EFFECT OF ALLOYING ELEMENTS ON PROPERTIES OF FERRITIC Fe-Cr ALLOYS FOR SOFC INTERCONNECTS

Akihiro Toji¹, Toshihiro Uehara¹, Takehiro Ohno²
¹Metallurgical Research Laboratory, Hitachi Metals, Ltd.
Yasugi-cho, Yasugi-shi, Shimane 692-8601, Japan
²Chubu-Tokai Branch, Hitachi Metals, Ltd.
Nishiki-2 chôme, Naka-ku, Nagoya, Aichi 460-0003, Japan

ABSTRACT

Ferritic Fe-Cr alloy is desired as interconnect material of SOFC because of its lower cost and workability. We developed a ferritic Fe-22Cr alloy with a small addition of La and Zr which has good oxidation resistance and good electrical conductivity at 750-1000 degrees C. For further improvement, we investigated the effect of alloying elements, Ti, Nb, Zr and La, on properties of ferritic Fe-Cr alloys. From the result of this study, ferritic Fe-Cr alloy with addition of the combination of La and Zr, indicated better oxidation resistance and electrical contact resistance than that with Ti and La and that with Nb, Zr and La.

INTRODUCTION

Fe-Cr ferritic alloys are candidates for interconnects because SOFC operating temperature is being reduced from about 1000°C to around 750°C. Commercially available alloys, however, do not have good combination of high temperature properties required for SOFCs such as good oxidation resistance, thermal expansion compatibility with ceramics, high electrical conductivity, etc. So we developed a ferritic Fe-22Cr alloy with small additions of La and Zr, ZMG232, for SOFC interconnects (1,2), and then improved the alloy, which has better combination of oxidation resistance and electrical conductivity after exposure in air at 750-1000°C, by decreasing its Si content (3). In this study, we investigated the effect of alloying elements on properties of ferritic Fe-Cr alloys for SOFC interconnects.

EXPERIMENTAL PROCEDURES

Ferritic Fe-Cr alloys with various contents of added elements such as Ti, Nb, Zr and La were prepared. Chemical compositions of alloys used in this study are shown in Table 1. Commercial alloys, 430 Alloy and 446 Alloy, were also prepared, as shown in Table 1, for comparison. In this study, ZMG232 with low Si content was used for better oxidation resistance. The alloys were vacuum induction melted and cast into 10 kg ingots. They were then hot-forged to 30 mm square bars and annealed at 780°C for 1 hour.

Oxidation tests were carried out in air at 750-1000°C for 100-1,000 hours. Columnar test specimens, 10 mm in diameter and 20 mm in length, were used for oxidation tests.
Oxidation weight gain without exfoliated scale and weight of the exfoliated scale were measured. After oxidation test, microstructures of specimens in cross section near surface were observed by means of optical microscopy and scanning electron microscopy (SEM). Contact resistance of plate specimens, with contact area of 10 mm square and 3 mm in thickness covered with Pt-paste for connection with a standard Pt-mesh, was measured in air at 750°C after preoxidation in air at 750°C for 1000 hours, and measured at 1000°C after preoxidation in air at 1000°C for 100 hours, using a four-point method. Mean coefficient of thermal expansion of columnar specimens, 5 mm in diameter and 19.5 mm in length, was measured using a thermal dilatometer from 30 to 1000°C.

### Table 1. Chemical compositions and mean coefficients of thermal expansion of alloys used in this study (mass%).

| alloy   | C   | Si  | Mn  | Ni  | Cr  | Al  | La   | others | Fe     | CTE<sub>30-1000°C</sub>×10<sup>-6</sup>/°C |
|---------|-----|-----|-----|-----|-----|-----|------|--------|--------|-----------------------------|
| ZMG232  | 0.02| 0.10| 0.47| 0.26| 22.14| 0.21| 0.04 | Zr=0.20| bal.   | 12.7                        |
| Fe22CrTi| 0.01| 0.11| 0.49| 0.27| 22.23| 0.16| 0.05 | Ti=0.10| bal.   | 12.9                        |
| Fe22CrNbZr| 0.02| 0.10| 0.55| 0.31| 22.09| 0.20| 0.08 | Nb=0.30, Zr=0.22 | bal. | 13.2                        |
| 446Alloy| 0.11| 0.32| 0.47| 0.11| 24.81| 0.21| -    | -      | bal.   | 13.1                        |
| 430Alloy| 0.02| 0.34| 0.48| 0.15| 16.97| 0.15| -    | -      | bal.   | 13.2                        |

(Note: ZMG is a trademark of Hitachi Metals, Ltd.)

### RESULTS AND DISCUSSIONS

Fig. 1 shows oxidation resistance and electrical contact resistance of specimens in air at 1000°C for 100 hours and at 750°C for 1000 hours. The figure in parentheses shows weight of exfoliated scale (mg/cm²). There is little difference in oxidation weight gains at 750°C for all alloys. On the other hand, 430 Alloy indicates the worst oxidation resistance at 1000°C. In comparison with 430 Alloy, other alloys such as 446 Alloy, ZMG232, Fe22CrTi and Fe22CrNbZr indicate good oxidation resistance at 1000°C. However only 446 Alloy had some exfoliated scale. Therefore, as shown in 446 Alloy, an increase in Cr only in 430 Alloy does not always give enough oxidation resistance at 1000°C. Since ZMG232, Fe22CrTi and Fe22CrNbZr had no exfoliated scale at 1000°C, it is clear that the addition of La does not form exfoliated scale and improves significantly oxidation resistance of Fe-22Cr alloy. The addition of Zr in Fe-22Cr alloy has more effect in improving oxidation resistance than Ti and Nb, because ZMG232 had the smallest oxidation weight gain in Fe-22Cr alloys containing La.

Contact resistances of 430 Alloy and ZMG232 were measured at 750°C after preoxidation in air. Although ZMG232 and 430 Alloy have comparable oxidation resistance at 750°C, ZMG232 has much lower contact resistance than 430 Alloy. It is thought that the difference in type and composition of oxide layers has some effect on these results of oxidation resistance and contact resistance. It is reported that high content of Fe in Mn rich spinel oxide layers formed at the surface of ZMG232 causes low contact resistance (4). Contact resistance at 1000°C after preoxidation in air was measured for all
the alloys except 430 Alloy. Because of a large exfoliation of scale, contact resistance of 430 Alloy at 1000°C could not be measured. Contact resistances of ZMG232, Fe22CrTi and Fe22CrNbZr at 1000°C were about 20 to 30 mΩ·cm², and ZMG232 and Fe22CrTi indicated the lowest contact resistance. Therefore it was concluded that ZMG232 containing La and Zr has the best combination of oxidation resistance and electrical conductivity.

Figure 1. Results of oxidation tests in air and electrical contact resistance at 750 and 1000°C.

Fig. 2 shows optical microstructures of the oxide layers in specimens after exposure in air at 1000°C for 100 hours. The oxide layer in ZMG232 with small additions of La and Zr was the thinnest in all specimens. The thickness of oxide layer shown in Fig. 2 corresponds to the oxidation weight gain and the contact resistance shown in Fig. 1.
Coated Ni for observation

Coated Ni for observation

Figure 2. Optical microstructure of oxide layer after exposure in air at 1000°C for 100 hours.

Fig. 3 shows the time dependence of square of thickness of the oxide layer in ZMG232 in air at 750°C up to 3000 hours. It is found that the growth rate of oxide layer in ZMG232 follows the parabolic law.

Fig. 3. Time dependence of the growth rate of oxide layer in ZMG232 at 750°C in air.

Fig. 4 (a-c) shows EDX element maps of the oxide layers in Fe22CrTi, Fe22CrNbZr, and ZMG232 after exposure in air at 1000°C for 100 hours. All specimens had Mn rich oxide layer at the top of them, Cr rich oxide layer under Mn rich oxide layer, and Al oxide particles dispersed in metal matrix under oxide layer. Mn rich oxide layer of ZMG232
was the thinnest in all specimens and contained a small amount of Fe that is effective for improving electrical conductivity. Fe22CrNbZr had much thicker Cr-rich oxide than Fe22CrTi and ZMG232, and condensed Nb layer between Cr-rich oxide scale and metal matrix. It is thought that thick Cr-rich oxide on Fe22CrNbZr causes slightly higher contact resistance. In Fe22CrTi, Ti oxide particles in metal matrix were observed. On the other hand, Fe22CrNbZr and ZMG232 had a few Zr oxide particles in metal matrix.

(a) ZMG232

(b) Fe22CrTi
CONCLUSIONS

In this study, ZMG232, a ferritic alloy containing Zr and La indicates better oxidation resistance and electrical contact resistance than ferritic alloys containing Ti and La, and containing Nb, Zr and La, after exposure in air at 1000°C. Therefore, ZMG232 is considered suitable for interconnect material in planar SOFC systems operated at about 750 to 1000°C. We will continue to improve the high temperature properties of ZMG232.

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