Improvement of Oxidation Resistance of Fe-Cr Ferritic Alloy Sheets for SOFC Interconnects

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Fe-Cr ferritic alloys are applied for interconnects of solid oxide fuel cells (SOFCs) operated at around medium temperatures. The oxidation behavior of sheets with various thicknesses of Fe-22%Cr ferritic alloy, ZMG232L, was investigated. The oxidation rate of thin sheet was much higher than that of thick one because Cr content decreased under oxide layer of edge part of thin sheet therefore Cr oxide became unstable and Fe was mainly oxidized. Such accelerated oxidation was improved mainly by reducing Mn, additionally by increasing Cr and adding W.

Key Words: Oxidation Behavior, Fe-Cr Ferritic Alloy, SOFC, Interconnects

1 Introduction

Recently, solid oxide fuel cells (SOFCs) are expected as a new and clean power generator with high efficiency. In late years according to reduction of operating temperature of SOFCs, metallic materials, especially Fe-Cr ferritic alloys, are promising as interconnect materials of SOFCs because of their low thermal expansion behavior close to ceramic parts, relatively good oxidation resistance, lower cost than ceramics, good workability, good machinability, and so on. However conventional Fe-Cr ferritic alloys such as type430 stainless steel do not have sufficient oxidation resistance at medium operating temperature of SOFCs. ZMG232L is one of the developed Fe-Cr ferritic alloys especially for SOFC metallic interconnects. ZMG232L is a Fe-22%Cr ferritic alloy with a small addition of Zr and La and reduction of Si and Al, which has good oxidation resistance and good electrical conductivity at elevated temperature in the range of about 700-1000°C required for SOFC interconnects. These metallic materials are usually machined or pressed into various shapes of interconnect parts. Thin sheets are often used in press forming. It is, however, possible for the oxidation resistance of thin sheet-type metallic materials to become lower as the sheet becomes thinner.

In this study the effect of thickness of sheet of ZMG232L on oxidation behavior was investigated. Moreover, improvement of oxidation resistance of thin Fe-Cr alloy sheet was carried out.

2 Experimental

The chemical compositions of ZMG232L and experimental alloys are shown in Table 1. These alloys were experimentally melted in vacuum and cast into ingots, and then hot forged, cold rolled into sheets with various thicknesses, and annealed. Test pieces for oxidation tests of 15 mm square were cut from these sheets and polished. The test piece was put in the container made of alumina one by one, and put into the electric furnace at 850°C in air. The oxidation weight gain of each test piece was measured after each 500 hours’ oxidation test. After 1000 hours’ test, the specimen was cut, plated with Ni, mounted in the resin, ground and polished, then the cross-sectional microstructure of oxidation layer was observed and analyzed with electron probe micro analysis (EPMA).

3 Results and Discussion

The oxidation weight gains at 850°C in air of ZMG232L sheet specimens with various thicknesses as a function of exposure time are shown in Fig. 1. No spalled scale was observed in all specimens. The oxidation weight gains of sheet specimens of not less than 0.5 mm thick increase with time according to the parabolic law. On the other hand, when the sheet specimens are thinner than about 0.2 mm, their oxidation weight gains rapidly increase with time. Thus, the oxidation is accelerated when the specimen is thin. Figure 2 shows SE-EPMA image in the cross-sectional microstructure of specimen of 0.1 mm thick of ZMG232L after exposure at 850°C for 1000 hours in air. In Fig. 2, white layers which cover the surface of specimen are Ni layers plated only for preparation of test piece for microstructure observation, and gray layers under the Ni layer are oxide layers. In the case of the sheet specimen of 0.1 mm thick, anomalous oxidation was observed only at the edge of the

| Table 1 Chemical compositions of alloys used in this study (mass %). |
|-------------------|---|---|---|---|---|---|---|---|---|
|                  | C  | Si | Mn | Ni | Cr | Al | Zr | La | W  | Fe |
| ZMG232L          | 0.02 | 0.08 | 0.46 | 0.34 | 21.8 | 0.05 | 0.19 | 0.05 | -  | bal. |
| 232K             | 0.02 < 0.01 | 0.01 | 0.36 | 21.9 | 0.01 | 0.27 | 0.05 | -  | bal. |
| 232K1            | 0.02 < 0.01 < 0.01 | 0.036 | 23.8 | 0.01 | 0.20 | 0.05 | -  | bal. |
| 232K2            | 0.03 < 0.01 < 0.01 | 0.036 | 23.8 | 0.02 | 0.23 | 0.06 | 1.95 | bal. |
sheet, which was formed both inside and outside of the edge of the specimen. This oxide formed out of the edge consists of Fe rich oxide. On the other hand, thin oxide layer which mainly consists of Cr-Mn spinel and chromia was observed, except for the edge part. Figure 3 shows Cr concentration analyzed with WDS at each position indicated in the cross section of microstructure in Fig. 2. Cr concentration at all parts in the alloy after exposure at 850°C for 1000 hours in air decreased because Cr was used to form the oxide layer at the alloy surface. Cr concentration in the alloy, however, significantly decreased to less than 16 mass% at the edge part although it still remained more than 16 mass% except for the edge part. The edge of the specimen are covered with Cr oxide at the early stage of oxidation, but Cr in the alloy matrix is used more to form the oxide layer because the edge has three surfaces. Furthermore thin specimen contains smaller amount of Cr than thick one. Thus Cr concentration at the edge is depleted rapidly and then stable Cr oxide layer cannot be formed. It was found that anomalous oxidation occurred because stable Cr oxide layer was not formed when Cr concentration in the alloy surface decreased to less than 16 mass%.

In order to improve the anomalous oxidation at the edge part of thin sheets, modification of chemical compositions of alloys were carried out. Improved alloys are 232K, 232K1, and 232K2 shown in Table 1. 232K has lower Mn concentration than ZMG232L. 232K1 has higher Cr concentration than 232K. 232K2 is the alloy that contains 2 mass%W in 232K1. The oxidation weight gains of these specimens of 0.1 mm thick after exposure at 850°C for 1000 hours in air are shown in Fig. 4. Specimen of 0.1 mm thick was selected to evaluate anomalous oxidation behavior within a short time. In this test, no spalled scale was also observed. As shown in Fig. 4, oxidation weight gains of 232K, 232K1, and 232K2 were much smaller than that of ZMG232L. Reduction of Mn concentration is effective to improve oxidation resistance of thin sheet. Among the alloys with low Mn, the increase of Cr concentration up to 24 mass% increases oxidation weight gain since oxidation weight gain of 232K1 was larger than that of 232K. Addition of 2 mass%W to the alloy with low Mn and high Cr, however, slightly decreases oxidation weight gain, when oxidation weight gain of 232K2 is compared with that of 232K1.
Figure 5 shows SE-EPMA image of cross-sectional microstructures of specimens of 0.1 mm thick of 232K, 232K1, and 232K2 after exposure at 850°C for 1000 hours in air. Oxide layers of these alloys were much thinner than that of ZMG232L, and no anomalous oxidation was observed both at the edge and at the plain surface of specimens of these alloys containing low Mn. This is the reason why oxidation weight gains of these alloys were much smaller than that of ZMG232L. Figure 6 shows Cr concentration analyzed with WDS at each position indicated in the cross-sectional microstructure in Fig. 5 (an example of analyzed positions is shown in Fig. 5 (a)). Cr concentrations at all parts in 232K containing 22 mass% Cr after exposure at 850°C for 1000 hours in air also decreased, but they are still more than 18 mass% even at the edge part of the specimen. Cr concentrations in 232K1 and 232K2 containing 24 mass% Cr after exposure at 850°C for 1000 hours in air are more than 19 mass% even at the edge of the specimens. Reducing Mn mainly hinders Cr from decreasing in the alloy during oxidation on the alloy surface at elevated temperature. Increasing Cr and adding W additionally improve anomalous oxidation. These effects of alloying elements are thought to relate to the forming rate of tight and uniform Cr oxide on the surface and diffusion rate of Cr in the alloy matrix. This result is, however, limited only to 1000 hours’ oxidation test at 850°C at this moment and the duration up to anomalous oxidation of 232K, 232K1, and 232K2 has not been found yet. Further investigation of oxidation behavior of these alloys is needed to clarify the effect of alloying elements on improving anomalous oxidation of thin sheet of Fe-Cr ferritic alloy.

4 Conclusion

Oxidation of thin specimen of ZMG232L at 850°C in air was accelerated as the thickness became small, and anomalous oxidation was observed at the edge of specimen of 0.1 mm thick after 1000 hours exposure. Mainly reducing Mn and additionally increasing Cr and adding W in this alloy significantly improved anomalous oxidation of 0.1 mm thick specimen at 850°C for 1000 hours in air.

References