ADHESION BEHAVIOUR OF THERMAL OXIDE SCALES GROWN ON FERRITIC STAINLESS STEELS PROPOSED AS INTERCONNECTS IN SOFCs

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ABSTRACT

Three grades of ferritic stainless steel proposed as interconnects in SOFCs, AISI 441, AISI 444 and Crofer 22 APU, were oxidized in dry air (cathode environment) at a working temperature of 800°C. The adhesion of oxide scales grown on these alloys was investigated by an in situ tensile test, allowing the continuous observation of surface failure. Adhesion energy was quantified to assess the resistance to spallation. In the range of oxide thickness from 0.5 to 1.2 \(\mu m\), values in the order of 10 to 100 \(J.m^{-2}\) were obtained with a general trend of adhesion energy decrease with increasing oxide thickness. Comparison of the grades showed that adhesion energy of Crofer 22 APU was slightly higher than that of AISI 441 and AISI 444, due to the presence of lanthanum as a minor addition.

INTRODUCTION

Because solid oxide fuel cells (SOFCs) have a working temperature of 650° to 900°C, stainless steels have emerged as competitive materials to be used as SOFC interconnects. However, the high-temperature lifetime of Cr-containing alloys is often limited by oxide scale spallation, which would be highly detrimental in such an application. Adhesion of oxide scales on alloys is usually assessed by the qualitative consideration of an oxide/metal interface or by direct measurement of spallation in service. Only a few testing methods have been developed to determine the interfacial fracture toughness of oxide scales such as the indentation test (1) or the inverted blister test (2,3). However, the first method is not really precise and the second needs thin metal specimens and a gluing procedure that does not allow measurements of very adhesive scales. The present work uses the in situ tensile test, allowing continuous observation of surface spallation during continuous applied strain. The adhesion behavior of oxide scales on interconnect alloys under this test was investigated, leading to the quantitative assessment of scale adhesion in term of adhesion energy.

EXPERIMENTAL

AISI 441 and AISI 444 stainless steels were supplied by Arcelor as sheets 2 and 1.2 mm thick, respectively. Crofer 22 APU was supplied by Thyssen Krupp VDM with a
thickness of 1 mm. Their chemical composition is reported in Table 1. It may be noted that the Cr content of AISI 441 and AISI 444 is about 18%, whereas it is around 23% for Crofer 22 APU. These alloys contain different minor elements, Ti and Nb for AISI 441, Ti and Mo for AISI 444, and Ti and La for Crofer 22 APU.

Table 1. Chemical composition of the studied interconnect alloys.

| Grade      | Cr   | Ni  | C  | Mn  | Si  | Al  | Ti  | Nb | Mo | Other |
|------------|------|-----|----|-----|-----|-----|-----|----|----|-------|
| AISI 441   | 17.8 | 0.10| 0.01| 0.24| 0.6 | 0.006| 0.13| 0.55| 0.01|       |
| AISI 444   | 17.7 | 0.9 | 0.4 | 0.22| 0.26| 2.00 |     |    |    |       |
| Crofer 22 APU | 22.8 | 0.16| 0.05| 0.45| 0.1 | 0.13 | 0.08| 0.01| La  |       |

For oxidation kinetics, specimens were prepared to the dimensions $2 \times 2$ mm$^2$. They were polished up to the 1200 SiC grit, rinsed in distilled water and alcohol, and finally dried in air. They were then oxidized at 800°C for times up to 500 hr in synthetic air with a linear flow rate of 1 mm/s$^{-1}$ in the laboratory tube.

For adhesion measurements, specimens were prepared by electro-erosion with special shape fitting to the tensile machine, their main axis parallel to the rolling direction of the sheet. The surface was prepared and oxidized by the same methods described above. The final pass of polishing was chosen parallel to the main sample axis. The oxidized specimen was then placed in the tensile machine sitting in the SEM chamber, and a constant strain rate was applied. The oxide surface was observed with backscattered electrons during strain, and regular pictures were captured at a 500X magnification.

RESULTS AND DISCUSSION

Figure 1 illustrates the mass gains of interconnect alloys oxidized in synthetic air at 800°C up to 500 hours. This plot exhibits parabolic behavior, with a higher parabolic rate constant for Crofer 22 APU than for AISI 444 and AISI 441. From mass gains, oxide thicknesses were calculated assuming pure chromia.

Figure 1. Oxidation kinetics of interconnect alloys oxidized in 1 atm synthetic air at 800°C; continuous lines are the best parabolic fits.
After oxidation, oxide scales exhibited room temperature residual stress, a combination of growth and thermal stresses. Because the stress value was required to quantify the adhesion energy by the tensile test, Raman spectroscopy was used to quantify stress in the scales under study (4). Results for all grades are reported in Figure 2. For each specimen, the measurement was repeated five times, and the values shown in the graph are averages of the range of the maximum and minimum stress measured. It appeared that the residual stress increased as a function of oxide thickness for very thin scales and tended to a constant compressive stress of about 1.75 GPa from oxide thickness of 0.75 μm, as already observed for ferritic stainless steels (5).

![Figure 2. Compressive residual stress in oxide scales on interconnect alloys versus oxide thickness; oxidation in 1 atm synthetic air at 800°C.](image)

The evolution of surface failure during the tensile test was captured in function of the imposed strain ($ε$). Figure 3 shows examples of such observations on scales grown in synthetic air at 800°C for 200 hours. For the three investigated grades, the first observation was regular transverse cracking perpendicular the strain axis, appearing after a given imposed strain. For oxide scales on AISI 441 and AISI 444, spallation was observed for higher strains, occurring on non-selective places over the entire zone of observation. The spalled fraction of surface area typically increased with increasing imposed strain. For Crofer 22 APU, it appeared that the major oxide failure was mainly transverse cracking, with very few spallations found only on lanthanum oxide nodules.

The critical strain initiating the first spallation ($ε_{in}$) was first plotted to qualitatively assess the spallation resistance of oxide scales. Figure 4 depicts $ε_{in}$ as a function of oxide thickness. It appeared that $ε_{in}$ decreased with increased oxide thickness, and the trend for scales on AISI 441 and AISI 444 were identical. Crofer 22 APU exhibited a different behavior, with no spallation for the thinnest scales and high critical strain values (3.3–3.5%) for the 1.1 μm oxide scales.

From these results, adhesion energy was quantitatively calculated using the theoretical framework recently described (6,7). In brief, it considers that energy was first stored along tensile and transverse directions of the oxide scale during growth and cool-down. After the tensile test was launched, stored energy was modified, first due to elastic deformation of the oxide scale, from the onset of strain to the strain at limit of elasticity of substrate. During this period, the oxide stored energy along the tensile direction first...
decreased, then increased, whereas it continuously increased along the transverse direction. After this stage, the oxide was still considered elastic, whereas the metal deformed plastically. The energy stored in this last stage was due to the elastic deformation of oxide from the beginning of plastic deformation of the substrate until the first spallation took place. In the case where the first spall occurred at the same strain that transverse cracking, both energy contributions were taken into account. In the case
where transverse cracking occurred before the first spallation, the stress in the loading direction was considered fully relaxed and the stored energy due to the stress in this direction totally released. The driving force for spallation was therefore oxide compressive loading in the transverse direction. Using the values of residual stress (from Figure 2) of elastic constants of metal and oxide and of metal elasticity (0.15%), the total elastic energy stored in oxide at the first spallation was then derived. Adhesion energy was finally quantified by multiplying the total stored energy by the oxide thickness.

Figure 5 exhibits the derived adhesion energy as a function of oxide thickness. The open symbols in the graph indicate that no spallation was observed during the test. For these situations, a minimum adhesion energy was calculated using the value of strain at the finish of the test. Adhesion energy was found to decrease with increased oxide thickness. Oxide scales on the two AISI grades exhibited similar adhesion energies, whereas scales on Crofer 22 APU seemed to be rather higher. This tendency was not as marked as the strain at spallation onset ($\varepsilon_{sn}$). The higher adhesion of the oxides on Crofer 22 APU was the probable result of the presence of reactive element lanthanum in this material, well known to improve scale adhesion as are many other reactive elements (8,9).

![Figure 4](image_url) Figure 4. Critical strain initiating first spallation as a function of oxide thickness; specimens oxidized in synthetic air at 800°C.

![Figure 5](image_url) Figure 5. Adhesion energy of oxide scales on interconnect alloys oxidized in synthetic air at 800°C; open symbols indicate minimum adhesion energy.
CONCLUSIONS

The in situ tensile test was applied to investigate the adhesion behavior of oxide scales grown at 800°C on interconnect alloys in dry air, representative of the cathodic side of interconnects. The resistance to spallation was first qualitatively assessed by the strain that initiated the first spallation ($\epsilon_{spall}$). The resistance to spallation of Crofer 22 APU was concluded to be higher than that of AISI 441 and AISI 444, whereas the resistance to spallation of both conventional alloys was nearly the same. The adhesion energy at $\epsilon_{spall}$ was further quantified. In the range of oxide thickness from 0.5 to 1.2 µm, adhesion values in the order of 10 to 100 J/m² were measured. The tendency of scale adherence considered by the adhesion energy was congruent to the spallation assessment by $\epsilon_{spall}$ but less marked.

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