JOURNAL OF MATERIALS SCIENCE **39** (2004) 4383–4386 LETTERS

Corrosion of intermetallic compound Fe40Al in molten LiCl and LiCl-Li_2O

R. Y. LIU, X. WANG, J. S. ZHANG, M. L. ZHU, H. Y. LI
Department of Material Engineering, Dalian University of Technology, Dalian 116024, People's Republic of China
E-mail: jszhang@dlut.edu.cn

A lithium reduction technique has been developed for the spent nuclear fuel management [1]. In this process the oxide (UO_2) is reduced to metallic form by the reaction with lithium dissolved in the molten LiCl at 750 °C. The strong basic Li_2O formed during the reduction process is soluble in salt. Thus, the accelerated corrosion of alloys resulting form the Li_2O in molten LiCl cause a serious problem in containment materials, resulting in the delay of the application of the new technique.

To date, only a few reports have been published on the corrosion of materials in molten LiCl-Li_2O, with the main objective to find a material that can be used to improve the vessel longevity for this new technology [1–3]. In these studies, corrosion behaviors of many iron-base and nickel-base alloys with good high-temperature oxidation resistance have been investigated in molten LiCl-Li_2O under air. Unfortunately, all these alloys experience serious corrosion in the melt.

Fe40(at%)Al-base intermetallics in presence of molten salts present better corrosion resistance when comparing them with common alloys [4]. Accordingly, this work was conducted to investigate the corrosion behavior of Fe40Al in molten LiCl and LiCl-Li_2O mixture by immersion experiments. Fe40Al was prepared by vacuum induction melting and casting into an ingot. The ingot was cut into specimens of 10 mm × 8 mm × 2 mm. All the specimens were finely ground and polished. Immersion experiments were carried out at 750 °C in molten LiCl or LiCl-3 wt%Li_2O. The concentration of Li_2O in the molten mixture was chosen to be 3 wt% which corresponded to approximately 100% theoretical UO_2 reduction [1]. LiCl and the mixture of LiCl and Li_2O, contained in alumina crucibles were dried at 350 °C for 24 h, and then held in the molten state at 750 °C. For every group of experiments, 25 g salt was contained in an alumina crucible of 25 ml. After a selected period of time, the corroded specimens were rinsed with distilled water, dipped in a solution containing hydrochloric acid and tetrabutylammonium iodide to strip corrosion products, dried and weighted by microbalance.

Fig. 1 shows the weight loss curves for the corrosion of Fe40Al in molten LiCl and LiCl-Li_2O at 750 °C in air. The presence of Li_2O significantly accelerates the corrosion of Fe40Al. In molten LiCl, the weight loss increased linearly with test time in the initial stage, and then increased parabolically after about 5 h. Similarly, in molten LiCl-Li_2O, a large weight loss is first obtained at short exposure times (about 1 h), and then the corrosion rate is very low following a parabolic rate law up to 25 h of corrosion. During the experiments, the spallation of the scales was observed in the two different melts (especially for molten LiCl-Li_2O), which would account for the fast corrosion in the initial stage of experiments.

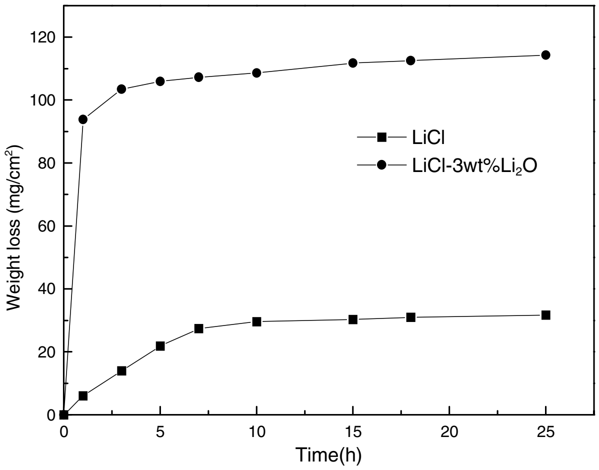

Figure 1 Weight loss curves of Fe40Al in molten LiCl and LiCl-Li_2O at 750 °C in air.

The X-ray diffraction (XRD) patterns of corrosion product of Fe40Al after immersion testing in molten LiCl and LiCl-Li_2O at 750 °C for 25 h is given in Fig. 2. Differences are found in the major corrosion products, i.e., α-$LiAlO_2$ plus α-Al_2O_3 in molten LiCl and γ-$LiAlO_2$ plus Fe in molten LiCl-Li_2O. According to

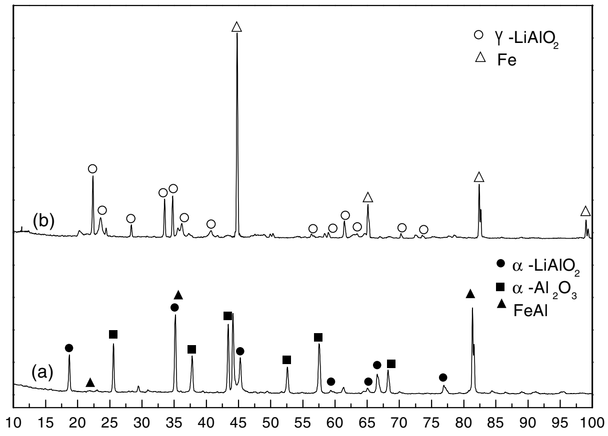

Figure 2 XRD patterns of Fe40Al corroded: (a) in molten LiCl and (b) in molten LiCl-Li_2O at 750 °C in air for 25 h.

0022–2461 © *2004 Kluwer Academic Publishers*

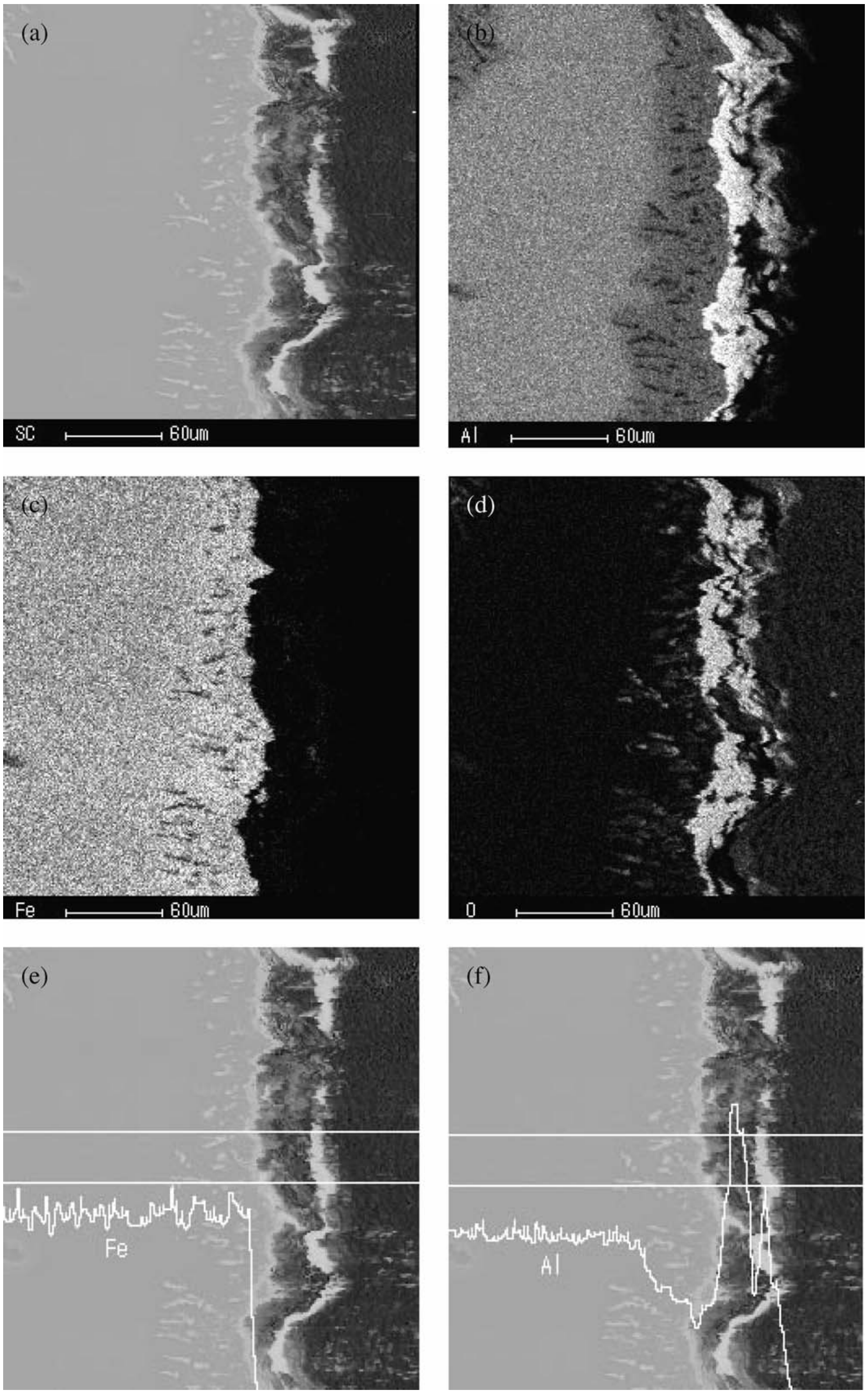

Figure 3 The cross-section of corrosion scale in molten LiCl at 750 °C in air for 25 h for Fe40Al by EPMA: (a) morphology, (b) Al distribution, (c) Fe distribution, (d) O distribution, (e) line profile of Fe and (f) line profile of Al.

the results of XRD analysis, it is logical to believe that only Al in Fe40Al was selectively corroded in both molten LiCl and LiCl-Li_2O.

The cross-sections of the specimens corroded in molten LiCl and LiCl-Li_2O were examined by electron probe microanalyzer (EPMA), and the results are shown in Figs 3 and 4, respectively. Fe40Al corroded in molten LiCl shows a porous external scale composed of Al and O (Li cannot be detected by EPMA) elements, plus an internal corrosion region. In combination with the XRD analysis, the external corrosion layer was composed of α-Al_2O_3 and α-$LiAlO_2$. It is reasonable to believe that the internal corrosion products should be the oxides of Al, because only Al in Fe40Al was selectively corroded. Based on the element distribution analysis (Fig. 3b, c, and d), some cracks were also detected in the corrosion scale. Moreover, the concentration gradient of Al was observed in substrate, as shown in Fig. 3e, indicating that diffusion of Al from the substrate to the scale takes place. In molten LiCl-Li_2O, only

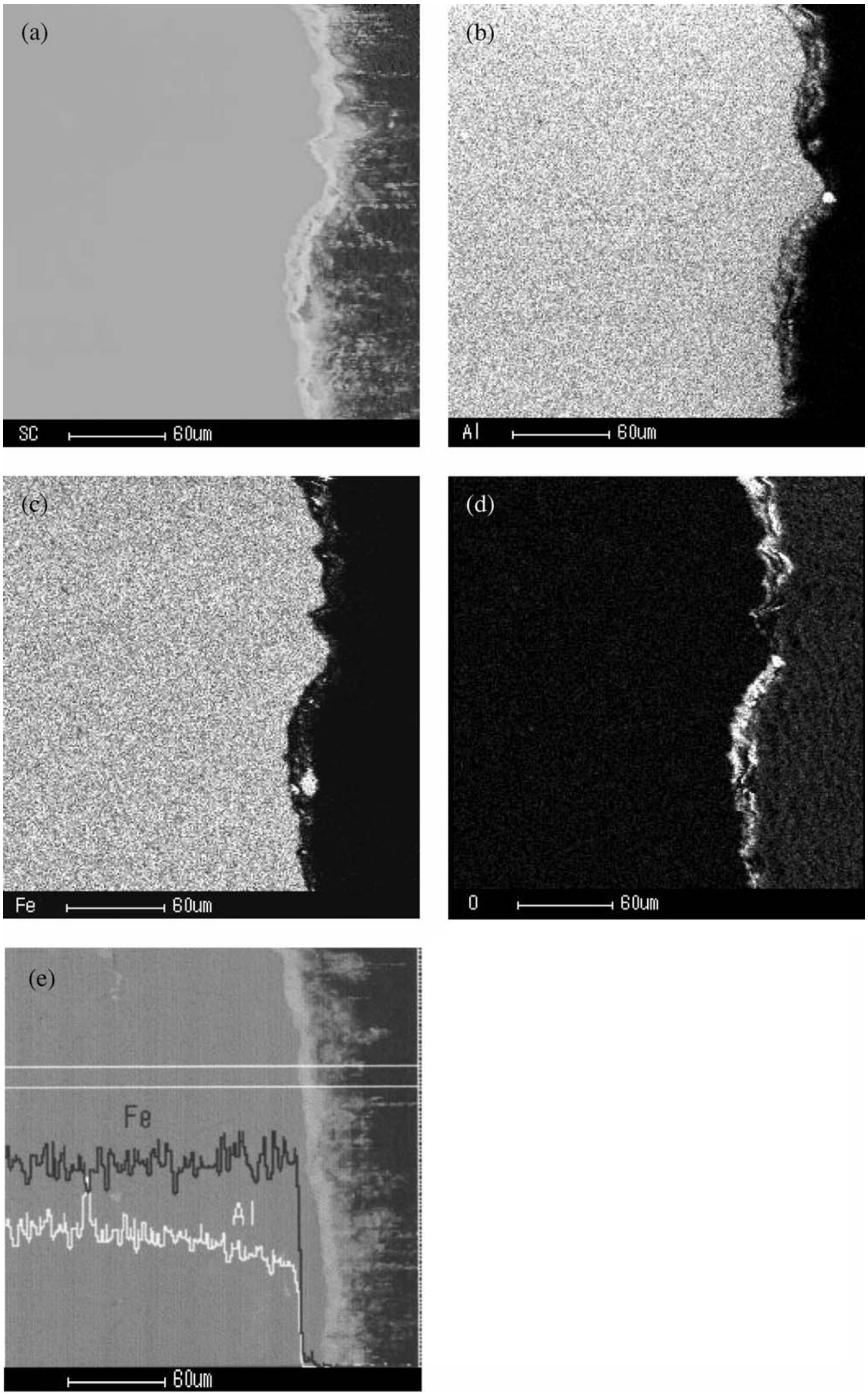

Figure 4 The cross-section of corrosion scale in molten LiCl-Li_2O at 750 °C in air for 25 h for Fe40Al by EPMA: (a) morphology, (b) Al distribution, (c) Fe distribution, (d) O distribution and (e) line profile of Fe and Al.

a thinner external scale containing Al and O elements were observed on the surface of the corroded specimen, as shown in Fig. 4a, b, c, and d. Combined with XRD analysis (Fig. 2b), the corrosion scale was composed of γ-$LiAlO_2$ and Fe after corrosion in molten LiCl-Li_2O. The concentration gradient of Al was also detected in the substrate, as shown in Fig. 4e.

Corrosion in molten salts is characterized by two steps [5]. The first is oxidation of the metal and the second is basic or acidic dissolution of oxide. Accordingly, Al in Fe40Al at first reacted with oxygen dissolved in the melts and formed Al_2O_3. The formation of Li-containing oxide in the corrosion scale is due to the basic dissolution of Al_2O_3 in contact with the melts, according to the following reaction [6]:

$$Al_2O_3 + Li_2O = 2LiAlO_2 \qquad (1)$$

Clearly, the molten LiCl-Li_2O mixture can provide adequate Li_2O. Furthermore, the supply of Li_2O in molten

LiCl is given by the following reaction [7]:

$$4\text{LiCl} + \text{O}_2 = 2\text{Li}_2\text{O} + 2\text{Cl}_2 \qquad (2)$$

According to reference [8], if the dissolution takes place, then the structure and integrity of the scale is damaged by the loss of some element or component and it is manifested by cracking and spalling of the scale. Accordingly, the cracks in Fig. 3 and the spallation of the scale come from the contribution of the basic dissolution of Al_2O_3.Thus it is logical to conclude that the fast corrosion in the initial stage of a test (as shown in Fig. 1) in the different melts is ascribed to the basic dissolution in contact with the melts. Based on reaction (1), it can be deduced that the higher activity of Li_2O in molten LiCl-Li_2O resulted in more severe corrosion compared to LiCl (Fig. 1). The parabolic curves in Fig. 1 after the initial stage could be explained by diffusion of Al in the latter stage of corrosion. The severe corrosion in the initial stage results in depletion of Al in the vicinity of the corrosion scale, and then Al must diffuse from the substrate to the interface of substrate/scale for the corrosion to continue. Based on Wagner's theory [9], when the corrosion rate follows the parabolic law, the corrosion process is controlled by diffusion mechanism. From the Wagner's theory and also from consideration made above, the parabolic curves (Figs 1a and b) in the latter stage of corrosion were determined by the diffusion of Al from the matrix to the corrosion scale.

In conclusion, Fe40Al was corroded at a higher corrosion rate in molten LiCl-Li_2O compared to that in molten LiCl. The corrosion of Fe40Al in different melts exhibited a similar trend: a very fast corrosion in the initial stage of corrosion, and then stabilized as parabolic law in the latter stage of corrosion. The fast corrosion in the initial stage was due to the basic dissolution of Al_2O_3, and the slow corrosion rate in the latter stage was controlled by the diffusion of Al from the substrate to corrosion scale.

Acknowledgments

The authors would like to thank Professors J. T. Guo, M. K. Lei, and D. H. Wang for technical assistance and helpful discussion.

References

1. J. E. INDACPCHEA and J. L. SMITH, *J. Mater. Res.* **14**(5) (1999) 1990.
2. S. H. CHO, S. C. PARK and J. S. ZHANG, *Korean J. Mater. Res.* **9** (1999) 556.
3. *Idem.*, *ibid.* **10** (2000) 471.
4. P. F. TORTORELLI and K. NATESAN, *Mater. Sci. Eng.* A **258** (1998) 115.
5. M. SPIEGEL, P. BIEDENKOPF and H. J. GRABKE, *Corros Sci.* **39** (1997) 1193.
6. S. XU, Y. ZHOU and X. HUANG, *J. Power Source.* **103** (2002) 230.
7. S. Z. DUAN and Y. Z. QIO, "Molten Salt Chemistry-Principle and Application" (The Metallurgical Industry Press Peking, 1990).
8. M. A. ESPINOSA and G. CARBAJAL, *Mater Corros.* **54** (2003) 304.
9. P. KOFSTAD, "High Temperature Corrosion" (Elsevier Applied Science London, 1988).

Received 19 August
and accepted 5 December 2003