TOTAL SOLUTION OF METALLIC MATERIALS FOR SOFCs

Toshihiro Uehara, Akihiro Toji, Ken Inoue, Motoi Yamaguchi*, Takehiro Ohno**

Metallurgical Research Laboratory, Hitachi Metals, Ltd

*Yasugi Works, Hitachi Metals, Ltd.
Yasugi-cho, Yasugi-shi, Shimane 692-8601, Japan

**Chubu Branch, Hitachi Metals, Ltd.
Meieki, Nakamura-ku, Nagoya, Aichi 450-0002, Japan

ABSTRACT

Several kinds of metallic materials with high temperature properties such as good oxidation resistance, high electrical conductivity, low thermal expansion coefficient, etc are expected to be used in SOFC systems. Some new alloys were developed in this study in order to solve the problems which conventional alloys are not able to conquer. Fe-Cr ferritic interconnector alloy, oxidation-resistant Ni-based alloy for capsule for gas separation, and low thermal expansion Fe-Ni-Co alloy compatible with YSZ for current collector are discussed here.

INTRODUCTION

Since SOFCs are operated at high temperatures in the range of about 700-1000°C, several kinds of metallic materials with high temperature properties such as good oxidation resistance, thermal expansion compatibility with ceramics, high electrical conductivity, etc, are expected to be used for SOFC systems. For example, Fe-Cr ferritic alloys are candidates for interconnector material at operating temperatures around 750°C. Commercial alloys, however, do not have good combination of these high temperature properties required for SOFCs. Therefore, development of new alloys is needed in order to solve the problems which conventional alloys are not able to conquer. Fe-Cr ferritic interconnector alloy (1), oxidation-resistant Ni-based alloy as capsule for gas separation, and low thermal expansion Fe-Ni-Co alloy compatible with YSZ for current collector are proposed here as examples of newly developed alloys.

DEVELOPMENT OF Fe-Cr FERRITIC INTERCONNECTOR ALLOY

For interconnector materials, good oxidation resistance, electrical conductivity, and low thermal expansion close to that of YSZ are required at the operating temperatures. A Fe-Cr ferritic alloy with low thermal expansion of about 13x10^-6/°C was selected and the effect of alloying elements on oxidation resistance and electrical conductivity was investigated in order to develop a new interconnector alloy.
Experimental Procedures

Ferritic Fe-Cr alloys containing various amounts of added elements such as Cr, Al, Ti, Zr, La, Y, and Ce were prepared. Chemical compositions of alloys used in this study are shown in Table 1. An austenitic Ni-based alloy, Alloy 600 was also prepared for comparison. These alloys were vacuum induction melted and cast into ingots of 10 kg respectively. And then they were hot-forged to 30 mm square bars and annealed.

Oxidation tests were carried out in air at 750-1000°C for 100-1000 hours. Columnar test specimens of 10 mm in diameter and 20 mm in length were used for oxidation tests. Oxidation weight gains without exfoliated scale and weights of exfoliated scale were measured. Contact resistance of plate specimens with contact area of 10 mm square and 5 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 of 5 mm in diameter and 19.5 mm in length was measured using a thermal dilatometer from 30°C to 1000°C.

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

| Alloy   | C  | Si | Mn | Ni | Cr | Al | Others | Fe   | CTE30-1000°C (x10^-6/C) |
|--------|----|----|----|----|----|----|--------|------|------------------------|
| 600    | 0.03 | 0.19 | 0.42 | bal. | 16.18 | 0.20 | Ti=0.33 | 8.96 | 16.7                   |
| FeCrAl | 0.06 | 0.49 | 0.60 | 0.21 | 19.78 | 3.53 | Ti=0.33 | bal. | -                      |
| 430    | 0.02 | 0.40 | 0.49 | 0.25 | 15.83 | 0.19 | -       | bal. | 13.0                   |
| FeCr-1 | 0.05 | 0.39 | 0.51 | 0.25 | 19.24 | 0.14 | Ti=0.50 | bal. | 13.0                   |
| FeCr-2 | 0.02 | 0.40 | 0.55 | 0.23 | 22.03 | 0.13 | Ti=0.51 | bal. | 13.0                   |
| FeCr-3 | 0.03 | 0.38 | 0.55 | 0.25 | 25.75 | 0.16 | Ti=0.54 | bal. | 13.0                   |
| FeCr-4 | 0.02 | 0.40 | 0.50 | 0.27 | 21.93 | 0.22 | Y=0.1   | bal. | -                      |
| FeCr-5 | 0.02 | 0.40 | 0.50 | 0.23 | 21.74 | 0.18 | Ce=0.02 | bal. | -                      |
| ZMG232 | 0.02 | 0.40 | 0.50 | 0.26 | 21.97 | 0.21 | Zr=0.22, La=0.04 | bal. | 12.8                   |

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

Results and Discussion

Figure 1 shows oxidation resistance and electrical contact resistance of specimens in air at 1000°C for 100 hours. FeCrAl had the best oxidation resistance of all of the specimens tested in this study, although it had very high contact resistance since FeCrAl forms Al rich oxide layer on the surface, with very low electrical conductivity at elevated temperature. 430 alloy had the worst oxidation resistance at 1000°C. Increase of Cr content and addition of Ti decrease weight of exfoliated scale, but oxidation resistance of alloys with Ti and high Cr is not always sufficient. Fe - 22% Cr alloy with small additions...
of Y, Ce, or both of Zr and La respectively has small oxidation weight gain and no exfoliated scale. Furthermore, Fe-Cr alloys with a small amount of Al, FeCr-1 - FeCr-5, and ZMG232, indicate very low contact resistance comparable to Alloy 600 because they form Cr rich oxide layer on the surface, which has enough electrical conductivity at elevated temperature. Oxidation resistance was also evaluated in the condition of 1000°C for 1000 hours in air (1) and this result indicated that only ZMG232 with La and Zr had no exfoliated scale. From these results, ZMG232, which is Fe-22%Cr ferritic alloy with small addition of Zr and La, was selected for interconnector.

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

Figure 2 shows the oxidation resistance and electrical contact resistance of ZMG232 and 430 alloy in air at 750 and 1000°C. Oxidation weight gain at 750°C for ZMG232 is almost the same as that in 430 alloy and no exfoliation of scales occurred in both alloys. On the other hand, electrical contact resistance of ZMG232 at 750 and 1000°C remains low and is much lower than that of 430 alloy. It is supposed that it is because the scales of both alloys consist mainly of chromia but the scale on ZMG232 is more adhesive and denser than that of 430 alloy.

Figure 3 shows the mean coefficient of thermal expansion from 30°C up to 1000°C. Mean coefficient of thermal expansion of ZMG232, is the as same as that of 430 alloy, but a little larger than that of YSZ, and much smaller than that of Alloy 600.
Since ZMG232 containing Zr and La indicates much better oxidation resistance and electrical contact resistance than 430 alloy and coefficient of thermal expansion close to YSZ, it is considered suitable for interconnector materials in planar-type SOFC system.

**Figure 2.** Results of oxidation tests in air and electrical contact resistance at 750 and 1000°C.

**Figure 3.** Mean coefficient of thermal expansion of ZMG232 compared with 430 alloy, Alloy 600 and YSZ.
DEVELOPMENT OF OXIDATION RESISTANT Ni-BASED ALLOY FOR CAPSULING FOR GAS SEPARATION

Oxidation resistant alloys will be used in SOFC system besides interconnector since SOFCs are operated at high temperatures in the range of about 700-1000°C. Furthermore, good mechanical properties are required for oxidation resistant alloys for SOFC because SOFC components are subjected to thermal cycles during operation. In this study the effect of small additions of alloying elements on oxidation resistance of conventional Ni-based alloy and of Alloy 600 in air at about 1000°C was investigated, in order to develop a new alloy with good oxidation resistance and mechanical properties for applications subjected to thermal cycles.

Experimental Procedures

Ni-based alloys with various amounts of added elements such as Cr, Al, Zr, and La were prepared. Table 2 shows chemical compositions used in this study. These alloys were vacuum induction melted and cast into ingots of 10 kg respectively. And then they were hot-forged and solution treated for oxidation test pieces. Hot-forged specimens were also cold rolled to sheet of 0.5 mm thick and solution treated for tensile test pieces. Oxidation tests were carried out in air at 1000°C for 100 hours. Columnar test specimens of 10 mm in diameter and 20 mm in length were used for oxidation tests. Oxidation weight gains without exfoliated scale, weights of exfoliated scale, and thickness of oxide layer were measured. Tensile test pieces (10 mm wide and 50 mm long in total, 5 mm wide and 20 mm long in gauge section) of ASL528 taken from the sheet were exposed at 700-1000°C for 100 hours 5 times in air and in H2/H2O (1/1) atmosphere, respectively, and oxidation weight gain was measured every 100 hours in air, and tensile test was carried out at room temperature after 500 hours in air and in H2/H2O.

Table 2. Chemical compositions of alloys used in this study (mass %).

| Alloy  | C    | Si   | Mn   | Ni   | Cr | Al | Fe | Others |
|-------|------|------|------|------|----|----|----|--------|
| Alloy 600 | 0.004 | 0.31 | 0.3  | bal. | 16.0 | 0.2 | 7.5 | 0.4Ti  |
| ASL528 | 0.030 | 0.30 | 0.27 | bal. | 16.0 | 0.2 | 7.1 | La + Zr |
| 600+Cr | 0.006 | 0.31 | 0.28 | bal. | 21.9 | 0.2 | 7.1 | -      |
| 600+Al | 0.005 | 0.30 | 0.27 | bal. | 16.0 | 3.4 | 7.2 | -      |

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

Results and Discussions

Oxidation resistance in air at 1000°C for 100 hours is shown in Figure 4. ASL528, 600 + Cr, and 600 + Al have much smaller oxidation weight gain and thinner oxide layer than Alloy 600, although all specimens except for ASL528 have exfoliated scale. It is found that small additions of La and Zr suppress the growth of oxide layer and improve the adhesion of oxide layer significantly. Tensile strength and elongation of ASL528 at room temperature are shown in Figure 5. Tensile strength and elongation remain almost constant when the exposure temperature increases from 700 to 1000°C both in air and in H2/H2O. These results, especially good elongation at room temperature after exposure at
700–1000°C, indicate that ASL528 has good heat crack resistance. In fact, the grain boundary oxidation and cracks along the grain boundary oxides near fracture section after tensile test were very small and at most about 20-30 μm deep after being at 1000°C for 500 hours both in air and in H2/H2O. Oxidation resistance of ASL528 at 700-1000°C for 100-500 hours in air is shown in Figure 6. Figure 6 indicates ASL528 has good oxidation resistance at temperatures in the range of 700-1000°C and the oxidation weight gain increases parabolically with time.

It is supposed that ASL528 is suitable for a metallic material applied for SOFC components, which are subjected to thermal cycles during operation since it has good oxidation resistance and heat crack resistance.

![Figure 4. Results of oxidation tests in air at 1000°C for 100 hours.](image)

![Figure 5. Tensile properties of ASL528 at RT after exposure at 700-1000°C for 500 hours in air and in H2/H2O.](image)
Pure Ni is usually used for current collection because of its good oxidation resistance in fuel gas atmosphere. But pure Ni has much higher coefficient of thermal expansion than ceramics such as YSZ. With regard to thermal expansion compatibility, an alloy with a lower thermal expansion will be a choice to replace pure Ni. Fe-Ni-Co low thermal expansion alloy is a candidate material for this application. But conventional alloys have low thermal expansion only below at most 400°C. In this study thermal expansion properties of Fe-Ni-Co alloys with various amounts of Ni and Co contents were investigated in order to optimize the whole thermal expansion behavior from room temperature to about 1000°C.

Experimental Procedures

Fe-Ni-Co alloys with various contents of Ni and Co were prepared. These alloys were vacuum induction melted and cast into ingots of 10 kg respectively. And then they were hot-forged and annealed. Thermal expansion curves of columnar specimens of 5 mm in diameter and 19.5 mm in length were measured using a thermal dilatometer from 30°C to 1000°C. Schematic thermal expansion curves of Fe-Ni-Co alloy and YSZ are shown in Figure 7. The hatched area surrounded by thermal expansion curves of Fe-Ni-Co alloy and YSZ is measured. To get a thermal expansion curve, which is the closest to that of YSZ, this area should be a minimum.

Results and Discussions

Fe-Ni-Co ternary phase diagram describing areas surrounded by thermal expansion curves of Fe-Ni-Co alloy and YSZ are shown in Figure 8. The measured area depends on Ni and Co contents significantly, and that this area is a minimum where Ni+Co is about 60 mass % and Ni content is lower than about 30 mass %. The best chemical composition of Fe-27.5Ni-32.5Co is selected from Figure 8. Thermal expansion curve of developed
alloy is shown in Figure 9, along with that of YSZ and pure Ni. The developed Fe-27.5Ni-32.5Co alloy has thermal expansion curve compatible with YSZ within the whole temperature range of 30-1000°C and it is much lower than that of pure Ni. Mean coefficient of thermal expansion of developed alloy and YSZ is 11.8x10^-6/C and 11x10^-6/C respectively and that of pure Ni is about 17x10^-6/C.

Thermal expansion behavior of the developed alloy matches very well with that of YSZ and hence this alloy is supposed to be suitable for current collector of SOFC. Evaluation of oxidation resistance in fuel gas atmosphere will be necessary.

![Figure 7. Schematic thermal expansion curves of Fe-Ni-Co alloy and YSZ and area surrounded by curves of Fe-Ni-Co alloy and YSZ.](image)

![Figure 8. Area surrounded by thermal expansion curves of Fe-Ni-Co alloy and YSZ described on the Fe-Ni-Co ternary phase diagram.](image)
CONCLUSIONS

Three kinds of new alloys such as Fe-Cr ferritic interconnector alloy, ZMG232, oxidation resistant Ni-based alloy for capsule for gas separation, ASL528, and low thermal expansion Fe-Ni-Co alloy compatible with YSZ for current collector were developed. Our metallic material technology should contribute to commercialization of SOFC technology in the near future.

REFERENCE

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