

Corrosion of Al-Fe Coatings for Wet-Seal Area in Molten Carbonate Fuel Cells

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The corrosion behavior of Al-Fe coatings was studied in the wet-seal atmosphere of molten carbonate fuel cells (MCFC). Fe-8Al, Fe-16Al, Fe-25Al, Fe-36Al, and Fe-70Al (in at.%) specimens were tested in Li/K carbonate at 650°C by a single cell test and an immersion test. In general, the corrosion resistance of the Al-Fe coatings was enhanced due to the formation of a protective LiAlO_2 layer. However, when the Al-Fe coatings didn't have sufficient content of aluminum enough for maintaining the protective layer, the corrosion resistance of the Al-Fe coatings was severely degraded by the growth of non-protective scales like LiFeO_2 . The test results revealed that the aluminum contents in the coatings should be higher than 25 at.% in order to form and maintain the protective LiAlO_2 layers.

Keywords : MCFC, Separator, wet-seal corrosion, Al-Fe coating

1. Introduction

The corrosion problem of separator plates is one of major problems to hinder a long-term performance of MCFC. Especially the wet-seal area of the separator undergoes the most severe corrosion.¹⁾ In general, aluminum-containing alloys or aluminum coated stainless steels have been applied to the wet-seal area.²⁾⁻⁵⁾ It has been reported that a small amount of aluminum addition is beneficial for corrosion resistance of wet-seal materials.^{2),3)} But the usage of aluminum-containing alloys is generally restricted by poor mechanical properties. A more practical approach is the application of aluminum coatings. Previous studies clearly showed that aluminum coatings (actually, Al-Fe phases) had high corrosion resistance against molten carbonate.⁶⁾⁻⁸⁾ There are, however, still some questions as to whether Al-Fe coatings keep the protective function during a long-term operation of MCFC. In order to develop more reliable wet-seal materials having a sufficient lifetime, a closer examination of the corrosion behavior of Al-Fe coatings is needed. The purpose of this study was to establish better understandings of the corrosion behavior of Al-Fe coatings in the MCFC wet-seal atmosphere, focusing on the influence of aluminum contents on the corrosion behavior of Al-Fe coatings.

2. Experimental

Commercial stainless steel AISI 316L was used as a separator plate, and the anode wet-seal area was selectively coated with aluminum by an evaporation process. Fig. 1 shows a schematic diagram of the aluminum-coated separator plate, which has the cell area of 100 cm². In the evaporation process, aluminum grains were placed in an alumina crucible, and vaporized by heating with an electron-beam gun. The separator plate was held at 350°C, the working pressure was maintained lower than 5×10^{-5} torr, and the deposition rate was controlled to be about 100 Å per second. The thickness of the aluminum coating layer was measured to be approximately 30 μm. Subsequently, the aluminum-coated separator was heat-treated

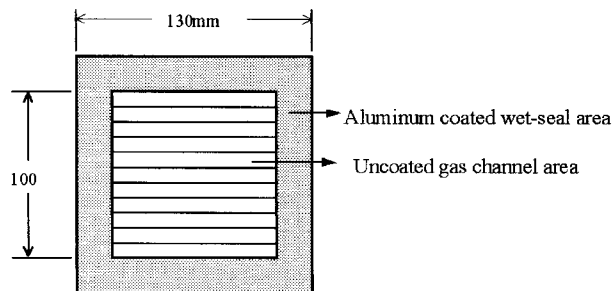


Fig. 1. Schematic diagram of aluminum coated separator for MCFC single cell

at 700°C for 3hrs in the atmosphere of 20H₂-80%N₂. After the heat treatment, the surface aluminum concentration was about 70 at.%. The separator was put to single cell operation at 650°C under the constant load of 150 mA/cm². The gas supply was 72H₂-18CO₂-10%H₂O for the anode, and 70Air-30%CO₂ for the cathode, respectively. For an electrolyte, 70Li₂CO₃-30mol%K₂CO₃ with LiAlO₂ matrix was used. During the single cell test, the corrosion kinetics of the aluminum-coated separator was determined by measuring scale thicknesses in metallographic cross sections. After 2500hr operation, the corrosion products and the coating layer were analyzed by scanning electron microscopy (SEM), X-ray deflection (XRD), and electron probe microanalysis (EPMA).

In addition to the single cell test, an immersion test was conducted to find out the effect of aluminum contents on the corrosion behavior of Al-Fe coatings. Al-Fe coated specimens containing various aluminum contents were prepared by a single-source evaporation method. The coated specimens were Fe-8Al, Fe-15Al, Fe-25Al and Fe-36 (in at.%) respectively. A cast specimen of Fe-25Al alloy was also prepared. For the immersion test, the coated specimens and the cast specimen were fully immersed in (0.62Li,0.38K)₂CO₃ eutectic melt at 650°C. After the immersion test, the corrosion products of Al-Fe coatings were identified by XRD, and the corrosion kinetics of Al-25Fe alloy was examined by measuring weight changes with immersion time.

3. Result and discussion

3.1 Single cell test

The single cell test was performed to investigate the corrosion behavior of an aluminum-coated separator in the MCFC wet-seal atmosphere. Fig. 2 shows the scale thickness data of uncoated separator (AISI 316L) and aluminum-coated separator after various operation times. The corrosion rate of the aluminum-coated separator was much lower. For example, the scale thickness of uncoated separator was about 50μm, while that of the aluminum-coated separator was about 8μm after 2,500hr operation. And the corrosion products on the uncoated separator consisted of two layers, outer layer of LiFeO₂ and inner layer of LiCrO₂, respectively while the aluminum-coated separator formed only LiAlO₂. It is known that aluminum is oxidized to form stable oxides such as LiAlO₂ or Al₂O₃ in molten Li/K carbonate. Possible oxidation reactions of the aluminum are as follows:

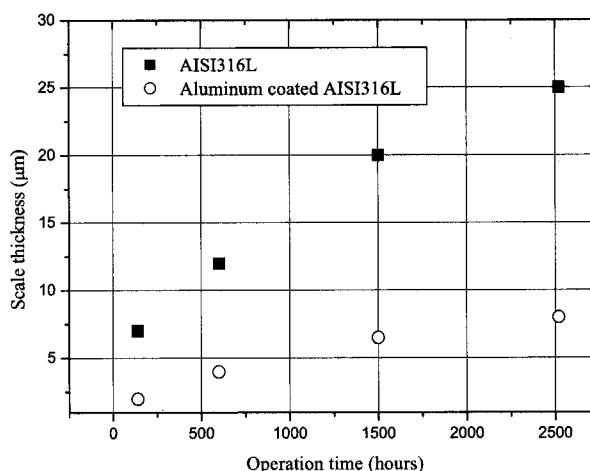
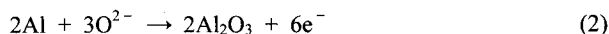


Fig. 2. Scale thickness of AISI 316L and aluminum coated AISI316L after various operation times of single cells



where the oxygen is supplied by the dissociation of carbonate ion ($\text{CO}_3^{2-} \rightarrow \text{RCO}_2 + \text{O}^{2-}$) or by the gas dissolved in molten carbonate.⁸⁾ The test results confirmed that the aluminum coating enhanced the corrosion resistance of AISI 316L by the formation of the protective LiAlO₂ layer.

As described above, the aluminum coating provided higher corrosion resistance. However, if the coating layer (i.e., Al-Fe phases) might not have sufficient aluminum content enough for the formation of stable LiAlO₂ layer, it could form non-protective iron oxides on the surface. This is because that the limit of LiAlO₂ formation on Al-Fe coatings depends on the aluminum content. This possibility is shown in Fig. 3. First of all, the coating layer at the region marked as C1 in Fig. 3(a) reveals uneven scale morphology, localized attack of the coating surface, and the growth of corrosion products inside the coating layer. This corrosion behavior is thought to be associated with inhomogeneous composition distribution and microstructural defects of the coating layer.⁷⁾ In any case, the coating layer at the region C1 could be undermined by the attack of carbonate salt and lose its outer part. Consequently it could be resulted into a thin coating layer like the region C2 in Fig. 3(a). Because the coating layer at the region C2 is thinner than normal coating layers, the surface concentration of aluminum is certainly lower. Aluminum concentration at the point #5 was measured to be 28 at.% by EPMA, while it was 41 at.% at the point #2. It is necessary for the coating layer to have a reservoir of the aluminum component forming a protective scale like LiAlO₂, and the protective scale should be able to continue to grow during the coating lifetime. In this

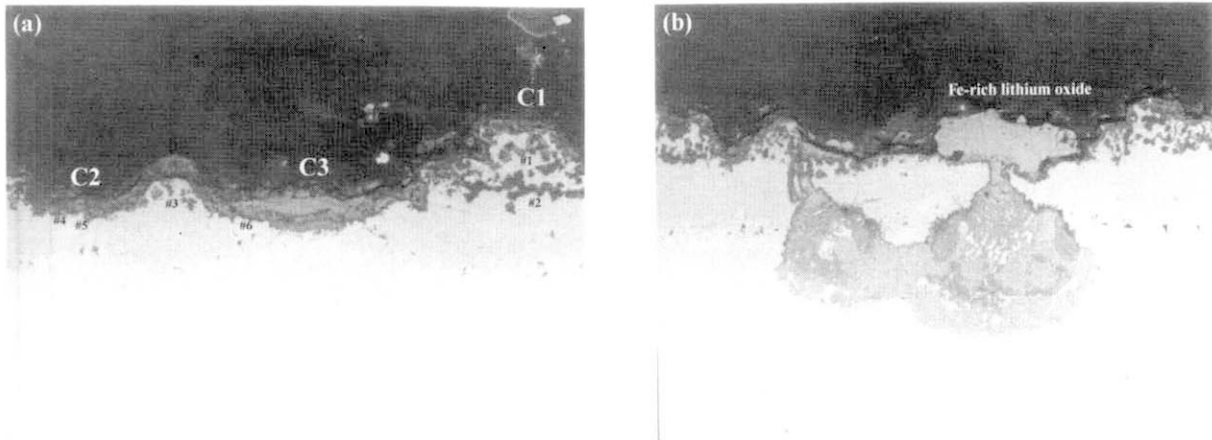


Fig. 3. Cross-sections of wet-seal area of the aluminum coated separator after 2,500hr operation, showing a corrosion sequence of degradation of the coating layer

respect, the region C2 may act as a position where iron oxides can be formed instead of LiAlO_2 . This is shown in the region C3 of Fig. 3(a). By further corrosion process, the iron oxide grew all the more, and oxygen could penetrate even through the scale and the coating layer into the substrate as shown in Fig. 3(b). In summary, the degradation of the coating layer could be initiated by localized attack, and the lack of aluminum concentration was followed at that region leading to the formation of iron oxide, finally pitting corrosion occurred.

3.2 Immersion test

The immersion test was carried out to examine the critical aluminum content for the formation of continuous protective LiAlO_2 layer in molten carbonate. Many studies have been conducted on oxidation behavior of iron-aluminum alloys in oxygen atmosphere, and revealed that what percentage of aluminum is required to form completely protective Al_2O_3 scales.^{9),10)} But, less work has been done on oxidation behavior in molten carbonate systems. Zeng¹¹⁾ reported that Fe-24.4Al-0.12B alloy (in wt%) formed external LiFeO_2 and inner Al_2O_3 after immersion in $(0.62\text{Li}/0.38\text{K})_2\text{CO}_3$ eutectic melt at 650°C for 100hrs. Frangini¹²⁾ pointed out that Fe-Al alloys with about 25 wt.% aluminum possessed long term corrosion resistance in molten carbonate. These results mean that aluminum contents play an important part in the corrosion behavior of Al-Fe alloys in the MCFC wet-seal atmosphere.

Fig. 4 shows the weight gain curves for the cast specimen of Fe-25Al in the eutectic melt at 650°C . The scale growth showed parabolic form up to about 50hours. On the further reaction, however, the Fe-25Al alloy started to corrode rapidly with larger weight gain. There are also scattered data in the figure probably due to spalled scales.

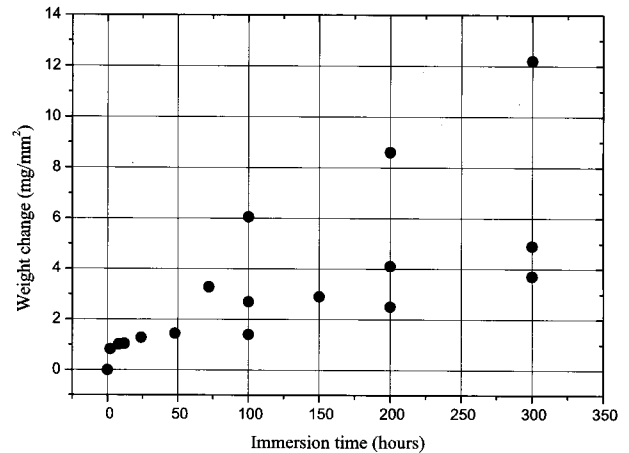


Fig. 4. Weight change versus immersion time of the Fe-25Al alloy specimen in the eutectic $(0.62\text{Li}/0.38\text{K})_2\text{CO}_3$ melt at 650°C

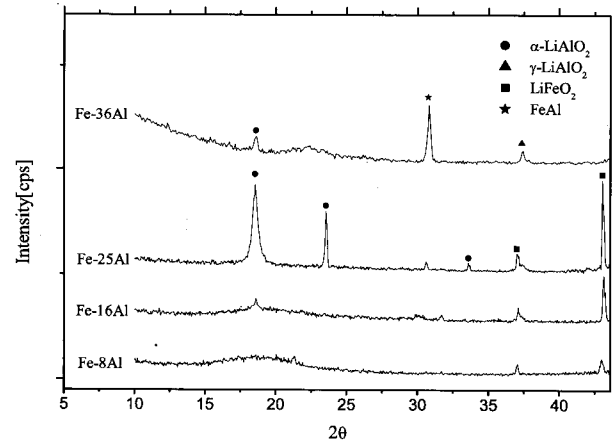


Fig. 5. XRD analysis of various Fe-Al coated specimens after immersion in the eutectic $(0.62\text{Li}/0.38\text{K})_2\text{CO}_3$ melt for 24hr at 650°C .

XRD showed that the scales consisted of LiFeO_2 and LiAlO_2 , indicating that the Fe-25Al alloy could not develop a stable LiAlO_2 oxide.

Fig. 5 shows the results of XRD on the Fe-Al coating specimens after 24hr immersion test in the eutectic melt at 650°C . First, Fe-8Al specimen showed sharp LiFeO_2 peaks and broad and weak peaks corresponding to LiAlO_2 phase. Sharp LiAlO_2 peaks began to appear in Fe-18Al specimen, and the intensities of LiAlO_2 peaks increased with increasing aluminum content in Al-Fe coatings. The corrosion products of Fe-25Al coating specimen consisted of LiFeO_2 , α - LiAlO_2 and γ - LiAlO_2 . By the way, only LiAlO_2 peaks were observed on the Fe-36Al specimen, indicating that LiAlO_2 scale completely formed on the surface. In conclusion, the test results imply that the critical aluminum content for the formation of a stable and protective LiAlO_2 in eutectic $(\text{Li/K})_2\text{CO}_3$ melt at 650°C should lie between 25 and 36 at.%.

4. Conclusion

The corrosion behavior of Al-Fe coatings was investigated by the single cell test and the immersion test in the MCFC wet-seal environment, focusing on the influence of aluminum contents on the corrosion behavior of Al-Fe coatings. In the single cell test, the aluminum-coated separator exhibited higher corrosion resistance than uncoated specimen due to the formation of a protective LiAlO_2 layer on the surface. However, the degradation of the coating layer was initiated by localized attack, leading to the lack of aluminum concentration and thus the formation of a non-protective iron oxide instead of LiAlO_2 . In the immersion test, the Al-Fe coatings containing 8 to 25 at.% aluminum formed predominantly LiFeO_2 and

corroded with large weight gain. When the aluminum content was 36 at.%, the Al-36Fe coating developed external LiAlO_2 scale. The results of the immersion test indicate that the critical aluminum level for the formation of a protective LiAlO_2 in eutectic $(\text{Li/K})_2\text{CO}_3$ melt at 650°C lies between 25 and 36 at.%.

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