

# Lifetime Evaluation of Al-Fe Coating in Wet-seal Environment of MCFC

JaeHo Jun, JoongHwan Jun, and KyooYoung Kim\*

*New Materials & Components Research Center,  
Research Institute of Industrial Science and Technology, Pohang, 790-600, Korea*

*\*Department of Materials Science & Engineering,  
Pohang University of Science and Technology, Pohang 790-784, Korea*

Aluminum source in an Al-Fe coating reacts with molten carbonate and develops a protective  $\text{LiAlO}_2$  layer on the coating surface during operation of molten carbonate fuel cells (MCFC). However, if aluminum content in an Al-Fe coating decreases to a critical level for some reasons during MCFC operation, a stable and continuous  $\text{LiAlO}_2$  protective layer can no longer be maintained. The aluminum content in an Al-Fe coating can be depleted by two different processes; one is by corrosion reaction at the surface between the aluminum source in the coating and molten carbonate, and the other is inward-diffusion of aluminum atoms within the coating into a substrate. In these two respects, therefore, the decreasing rate of aluminum concentration in an Al-Fe coating was measured, and then the influences of these two aspects on the lifetime of Al-Fe coating were investigated, respectively.

**Keywords** : molten carbonate fuel cell, Al-Fe coating, lifetime evaluation

## 1. Introduction

Separator plates of molten carbonate fuel cells (MCFC) are usually made of stainless steels such as AISI 316L or AISI 310S, but these materials are not suitable to use because they corrode rapidly in the wet-seal environments of MCFC.<sup>1)-3)</sup> Al-Fe coatings, therefore, have been applied to separators of MCFC.<sup>4)-6)</sup> In order that an Al-Fe coating maintains its protective function for the durability requirement of  $4 \times 10^4$ h, the coating needs to contain enough aluminum to form a protective  $\text{LiAlO}_2$  layer. However, if any coating does not originally contain enough aluminum content, or the aluminum content in the coating decreases to a critical level by some reasons during MCFC operation, a stable and continuous  $\text{LiAlO}_2$  protective layer cannot be maintained any longer. Instead, less protective layers such as  $\text{LiFeO}_2$  build-up, indicating that the coating loses its endowed function. Sasaki *et al.*<sup>7)</sup> examined the corrosion behavior of various Fe-Cr-Ni-Al alloys in the eutectic  $(\text{Li,K})_2\text{CO}_3$  melt for 1000h at  $650^\circ\text{C}$ . In their results, stable  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  were formed on the surface of a Fe-Cr-Ni-18.6Al (wt%) alloy, but iron oxide was observed for a Fe-Ni-4.7Al alloy and a Fe-Ni-Cr-10.5Al (wt%) alloy. Also, in the study by Frangini,<sup>8)</sup> an Fe-23.2Al-Zr-C-B (wt%) alloy showed a high corrosion resistance due to

the fact that a continuous aluminum oxide was formed on the surface in the eutectic  $(\text{Li,K})_2\text{CO}_3$  melt at  $650^\circ\text{C}$ . On the other hand, Zeng *et al.*<sup>9)</sup> reported that corrosion products formed on a Fe-24.4Al-0.12B (wt%) alloy were consisted of external  $\text{LiFeO}_2$  and inner  $\text{Al}_2\text{O}_3$  after an immersion test in the eutectic  $(\text{Li,K})_2\text{CO}_3$  melt for 100h. These results mentioned above reveal clearly that nature of corrosion products formed on a surface in the eutectic  $(\text{Li,K})_2\text{CO}_3$  melt at  $650^\circ\text{C}$  depends on aluminum contents in coatings or alloys. In other words, a protective  $\text{LiAlO}_2$  layer would not form on the surface if coatings or alloys do not contain sufficient aluminum

Over a long term operation of MCFC, a decrease in aluminum concentration in an Al-Fe coating can take place by following two main factors. First, aluminum concentration decreases while corrosion products are forming on the surface by a continuous chemical reaction between aluminum source in the coating and molten carbonate salt outside. Second, it also happens while aluminum atoms within the coating layer are diffusing inward a substrate. In this study, therefore, the decreasing rate of aluminum concentration in an Al-Fe coating was measured with respect to both the corrosion process and the inward diffusion process, respectively. And then, influences of two factors on the lifetime of an Al-Fe coating was inve-

stigated individually, with the assumption that the protective function of an Al-Fe coating ends when the aluminum concentration at the coating surface reaches a critical aluminum level.

## 2. Experimental procedures

### 2.1 Critical aluminum level

Four Al-Fe coated specimens containing various amounts of aluminum (viz. Fe-8Al, Fe-15Al, Fe-25Al and Fe-36Al (at%)) were prepared by using a single-source evaporation method.<sup>10)</sup> The Al-Fe coatings were fully immersed in the eutectic carbonate mixture of 62 mol  $\text{Li}_2\text{CO}_3$  and 38 mol  $\text{K}_2\text{CO}_3$  at  $650^\circ\text{C}$ . Following the immersion test, the corrosion products formed on the coated specimens were identified to find out the critical aluminum level for the formation of a protective  $\text{LiAlO}_2$  layer.

### 2.2 Al-Fe coating specimen

Aluminum was coated with a thickness of approximately  $30\mu\text{m}$  on a commercialized stainless steel (AISI 316) by using an electron-beam evaporation method. During the aluminum coating process, the vacuum level of a chamber was maintained below  $5 \times 10^{-5}$  torr, and the temperature of the substrate was kept at  $350^\circ\text{C}$ . To change the pure Al coating layer into an Al-Fe coating layer, the aluminum coated AISI 316L specimen was placed in a vacuum furnace under  $10^{-4}$  torr and heat-treated for 3h at  $850^\circ\text{C}$ . After the heat-treatment, the  $30\mu\text{m}$ -aluminum coating layer is changed into the B2-AlFe coating layer with a thickness of approximately  $50\mu\text{m}$ . Composition of the top coating surface is analyzed as 50.2Al-36.6Fe-7.6Cr-5.6Ni (at%), and aluminums are distributed uniformly in the range of 47~50 at% throughout the Al-Fe coating layer.

### 2.3 Evaluation of Al-Fe coating's lifetime

The Al-Fe coating specimen was used to investigate the influences of following two factors on the coating's lifetime: 1) corrosion reaction between aluminum and molten carbonate at the surface, and 2) inward diffusion of aluminum into the substrate. Firstly, in order to measure the decreasing rate of aluminum concentration due to the corrosion reaction at the surface, corrosion kinetics was examined by measuring weight changes versus immersion time in the eutectic carbonate mixture of 62 mol  $\text{Li}_2\text{CO}_3$  and 38 mol  $\text{K}_2\text{CO}_3$  at  $650^\circ\text{C}$ . Then, the change of aluminum content in the coating was calculated by combining the weight change data with a depleted amount of aluminum in the coating. Secondly, in order to measure the decreasing rate of aluminum concentration due to the inward diffusion of aluminum into the substrate, a diffusion test was con-

ducted in an argon gas atmosphere up to 8000h at  $650^\circ\text{C}$ , and the change of aluminum concentration at the surface was analyzed by EDS. Ultimately, influences of two factors on the Al-Fe coating's lifetime were investigated individually, based on the assumption that an Al-Fe coating's lifetime is the time which is taken until an initial aluminum content has decreased to a critical level.

## 3. Results and discussion

### 3.1 Critical aluminum level

An immersion test was carried out to examine a critical aluminum content required for the formation of a continuous protective  $\text{LiAlO}_2$  layer in molten carbonate. Fig. 1 shows the results of XRD on Fe-Al coating specimens after a 24 h immersion test in the eutectic Li/K carbonate melt at  $650^\circ\text{C}$ . The XRD results reveal that the Fe-8Al specimen showed sharp  $\text{LiFeO}_2$  peaks and broad and weak  $\text{LiAlO}_2$  peaks. The sharp  $\text{LiAlO}_2$  peaks began to appear in the Fe-18Al specimen. The intensities of  $\text{LiAlO}_2$  peaks increased with aluminum content in the Al-Fe coatings. The corrosion products of the Fe-25Al coating specimen consisted of  $\text{LiFeO}_2$ ,  $\alpha\text{-LiAlO}_2$  and  $\gamma\text{-LiAlO}_2$ . In addition, only  $\text{LiAlO}_2$  peaks were observed from the Fe-36Al specimen, indicating that  $\text{LiAlO}_2$  scale formed completely on the surface. It was observed from the test results that aluminum contents required for the formation of a stable and protective  $\text{LiAlO}_2$  in the eutectic Li/K carbonate melt at  $650^\circ\text{C}$  should be higher than 25 at%.

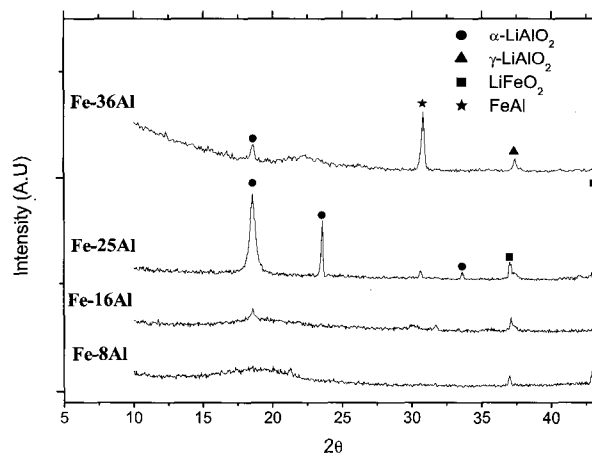


Fig. 1. XRD analysis of various Fe-Al coated specimens after immersion in eutectic  $(\text{Li,K})_2\text{CO}_3$  melt at  $650^\circ\text{C}$  for 24 h.

### 3.2 Influence of corrosion

If an Al-Fe coating forms a compact and continuous oxide on the surface by the chemical reaction with molten

carbonate without any degradation by local corrosion, the effective lifetime of the coating can be estimated by examining corrosion kinetics of the coating. If the oxidation of an Al-Fe coating follows a parabolic law in the eutectic  $(\text{Li,K})_2\text{CO}_3$  melt at  $650^\circ\text{C}$ , the change of aluminum content ( $\Delta C = C_o - C_t$ ) in the coating after a given time can be calculated by balancing the weight change ( $\Delta m$ ) for an oxide growth with the depleted amount of aluminum in the coating, then the following can be written.<sup>11),12)</sup>

$$A \cdot \Delta m = A \cdot k_p \cdot t^{0.5} = \frac{C_o - C_t}{100} \cdot \rho \cdot h \quad (1)$$

where  $C_o$  is the initial aluminum concentration (wt%),  $C_t$  is the aluminum concentration at time  $t$ ,  $\rho$  is the density of the coating layer,  $h$  is the coating thickness, and  $A$  is a constant based on the atomic weight ratio of aluminum and outside reactants like oxygen and/or lithium (i.e.  $\text{Al}_2\text{O}_3 = 1.125$  and  $\text{LiAlO}_2 = 0.692$ ). Therefore, the decreasing rate of aluminum concentration influenced by the corrosion process can be predicted from Eq. (1). In a real case, the aluminum decreasing by the inward diffusion of aluminum atoms into a substrate should be considered. However, Eq. (1) can be applied usefully in estimating the decreasing rate of aluminum only due to the corrosion reaction. Furthermore, it may be noted that when the aluminum concentration reaches a critical aluminum level ( $C_{Al}$ ), the protective function of the Al-Fe coating ends as described in the introduction chapter. In this respect, the lifetime of the Al-Fe coating can be calculated from Eq. (1), introducing the values of  $C_o$ ,  $C_{Al}$ , and  $k_p$ .

Fig. 2 shows weight changes versus immersion time for the Al-Fe coating specimen in the eutectic  $(\text{Li,K})_2\text{CO}_3$  melt at  $650^\circ\text{C}$ . As shown in Fig. 2, the weight per unit surface

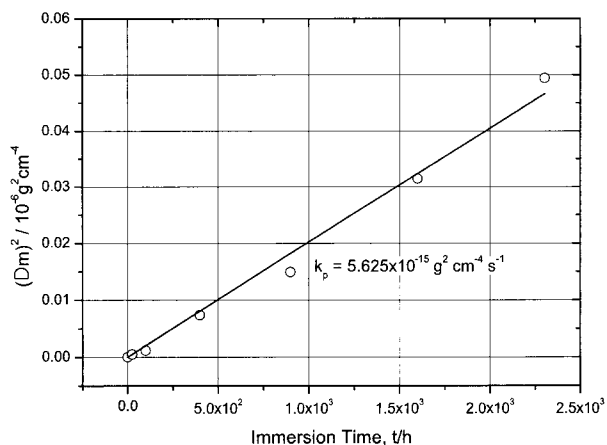


Fig. 2. Parabolic rate constant for corrosion of an Al-Fe coating in eutectic  $(\text{Li,K})_2\text{CO}_3$  melt at  $650^\circ\text{C}$ .

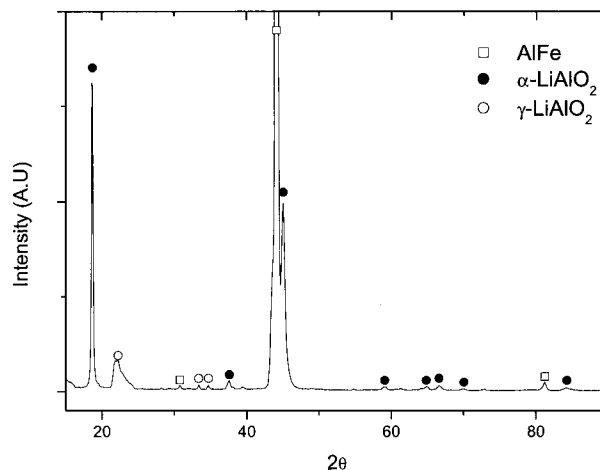


Fig. 3. XRD analysis for an Al-Fe coating after immersion in eutectic  $(\text{Li,K})_2\text{CO}_3$  melt for 4000h at  $650^\circ\text{C}$ .

area increases linearly with the square root of time, indicating that the scales formed on the Al-Fe coating in the eutectic  $(\text{Li,K})_2\text{CO}_3$  melt at  $650^\circ\text{C}$  grow in conformity with a parabolic law. Fig. 3 shows the result of XRD analysis for the Al-Fe coating specimen after an immersion test of 4000h, and reveals that the surface scale formed on the Al-Fe coating is  $\alpha$  and  $\gamma$ - $\text{LiAlO}_2$ . Especially, the value of the parabolic rate constant ( $k_p$ ) for the Al-Fe coating in the eutectic  $(\text{Li,K})_2\text{CO}_3$  at  $650^\circ\text{C}$  is measured as approximately  $5.625 \times 10^{-15} \text{g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$  from the least square fit of the data in Fig. 2.

Now, as the values of  $k_p$ ,  $C_o$ , and  $h$  were determined, the lifetime of the Al-Fe coating in the eutectic  $(\text{Li,K})_2\text{CO}_3$  at  $650^\circ\text{C}$  can be calculated. For example, it can be considered that an Al-Fe coating has following properties: 50.2 at% (32.8 wt%) for an initial aluminum concentration ( $C_o$ ),  $50\mu\text{m}$  for a thickness ( $h$ ),  $5.625 \times 10^{-15} \text{g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$  for a parabolic rate constant ( $k_p$ ), and  $5.59 \text{g} \cdot \text{cm}^{-3}$  for a density ( $\rho$ ) taken from an  $\text{Al}_{50}\text{Fe}_{50}$  alloy.<sup>13)</sup> Additionally, taking 25 at% (13.9 wt%) for a critical aluminum concentration ( $C_{Al}$ ) into account (Fig. 1), then the calculated lifetime of the Al-Fe coating is  $2.8 \times 10^6 \text{h}$ . This value is very high considering the durability requirement of  $4 \times 10^4 \text{h}$  for commercial MCFC applications, although it should be considered that the lifetime of the coating is in proportion to the square of a coating thickness as seen from Eq. (1). Consequently, it can be summarized that the influence of corrosion on the lifetime of the Al-Fe coating is not so serious, and this is basically due to the fact that the Al-Fe coating has a small parabolic rate constant of  $5.625 \times 10^{-15} \text{g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$  in the eutectic  $(\text{Li,K})_2\text{CO}_3$  melt at  $650^\circ\text{C}$ .

### 3.3 Influence of inward diffusion

In the previous section, the influence of corrosion on the lifetime of an Al-Fe coating was discussed. However, aluminum concentration in an Al-Fe coating can be also decreased by the inward diffusion of aluminum atoms into a substrate as well as the corrosion reaction between aluminum and molten carbonate at the surface. Accordingly, in this section, the decreasing rate of the aluminum concentration caused by the diffusion process was investigated, and then the influences of inward diffusion on the lifetime of an Al-Fe coating was studied.

To find out the decreasing rate of aluminum concentration caused by the inward-diffusion of aluminum within an Al-Fe coating, the diffusion behavior of aluminum in an Al-Fe coating layer should be examined. In fact, not only Al atoms diffuse inward a substrate, but also Fe, Ni and Cr atoms diffuse outward an Al-Fe coating layer from a substrate during MCFC operation. Plus, the diffusion coefficient of aluminum in an Al-Fe coating changes as aluminum concentration changes, and phase transformation can take place. Because of all these phenomena, it is very complicated to express an accurate diffusion model in a mathematical equation. Therefore, a simple Al-Fe coating system with following characteristics is introduced in this study. It is assumed that the Al-Fe coating has a uniform composition with an AlFe phase and a thickness of  $h$ . It is also assumed that the diffusion coefficient ( $D$ ) of aluminum does not change with diffusion time. In other words, at initial time ( $t = 0$ ), there is a uniform aluminum composition of  $C_0$  within the Al-Fe coating layer ( $0 \leq x \leq h$ ), and no aluminum exists in a substrate ( $x > h$ ). And, for a boundary condition, the concentration gradient at the surface of the coating ( $x = 0$ ) is not existed as time increases ( $t > 0$ ). Next, the aluminum concentration at the top surface is the important factor determining what kinds of corrosion product form in the eutectic  $(Li,K)_2CO_3$  melt at  $650^\circ C$ . Therefore, when the aluminum concentration at the surface ( $C_s$ ) is calculated at  $x = 0$ , the following equation can be obtained via Fick's second law.<sup>14),15)</sup>

$$\left(\frac{C_s}{C_0}\right)_{x=0} = erf\left(\frac{h}{2\sqrt{Dt}}\right) \quad (2)$$

Looking at Eq. (2), it can be noticed that the surface aluminum concentration ( $C_s$ ) is proportional to an error function, and the value of  $C_s$  can be calculated if the initial aluminum concentration ( $C_0$ ) and the diffusion coefficient ( $D$ ) of aluminum in the coating layer are known. Moreover, the lifetime of the Al-Fe coating can be estimated, substituting a critical aluminum concentration ( $C_{Al}$ ) as  $C_s$ .

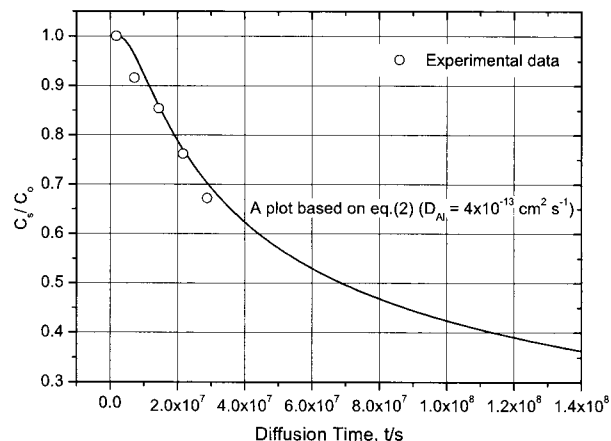


Fig. 4. Surface aluminum concentration changes versus diffusion time for an Al-Fe coating at  $650^\circ C$ . The solid line represents calculated values based on eq. (2).

Besides, it can be seen that the lifetime of the coating is proportional to the square of a coating thickness.

To examine the decreasing rate of aluminum concentration by the inward diffusion of aluminum, the Al-Fe coating specimen (viz.  $30\mu m$ -aluminum coating followed by heat treatment for 3h at  $850^\circ C$ ) was exposed in an inert gas atmosphere at  $650^\circ C$ . At the same time, aluminum concentrations versus diffusion time at the coating surface were measured by EDS. Fig. 4 shows the experimental data for aluminum concentration changes ( $C_s/C_0$ ) at the surface, and the calculated values based on Eq. (2) are presented together with the experimental data in Fig. 4. First of all, Fig. 4 shows that the decrease in aluminum concentration at 2000h is lower than the predicted value. This is thought to be associated with microstructure of the coating. Namely, the initial Al-Fe coating right after the heat-treatment seems to contain a loose microstructure providing rapid diffusion paths. However, as time passed 4000h, a trend is seen that the experimental data started to follow the plot based on Eq. (2). At this point, the diffusion coefficient of aluminum corresponds to about  $4 \times 10^{-13} cm^2 \cdot sec^{-1}$ . The measured aluminum concentration after 8000h starts to deviate from the calculated values. This can be attributed to the fact that aluminum concentration in the coating layer decreased with diffusion time, resulting in the increase of aluminum diffusivity. In general, when aluminum content decreases in an AlFe alloy, the long-range order parameter of B2-AlFe phase also decreases, then the aluminum diffusivity also increases.<sup>16),17)</sup> Looking into recent diffusion studies in Al-Fe phases, Mehrer *et al.*<sup>16),17)</sup> measured the diffusion coefficient of aluminum over wide temperature ranges by using 114m In as a substitute of aluminum, for which an

affordable radiotracer is not available. According to the result, the self-diffusion coefficient is approximately  $1.6 \times 10^{-13} \text{ cm}^2 \cdot \text{sec}^{-1}$  and  $1.8 \times 10^{-12} \text{ cm}^2 \cdot \text{sec}^{-1}$  for  $\text{Fe}_{50}\text{Al}_{50}$  and  $\text{Fe}_{73.5}\text{Al}_{26.5}$  alloy, respectively, at  $650^\circ\text{C}$ .

Although it is difficult to predict precisely the decreasing rate of aluminum concentration due to various reasons mentioned above, the influence of the inward-diffusion of aluminum on the lifetime of the Al-Fe coating can be estimated to some degree from the experimental data in Fig. 4 and Eq. (2). For instance, an Al-Fe coating, which has a thickness ( $h$ ) of  $50\mu\text{m}$  and a surface aluminum concentration ( $C_0$ ) of 50.2 at%, can be considered. In addition, it is assumed that a critical aluminum concentration ( $C_{Al}$ ) is 25 at% by using the previous result (Fig. 1). Then, the lifetime of the Al-Fe coating is  $1.9 \times 10^4 \text{ h}$  for a diffusion coefficient of  $4 \times 10^{-13} \text{ cm}^2 \cdot \text{sec}^{-1}$  obtained from the results in Fig. 4, and  $4.8 \times 10^4 \text{ h}$  for a diffusion coefficient of  $1.6 \times 10^{-13} \text{ cm}^2 \cdot \text{sec}^{-1}$  taken from the result in  $\text{Fe}_{50}\text{Al}_{50}$  alloy by Mehrer *et al.*<sup>16)</sup> These values are smaller than the value that was calculated in the case of the influence of the surface corrosion on the lifetime of the Al-Fe coating. This means that the decreasing rate of aluminum caused by the inward diffusion of aluminum is much higher than that of aluminum caused by the surface corrosion. Consequently, it can be stated that the inward diffusion of aluminum has a predominant influence on the lifetime of the Al-Fe coating.

#### 4. Summary

In order to estimate the lifetime of an Al-Fe coating in the eutectic  $(\text{Li,K})_2\text{CO}_3$  melt at  $650^\circ\text{C}$ , an Al-Fe coating specimen was used, which has a thickness of approximately  $50\mu\text{m}$  and a surface aluminum concentration of 50.2 at%. First of all, this study is based on the assumption that when an initial aluminum concentration at the coating surface decreases to a critical level (i.e. 25 at%) not able to form a protective  $\text{LiAlO}_2$  layer, the coating loses its protective function and this point of time is defined as the lifetime of the coating. Firstly, in the aspect of the surface corrosion reaction, the lifetime of the Al-Fe coating was estimated at  $2.8 \times 10^6 \text{ h}$ . This result means that the influence of the surface corrosion on the coating's lifetime is not so high considering that the durability requirement of commercial MCFC application is  $4 \times 10^4 \text{ h}$ . In addition, the basic reason for the result is that the Al-Fe coating has a small parabolic rate constant of  $5.625 \times$

$10^{-15} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$  in the eutectic  $(\text{Li,K})_2\text{CO}_3$  melt at  $650^\circ\text{C}$ . Secondly, regarding the inward diffusion of aluminum, the lifetime of the Al-Fe coating could be expected about  $4.8 \times 10^4 \text{ h}$  from a diffusion test and a simple diffusion model. This result indicates that the influence of the inward-diffusion is much larger than that of the surface corrosion reaction on the lifetime of the Al-Fe coating in the eutectic  $(\text{Li,K})_2\text{CO}_3$  at  $650^\circ\text{C}$ .

#### References

1. J. R. Selman, Fuel Cell Systems, p.345, Plenum Press, New York, 1993.
2. J. P. T. Huijsmans, G. J. Kraaij, R. C. Makkus, G. Rietveld, E. F. Sitters, and H. Th. J. Reijers, *J. of Power Sources* **86**, 117 (2000).
3. R. A. Donado, L. G. Marianowski, H. C. Maru, and J. R. Selman, *J. Electrochem. Soc.*, **131**, 2535 (1984).
4. C. Y. Yuh, R. Johnsen, M. Farooque, and H. C. Maru, *Proc. Symp. Molten Carbonate Fuel Cell Technology*, p. 158, The Electrochemical Society, Pennington, NJ (1993).
5. M. Yamamoto, N. Fujimoto, Y. Uenatsu, and T. Nagoya, *Nisshin Steel Technical Report*, **73**, 18 (1996).
6. J. E. Indacochea, I. Bloom, M. Krumpelt, and T. G. Benjamin, *J. Mater. Res.*, **13**, 1834 (1998).
7. M. Sasaki, S. Ohta, M. Asno, and N. Igata, *Cor. Eng.*, **45**, 231 (1996).
8. S. Frangini, *Oxid. Met.*, **53**, 139 (2000).
9. C. L. Zeng, W. Wang, and W. T. Wu, *Oxid. Met.*, **53**, 289 (2000).
10. S. Schiller, U. Heisig, and S. Panzer, *Electron Beam Technology*, p. 100, John Wiley & Sons, Inc., New York, 1982.
11. W. J. Quadackers and K. Bongartz, *Werkstoffe und Korrosion*, **45**, 232 (1994).
12. P. F. Tortorelli and K. Natesan, *Mater. Sci. & Eng.*, **A258**, 115 (1998).
13. E. Payne and P. D. Desai, Properties of Intermetallic Alloys, Chapter 2, Metal Information Analysis Center, CINDAS, Indiana, 1994.
14. D. Gupta and P. S. Ho, Diffusion Phenomena in Thin Films and Microelectronic Materials, Chapter 1, NOYES Publications, NJ, 1988.
15. K. Matsumoto, A. Matsuoka, and K. Nakagawa, *Denki Kagaku*, **66**, 537 (1998).
16. Mehrer, M. Eggersmann, A. Gude, M. Salamon, and B. Sepiol, *Mater., Sci. & Eng.*, **A239-240**, 889 (1997).
17. M. Eggersmann and H. Mehrer, *Met. Phys. Adv. Tech.*, **19**, 113 (2001).