ELECTROLYTIC DEPOSITION OF OXIDE COATINGS FOR SOLID OXIDE FUEL CELL INTERCONNECTS

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ABSTRACT

Composite yttria-silver coatings and praseodymia coatings were applied to 430 stainless steel by cathodic electrolytic deposition. Crack-free 0.5-1 µm thick coatings were obtained from chloride salts in aqueous or water-ethanol solutions. The electrical conductivity and oxidation behavior at 750°C of coated and uncoated samples were investigated. Coated samples oxidized for 24 h developed a scale thickness of approximately 1 µm and an area-specific resistance (ASR) of less than 0.1 ohm-cm², compared to uncoated samples which had a scale thickness near 1.3 µm and an ASR near 0.2 ohm-cm². The scale growth followed parabolic oxidation kinetics up to 168 h, spalling of the scale was evident. Another group of coated samples was initially heated in intermittent steps to 750°C over a period of hours. These samples showed better oxidation performance with good scale adhesion and had a scale thickness of less than 0.1 µm and an ASR of less than 0.1 ohm-cm².

INTRODUCTION

It is common practice to use ferritic stainless steels as interconnect materials due to matching coefficient of thermal expansion with the electrolyte [1-3]. However, chromia-forming alloys form volatile Cr(VI) species under SOFC operating environments [4-5]. The reduction of the Cr(VI) species to Cr₂O₃ results in poisoning of the triple phase boundary and deterioration of cell performance. Moreover, the ASR (area-specific resistance) of the interconnects and oxide electrodes approaches the tolerance limit for practical SOFCs with minimal oxidation [6]. Therefore, a protective coating for the metallic interconnect, which is also electronically conductive, non-volatile and chemically compatible with other cell components, is the most direct solution to the problem.

Many investigations have shown that the addition of rare earth elements to Cr-containing alloys either in the bulk or on the surface can significantly decrease the growth rate of Cr oxide films [7-8]. In this work, yttria-silver coatings and praseodymia coatings have been applied by cathodic electrolytic deposition. We have found that oxides of Y and Pr react with Cr oxide to produce perovskites. This appears to be a promising strategy to reduce the evaporation of Cr species and subsequent degradation of cell performance.

EXPERIMENTAL

The alloy samples were commercial 430 stainless steel with a composition of Fe-17% Cr,
0.6% Si, 0.7% Mn (in wt%) and sample dimension of $1 \times 1 \times 0.1$ cm.

For yttria-silver coatings, electrolytic deposition was performed from mixed $Y(NO_3)_3$ and $AgNO_3$ (commercial purity) aqueous solutions in galvanostatic mode. Different molar ratios of $Y(NO_3)_3$ to $AgNO_3$ were tested. Multilayer deposits were formed by repeated deposition steps. For deposition of praseodymia, commercial grade $PrCl_3$ and poly (dimethyldiallylammonium chloride) polymer binder (PDDA, average $M_w = 400,000-500,000$, 20%), were used as starting materials. Electrolytic deposition was performed from ethanol solutions of $PrCl_3$ in galvanostatic mode. In both cases, both sides of the sample were coated.

In order to investigate the influence of heating rate on the oxidation and electrical behavior of coated samples, two heating processes were followed:

1) Continuous heating: temperature increased from room temperature to $750^\circ$ C continuously in one hour.

2) Intermittent heating: temperature was increased to $750^\circ$ C step by step, holding at $200^\circ$ C, $300^\circ$ C, $380^\circ$ C, $460^\circ$ C, $540^\circ$ C, $620^\circ$ C, $700^\circ$ C for 30 minutes.

Samples were examined after oxidation in stagnant air for 24, 168 and 744 h. After each interval, the ASR was measured at $750^\circ$ C using the four-probe method. To reduce the contact resistance, both sides of the samples were sputtered with gold film before ASR measurement. A current of 0.1 A was applied and the voltage drop across the sample was measured. After ASR measurement, the surface morphology and cross-section of the coatings were examined by a Philips 515 scanning electron microscope (SEM). The composition of the coating was analyzed by energy dispersive spectroscopy (EDS). The phase content was determined by a Bruker D8 Advanced X-ray diffractometer using Cu Ka1. Green deposits were removed from the substrate and dried at room temperature for 7 days before XRD analysis.

RESULTS AND DISCUSSION

Continuous Heating

Uncoated samples. Uncoated 430 stainless steel samples were oxidized at $750^\circ$C as standards. The ASR was near 0.2 ohm·cm$^2$ after 24 h oxidation and 50.9 ohm·cm$^2$ after 168 h oxidation. The surface morphology of uncoated samples after oxidation is shown in Fig. 1. SEM observation revealed the formation of nodules on the surface; these nodules became larger and more numerous with time. The thickness of the continuous oxide scale (apart from nodules) after 24 h oxidation was 1.3 μm, and after 168 h it was 3.9 μm. XRD revealed that the nodules were $(Fe,Cr)_2O_3$ corundum (Fig. 2). Apparently, the growth of the nodules on the surface damages the integrity of the oxide scale and reduces its protective ability. It is evident that 430 stainless steel cannot effectively protect itself from severe oxidation at $750^\circ$C. The formation of the oxide nodules resulted in a large increase of electrical resistance of uncoated samples.

Yttria-Silver coated samples. The ASR of the yttria-silver coated samples after oxidation at $750^\circ$C is shown in Fig. 3. The ASR of coated samples was lower by half after 24 h and by a factor of 500 after 168 h oxidation, compared with uncoated samples. The surface
morphology of the coated samples was nearly the same after different oxidation time. The sample surface was covered with worm-like ridges (Fig. 4), a phenomenon called convolution morphology [9,10]. The white speckles on the surface are gold which is due to the gold sputtering. XRD analysis showed no Y₂O₃ on the surface after oxidation, only chromium oxide, spinel and perovskite (Fig. 6). As the difference among the diffraction angles of Ag, Au and the BCC substrate alloy peaks is very small, it is impossible to distinguish between them. SEM photos of the cross-section show that these oxide scales are continuous and dense (Fig. 5). However, in some regions, they buckled from the surface, leaving a gap between the scale and the substrate (Fig. 5b). It can be hypothesized that there is some ductility of the oxide scale to conform to the surface because the oxide scales are still continuous even when they buckle up from the surface. The thickness of oxide scales after oxidation for 24 h averaged 1.1 μm, and the thickness of oxide scales after oxidation for 168 h was about 1.4 μm. The growth rate of the oxide scales of coated samples is 2.78 times slower than uncoated samples.

SEM photos show no evidence of large oxide nodules on the surface. It seems that yttrium on the surface prevents the formation of porous oxides and facilitates the formation of continuous and dense oxide scales. According to XRD results, it is clearly not the Y₂O₃-Ag coating itself that provides the protection for the substrate, but rather the formation of continuous and dense oxide scales on the surface that impede the further severe oxidation of the substrate. This might be the reason why the electrical resistance of coated samples showed little change when oxidation time extended from 24 hours to 168 h.

**Praseodymia coated samples.** The ASR of the praseodymia coated samples after oxidation at 750°C is shown in fig. 7. Fig. 8 shows that there are also many ridges formed on the surface of samples after oxidation. Cross-section images show that the coating is continuous (fig. 9), and in some regions, the coating was detached from the surface. From the SEM photos, it appears that the oxide scale has remarkable ductility that allows buckling instead of cracking, maintaining continuous coverage of the substrate. The thickness of the oxide scale after 24 h oxidation averaged 0.7 μm, and 1.2 μm after 168 h oxidation. XRD patterns (fig. 10) show that the coating is composed of PrCrO₃, corundum and spinel phase after 168 hours oxidation. It is clear that Pr oxide reacts with Cr oxide to produce PrCrO₃ during high temperature oxidation. It is evident that formation of these kinds of oxide scale effectively decreases the oxidation rate and ASR of coated samples compared with uncoated samples.

However, whether the praseodymia coated samples or yttria-silver coated samples were heavily oxidized through continuous initial heat up after 744 h oxidation, and their ASR can not be obtained.

**Intermittent Heating**

Through intermittent initial heating (Figs. 3 and 7), the resulting ASR of coated samples even after 744 h oxidation was lower than that of samples after 168 h oxidation at 750°C following the standard heat up. The surface of samples was smooth, and there was no evidence of convoluted morphology on both kinds of coated samples (fig. 11 and 12). The crystals formed on the surface were found to be Cr oxide. The thickness of oxide scales on yttria-silver coated samples averaged 0.7 μm and the thickness of oxide scales on praseodymia coated samples averaged 1.2 μm after 744 h. Compared with the coated samples after 168 h oxidation prepared by continuous initial heat up, the thickness of oxide...
scales did not change significantly. It can be concluded that initial heating sequence greatly influences the oxide scale morphology and electrical behavior of the coated samples. Not only the convolution morphology but also the buckling of the oxide scales from the substrate can be totally avoided even after 744 h oxidation by the intermittent heat up. It is clear that intermittent heating method not only improves coating adhesion greatly, but also decreases the growth rate of the oxide scales.

CONCLUSIONS

Rare earth oxide coatings were obtained through cathodic electrolytic deposition. The coatings reacted with the growing chromium oxide scale at 750°C to produce the perovskites phase, which is predicted to suppress the evaporation of volatile Cr-species. It was demonstrated that the coatings helped to form continuous and dense oxide scales on the sample surface that decrease the oxidation rate and the ASR of coated samples, compared with that of uncoated samples.

Heating process has a great influence on the oxidation and electrical behavior of coated samples. The results show that intermittent initial heating can prevent formation of convolution morphology, which increases the adhesion of oxide scales and the oxidation protection of the coated samples. The ASR (0.09 ohm·cm²) of coated samples after 744 h oxidation prepared through intermittent heat up was nearly the same as that (average 0.1 ohm·cm²) of coated samples after 168 h oxidation by continuous heat up. The rare earth oxide coatings are thus promising for protecting metallic interconnects at intermediate temperatures.

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Figure 1. Surface morphology of uncoated samples after oxidation at 750°C.

(a) After 24 hour oxidation  
(b) After 168 hour oxidation

Figure 2 XRD pattern of uncoated samples after oxidation at 750°C for 168 h.

Figure 3. The influence of oxidation on the ASR of yttria-silver coated samples. The data after 744 h oxidation was obtained through initial intermittent heat up.
Figure 4. Surface morphology of yttria-silver coated sample after 168 h oxidation.

Figure 5. Cross-section of yttria-silver coated samples after oxidation for 168 h.

Figure 6. XRD pattern of yttria-silver coated samples after 168 h oxidation.
Figure 7. The influence of pre-oxidation on the ASR of praseodymia coated samples. The data after 744 h oxidation was obtained through initial intermittent heat up.

Figure 8. Surface morphology of praseodymia coated samples after 168 h oxidation.

Figure 9. Cross-section image of praseodymia coated samples after 168 h oxidation.
Figure 10. XRD pattern of praseodymia coated samples after 168 h oxidation.

Figure 11. Surface morphology of yttria-silver coated sample after 744 h oxidation.

Figure 12. Surface morphology of praseodymia coated sample after 744 h oxidation.