	–	–
ODS4	0.02	0.01	0.03	<0.005	0.002	15.8	1.9	0.09	0.003	0.34	–	–	–	–	–	–
ODS5	0.04	0.01	0.01	<0.005	0.002	16.0	–	0.09	0.007	0.34	–	–	–	–	–	–
12Cr steel	0.11	0.27	0.64	0.016	0.002	10.54	–	–	0.071	–	0.33	0.34	1.76	1	0.19	0.048

Table 2
Test conditions.

	ODS1-5	12Cr steel
Duration (h)	1000, 3000	800, 2000, 5000
Temperature (°C)	550, 650	550
Oxygen concentration (wt%)	1×10^{-8}, 1×10^{-6}	1×10^{-8}

3. Results

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

SEM images of ODS1-5 after 3000 h are presented in Fig. 1. In the ODS steels containing Al (ODS1-4), no dissolution effect was observed. EDX line scan analysis indicated that their surfaces are protected mainly by a thin Al oxide layer. Below this layer, Al–Cr or Al–Cr–Fe oxides were detected in parts of ODS1 and 2 and completely in ODS4. On the surface of ODS3, containing the largest amounts of Al and Cr, such extended oxide regions were hardly observed. ODS5, which contained no Al, showed the worst compatibility. The white areas in Fig. 1 indicate the dissolution attack in the material bulk.

3.2. Corrosion behavior of ODS and 12Cr steels in LBE containing 10^{-8} wt% oxygen at 550 °C

SEM images of ODS1-5 after 3000 h are shown in Fig. 2. Very thin scales protect the entire surfaces of ODS1-3 from dissolution. The oxide scales on the surfaces of ODS1 and 2 were too thin to be detected by EDX analysis, but a protective Al oxide scale, thinner than 0.5 μm, was observed on the surface of ODS3. ODS4 had a thin protective Al oxide scale but suffered from local dissolution attacks. ODS5 showed dissolution attack over a large part of its surface after only 1000 h. After 3000 h, almost the entire surface was attacked by LBE. Fig. 3 shows SEM images of cross-sections of the 12Cr steel. Although the entire surface was attacked after 800 h, the depth of dissolution attack was less than about 1 μm. Even after 5000 h, the extent was not significant.

3.3. Corrosion behavior of ODS steels in LBE containing 10^{-6} wt% oxygen at 650 °C

SEM images of ODS1-5 after 3000 h are shown in Fig. 4. Thin Al oxide scales covered most parts of the surfaces of the ODS steels containing Al (ODS1-4). The remaining parts were covered by Al–Cr oxide scales. We observed no dissolution effect on any of these steels. As for ODS1, 2 and 4, Fig. 4 clearly depicts internal oxidations below the thin outer oxide scales. ODS3, however, showed no internal oxidation and only a few Al oxide inclusions. Similar to other ODS steels, no dissolution attack was observed on ODS5 because the surface was protected by a Cr oxide layer. The Cr oxide scale was thinner than that of ODS5 exposed to LBE containing 10^{-6} wt% oxygen at 550 °C. Occasionally, some Fe–Cr oxide structures appeared below the Cr oxide layer.

3.4. Corrosion behavior of ODS steels in LBE containing 10^{-8} wt% oxygen at 650 °C

SEM images of ODS1-5 after 3000 h are shown in Fig. 5. ODS1-3 showed good corrosion resistance, similar to those in the other exposure test conditions. Although the surface of ODS4 after 1000 h seemed to be almost completely covered by a thin, non-

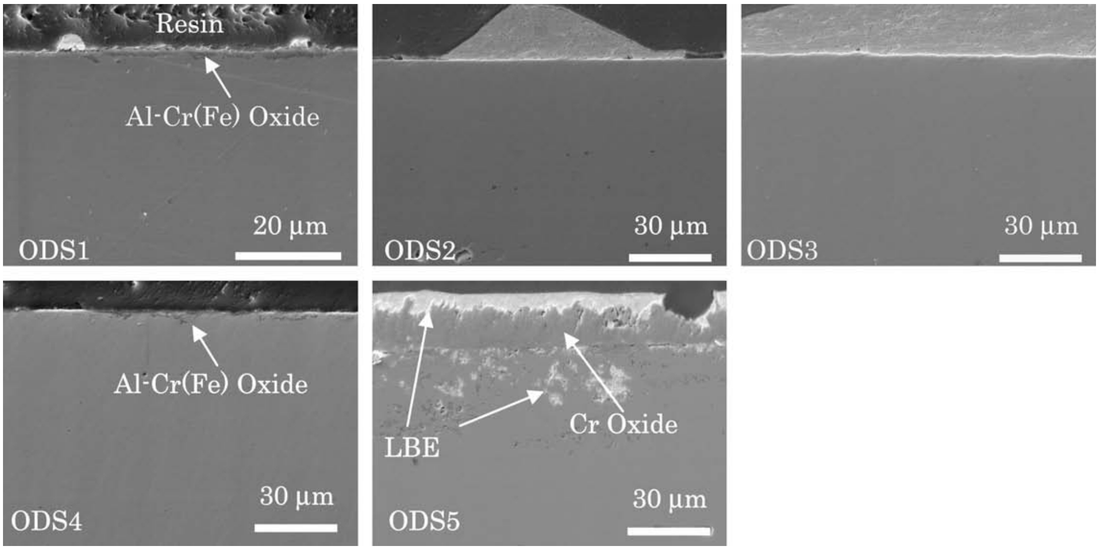

Fig. 1. SEM cross-sections of ODS steel specimens after 3000 h of exposure to LBE containing 10^{-6} wt% oxygen at 550 °C.

detectable oxide scale, we observed dissolution attack on about 40% of its surface after 3000 h. Oxide layers covered the remaining parts of the surface. ODS5 showed dissolution attack on about 70% of its surface after 1000 h. After 3000 h, dissolution attack and LBE infiltration covered the entire surface, and almost no oxide scale remained.

4. Discussion

The 12Cr steel showed good corrosion resistance even after 5000 h of exposure to LBE containing 10^{-8} wt% oxygen at 550 °C. We had previously reported that a martensitic 9Cr-ODS steel not containing Al showed good corrosion resistance for up to 2000 h

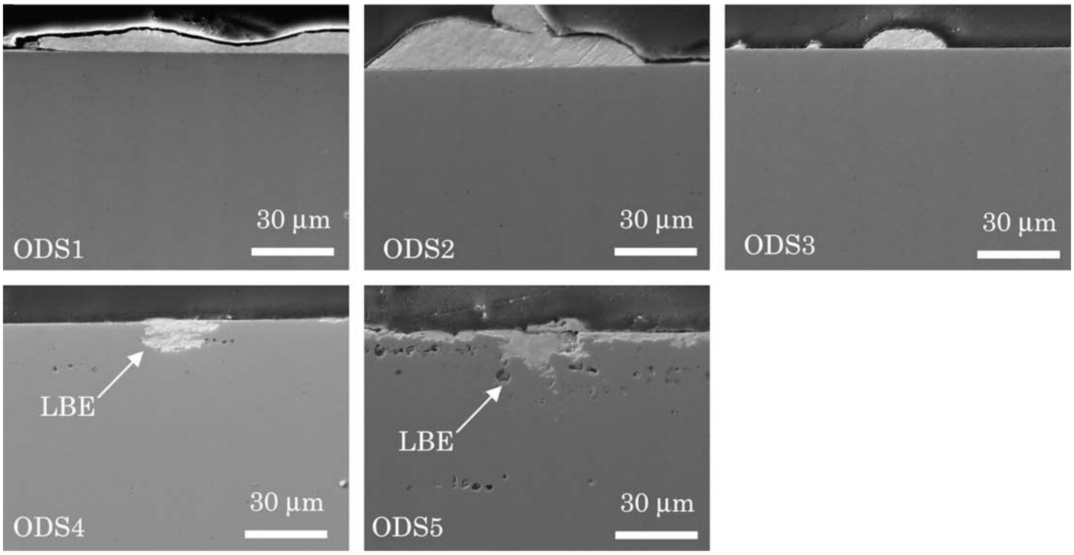

Fig. 2. SEM cross-sections of ODS steel specimens after 3000 h of exposure to LBE containing 10^{-8} wt% oxygen at 550 °C.

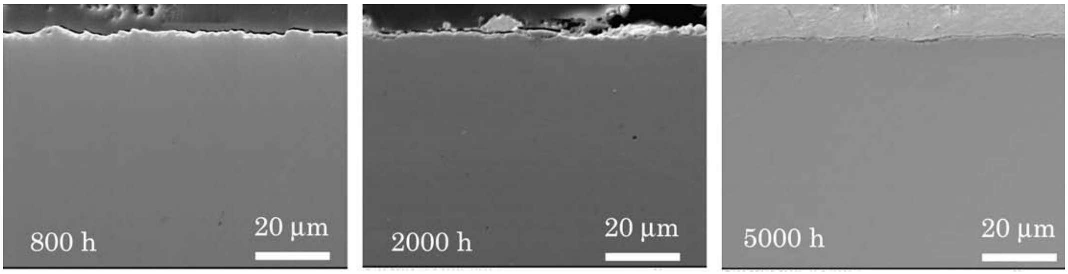

Fig. 3. SEM cross-sections of 12Cr steel specimens after exposure to LBE containing 10^{-8} wt% oxygen at 550 °C.

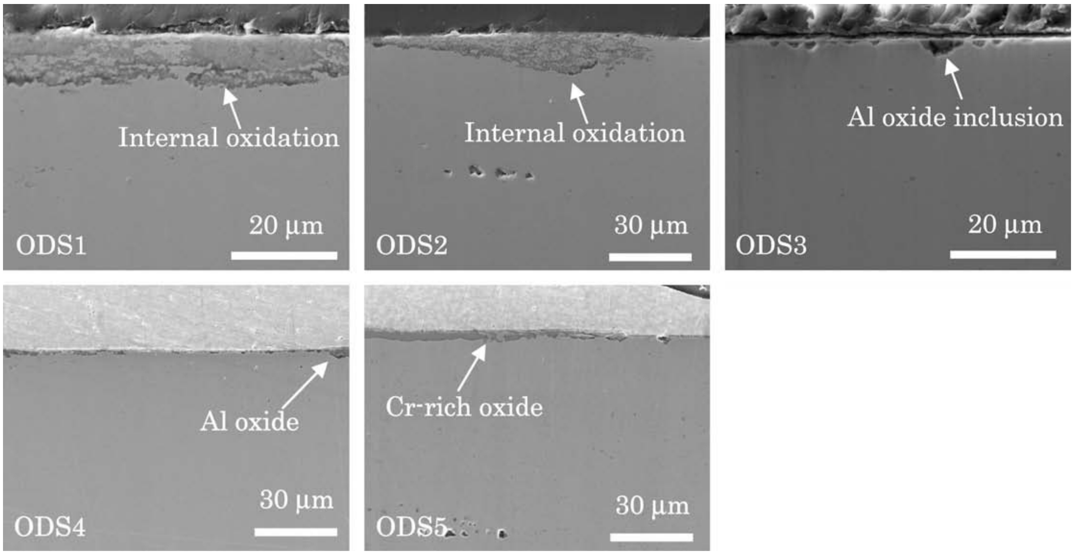

Fig. 4. SEM cross-sections of ODS steel specimens after 3000 h of exposure to LBE containing 10^{-6} wt% oxygen at 650 °C.

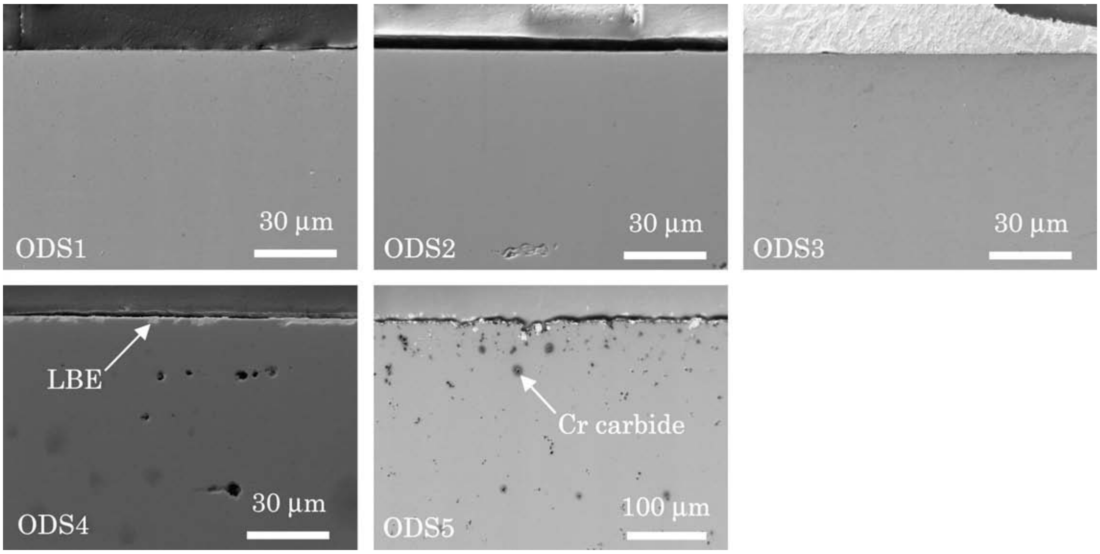

Fig. 5. SEM cross-sections of ODS steel specimens after 3000 h of exposure to LBE containing 10^{-8} wt% oxygen at 650 °C.

of exposure at 650 °C in LBE with 10^{-8} wt% oxygen [7]. Kurata et al. conducted static corrosion tests in oxygen-saturated LBE at 450 and 550 °C for 3000 h with various ferritic steels containing 0–16 wt% Cr and concluded that the corrosion depth decreases with increasing Cr concentration [8]. Therefore, we had expected that ODS5, containing about 16 wt% Cr and no Al, would show good corrosion resistance; however, its corrosion resistance was relatively low, except for one exposure condition. Thus, solely increasing Cr concentration may not improve the corrosion resistance of ODS steels in LBE. On the other hand, ODS1, containing almost the same Cr concentration as ODS5 and 3.4 wt% Al, showed very good corrosion resistance for up to 3000 h under all conditions. Comparing ODS1-3 which contain almost the same Al concentration (~3.5 wt%) and different Cr concentration (14–17 wt%), all of them showed good corrosion resistance; however, internal oxidation seems to decrease with increasing Cr concentration. Zhang et al. reported that an increase in Cr concentration promotes the formation of stable Al oxide scales [9]. Such scales on the surface of an ODS steel with higher Cr concentration will prevent oxygen diffusion through the scale and therefore reduce internal oxidation. From the viewpoint of resistance to LBE corrosion, an ODS steel with about 16 wt% Cr and 3.5 wt% Al is very promising. We plan to continue the exposure experiments to examine the corrosion resistance of these steels for longer durations.

5. Conclusion

Protective Al oxide scales were formed on the surfaces of the ODS steels with 3.5 wt% Al and 14–17 wt% Cr, and no dissolution attack was seen in any of the cases. Addition of Al is very effective in improving the corrosion resistance of ODS steels in LBE. On the other hand, the ODS steel with 16 wt% Cr and no Al showed no corrosion resistance except in the case of exposure to LBE with 10^{-6} wt% oxygen at 650 °C. Thus, the corrosion resistance of ODS steels in LBE may not be improved by solely increasing Cr concentration.

Acknowledgements

Present study includes 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).

References

[1] L. Soler, F.J. Martın, F. Hernandez, D. Gomez-Briceno, J. Nucl. Mater. 335 (2004) 174.
[2] G. Müller, A. Heinzel, J. Konys, G. Schumacher, A. Weisenburger, F. Zimmermann, V. Engelko, A. Rusanov, V. Markov, J. Nucl. Mater. 335 (2004) 163.
[3] C. Fazio, G. Benamati, C. Martini, G. Palombarini, J. Nucl. Mater. 296 (2001) 243.
[4] G. Müller, G. Schumacher, F. Zimmermann, J. Nucl. Mater. 278 (2000) 85.
[5] G. Müller, A. Heinzel, J. Konys, G. Schumacher, A. Weisenburger, F. Zimmermann, V. Engelko, A. Rusanov, V. Markov, J. Nucl. Mater. 301 (2002) 40.
[6] Y. Nishi, T. Furukawa, K. Aoto, I. Kinoshita, A. Kimura, S. Ukai, M. Fujiwara, in: Proceedings of 2006 JSME Annual Meeting, vol. 3, 2006, p. 37 (in Japanese).
[7] T. Furukawa, G. Müller, G. Schmacher, A. Weisenburger, A. Heinzel, K. Aoto, J. Nucl. Mater. 335 (2004) 189.
[8] Y. Kurata, M. Futakawa, S. Saito, J. Nucl. Mater. 343 (2005) 333.
[9] Z.G. Zhang, F. Gesmundo, P.Y. Hou, Y. Niu, Corros. Sci. 48 (2006) 741.