



Chromia scale adhesion on 430 stainless steel: Effect of different surface treatments

I. Belogolovsky, P.Y. Hou*, C.P. Jacobson, S.J. Visco

Materials Sciences Division, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, CA 94720, United States

ARTICLE INFO

Article history:

Received 23 February 2008
Received in revised form 21 March 2008
Accepted 25 March 2008
Available online 8 April 2008

Keywords:

Oxidation
Reactive element
Oxide–metal interface
Porosity

ABSTRACT

In the context of solid oxide fuel cell (SOFC) applications, the adhesion strength and failure location of chromia scale that developed on 430 stainless steel after various surface modifications prior to oxidations between 600 and 800 °C were evaluated. Results demonstrated that the tensile strength and nature of adhesion of the oxide/alloy interface on 430 stainless steel can be compromised by polishing, but can be improved by reducing surface impurities, increasing surface roughness and applying a coating that contains a reactive element, such as Y-nitrate. Optimally, a combination of firing in a reducing atmosphere and applying a thin yttrium nitrate coating was found to be especially effective. These findings identify surface modification techniques that improve scale adhesion for Cr₂O₃-forming metallic interconnects whether independently or beneath a protective coating.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Over the last decade, much research has focused on introducing metallic components into ceramic-based solid oxide fuel cells (SOFCs) to cut production costs so that they can be a viable source of clean energy in future markets [1,2]. Many interconnect alloys have been studied, and it has been shown repeatedly that ferritic stainless steels that form chromia on their surface are the best option, because of the relatively high conductivity and slow growth of the chromium oxide, Cr₂O₃, the close match of the thermal expansion coefficient of the steel with that of other cell components, and, vitally, low cost. However, when metallic parts are used, SOFC must be operated at an intermediate temperature range, about 600–800 °C; on the one hand, to ensure sufficient conductivity of the Cr₂O₃ layer, and on the other, to avoid faster growth of Cr₂O₃ and excessive evaporation of Cr containing species at higher temperatures. Chromium is known to deposit onto and poison the cathode of the cell and therefore degrade cell performance, and this problem is the biggest obstacle with Cr₂O₃-forming metallic interconnects [3,4]. Protective coatings have been investigated to combat Cr evaporation and some success has been achieved [5,6]. Some of these coatings are even capable of reducing the chromia growth rate and enhancing the scale conductivity [6].

While maintaining a slow-growing, highly conductive Cr₂O₃ scale with low evaporation rates are vital, it is also important that

the scale remain adherent to the alloy especially under thermal cycling conditions. A loss in adhesion means a loss in contact, and consequently, a reduction in conductivity. Extensive delamination and spallation of Cr₂O₃ scales due to poor adhesion is known to take place during cooling under the compressive thermal stress that develops from the thermal expansion mismatch between the Cr₂O₃ and the alloy [7,8]. When the oxide detached areas are exposed to high temperatures again, they oxidize much faster, since oxidation rate scales parabolically with oxide thickness. Repeated delamination and re-oxidation can eventually deplete the alloy near surface Cr content and cause breakaway oxidation, where fast growing Fe-rich oxides form locally and disrupt the SOFC integrity. It is therefore imperative that the adhesion property of a potential SOFC metallic interconnect be investigated, and ways of improving it be evaluated.

Application of surface coatings containing a reactive element, such as Y, Hf or Ce, has been proven to improve Cr₂O₃ scale adhesion, but mainly at temperatures greater than 900 °C [9,10]. Surface treatments, particularly those that remove alloy or surface impurities, have also been shown to improve oxide scale adhesion [11,12], although these results were often obtained from Al₂O₃-forming alloys. The purpose of this work is to research the effects of several common surface treatments, including those routinely used by industry, on a 430 ferritic stainless steel interconnect material, in order to find the best surface preparation technique as an optimizing precursor to combat Cr₂O₃ scale adhesion. Seven surface treatments with or without a coating were applied to 430 stainless steel substrates. The steel contains 16–18 wt.% Cr and oxidizes to form a complete Cr₂O₃ layer [13]. Long-term oxidation effects on scale adhesion of surface-treated and untreated sam-

* Corresponding author. Tel.: +1 510 486 5560; fax: +1 510 486 4881.
E-mail address: pyhou@lbl.gov (P.Y. Hou).

Table 1
Description of sample surface treatments prior to oxidation

Untreated	As-received, surface cleaned by sonicating in acetone then rinsing in ethanol
600 grit	Polished to 600 grit on SiC paper, then cleaned in acetone and ethanol
240 grit	Polished to 240 grit on SiC paper, then cleaned in acetone and ethanol
Electropolished	As-received sample cleaned in degreasing D909 solution (mainly sodium phosphate, held at 60 °C), then placed as the anode under 7 V in 95% H ₃ PO ₄ /5% H ₂ SO ₄ at 57 °C for ~1 min; sample was immersed in D909 again to neutralize the surface acidity, then rinsed with water
Acid pickled	As-received sample cleaned in degreasing D909 solution, dipped in nitric/HF solution for ~5 min; surface was then neutralized in D909 and rinsed with water
Sandblasted	As-received sample sandblasted with air-carried glass beads; surface cleaned by blowing off excess particles
Reduced	As-received, cleaned sample heat-treated in hydrogen at 790 °C for 45 min, then furnace cooled over several minutes to room temperature
Untreated, Yttrium-nitrate	As-received, surface cleaned sample dip-coated twice with an aqueous yttrium nitrate solution (drying under a heat lamp between coats), then fired in air at 500 °C for 1 h
600 grit, Yttrium-nitrate	Surface polished to 600 grit, cleaned, and then dip-coated twice with the yttrium nitrate solution, followed by air firing at 500 °C for 1 h
Reduced, Yttrium-nitrate	Reduced sample dip-coated twice with the Y-nitrate solution; fired at 500 °C for 1 h after coating

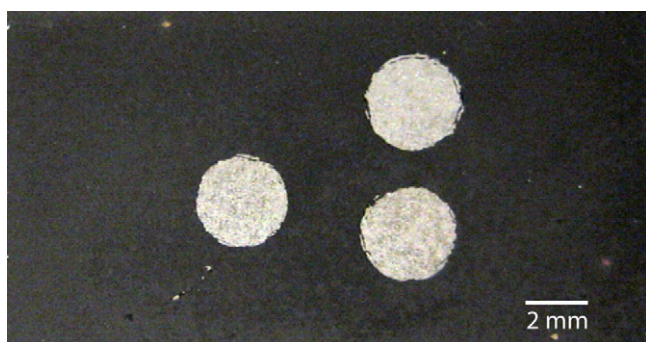


Fig. 1. Example of pull tests performed on oxidized sample, showing metallic alloy surfaces under each pull stub. The sample was polished to a 600 grit finish and then oxidized at 800 °C for 458 h.

ples were evaluated in the range of 600–800 °C SOFC operating temperatures.

2. Experimental

The substrate used for this study was a 250- μm thick 430 stainless steel sheet from Allegheny Ludlum. It is a low carbon ferritic stainless steel containing 16–18% Cr, 0.75% Ni, 0.12% C, 1% Mn and 1% Si with the balance of Fe. Samples 1 cm \times 2 cm or 2 cm \times 3 cm dimensions were cut from the sheet for testing. The as-received steel surface served as a baseline for comparing the rel-

ative effectiveness of various surface treatments. All samples were ultrasonically cleaned in acetone and then rinsed with isopropyl alcohol prior to processing.

Table 1 lists and describes all surface treatments applied to the as-received steel surface. Oxidation tests were conducted in static laboratory air. Each sample was hung from a thin wire and quickly lowered into a hot vertical furnace. At the end of the oxidation run, the sample was pulled out of the furnace to cool. Heating and cooling rates were high, with an average level greater than 300 °C min⁻¹. To examine the effect of temperature and time on spallation, samples were tested at different temperatures, ranging from 600 to 850 °C. Whether spallation had occurred during cooling was determined from optical and/or SEM observations of the oxidized surfaces. To compare the effect of surface treatments on scale adhesion, the samples were oxidized at 800 °C for 458 h, and then tested with a tensile pull tester.

Tensile testing was performed using a Quad Group Sebastian Five instrument, in a configuration illustrated elsewhere [14]. Preparation involved attaching a 2.70-mm diameter pull stub, pre-coated with an adhesive, to the sample, curing the stub-on-sample assembly in a low-temperature oven at 150 °C for 70 min, and letting the assembly cool for at least 1 h before testing. Tensile testing was achieved by vertically pulling the stub with increasing force until it detached from the sample; the force at which failure occurred was recorded. The pulled area on the sample and the stub surface were examined using an optical microscope. Sample surfaces that were shining and appeared metallic with a corresponding dark oxide layer on the stub were considered to have

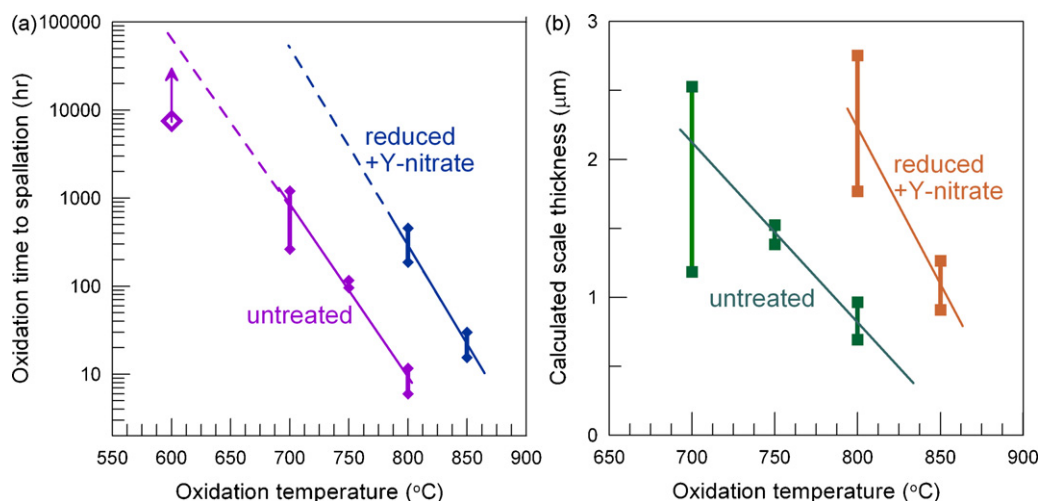


Fig. 2. Range of oxidation time (a) and scale thickness (b), at which spallation took place after isothermal oxidation and fast cooling to room temperature, for the untreated and the reduced plus yttrium nitrate coated 430 stainless steel. The untreated sample oxidized at 600 °C for the longest time did not show any spallation; the arrow points to expected longer failure time.

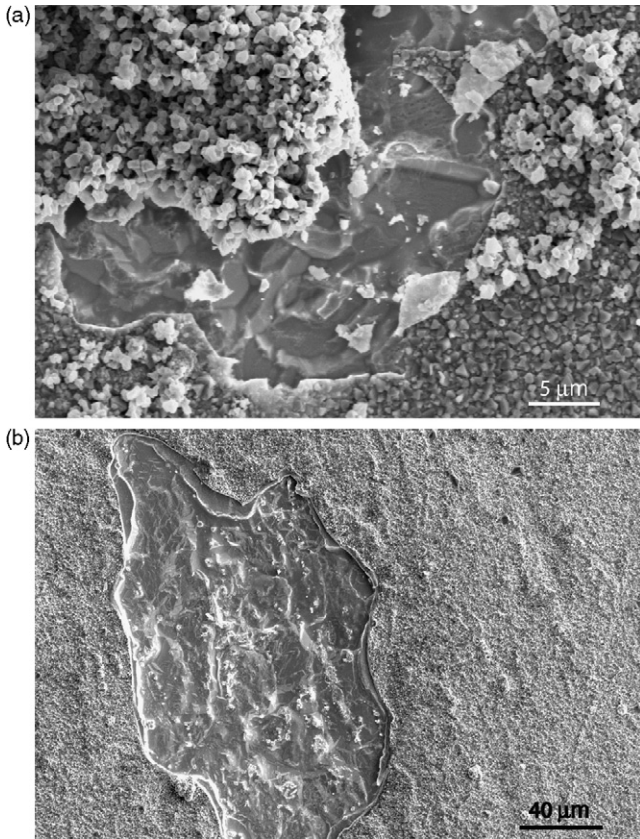


Fig. 3. SEM images of areas spalled during rapid cooling after isothermal oxidation at 800 °C for (a) 14 h and (b) 170 h.

failed at the oxide/metal interface. From the area fraction of such failure over the entire pulled area, a percentage of interfacial delamination was determined. At least three stubs were tested on each sample. Fig. 1 gives an example of a pull-tested sample, where pieces of the oxide scale were pulled away exposing alloy surfaces under the pull stubs.

3. Results and discussions

As-received, cleaned surfaces of the 430 stainless steel (identified as “untreated”) were examined for the presence of oxide

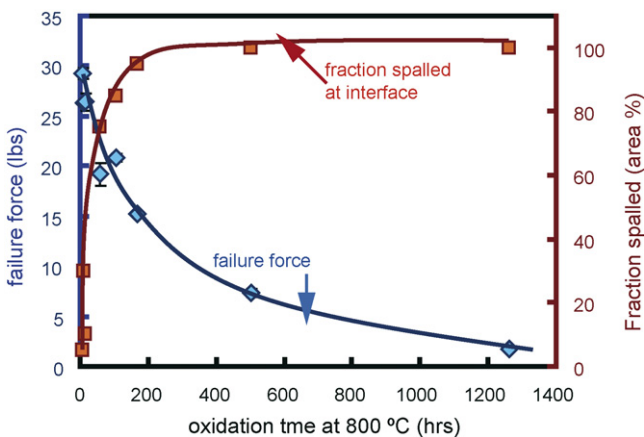


Fig. 4. Effect of oxidation time on the adhesion of oxide scales formed at 800 °C on untreated 430 alloy, evaluated by tensile pull testing.

spallation after different times of isothermal oxidation and fast cooling to room temperature. Since these examinations were made under an optical microscope, only spallation to the oxide/metal interface is noted from its high reflectivity, and the minimum detectable size (verified by SEM) was ~10 μm. Fig. 2(a) displays the range of oxidation time at each tested temperature where scale spallation would occur. The upper limit of each range represents samples whose scale showed spallation, and the lower limits are from samples without any noticeable spalls. The ranges can obviously be tightened if more samples were tested between them. The longest oxidation time at 600 °C was 7500 h, but the scale showed no spallation. Actual failure time is therefore expected to be longer, up to 60,000 h according to the trend line drawn from higher temperatures. The effect of a surface reduction followed by a thin yttrium nitrate coating will be discussed later. For the untreated, it is seen that the critical time for spallation increased by orders of magnitude with lowered oxidation temperatures. Using oxidation kinetics obtained from previous studies [6,13], equivalent oxide thicknesses were calculated assuming the scale was fully dense Cr₂O₃; results are given in Fig. 2(b). Again, the critical spallation thickness decreased with an increasing temperature, which indicates that the drastic drop in failure time at the higher temperatures seen in (a) is not a mere outcome of higher oxide growth rates. Additional factors must be involved; they may be higher thermal stresses that acted as stronger driving forces for spallation, and/or the development of more interfacial defects at higher oxidation temperatures.

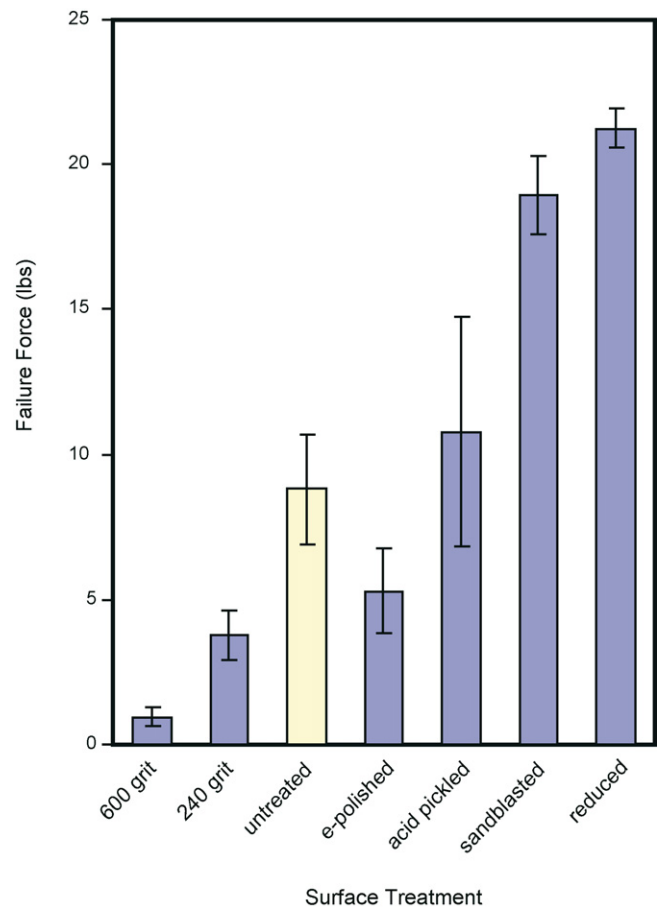


Fig. 5. Effect of surface treatments on the tensile failure load of oxide scales formed on 430 steel after 458 h oxidation at 800 °C in air.

Fig. 3 shows areas that spalled on cooling followed by oxidation at 800 °C. The sample in (a) was oxidized for 14 h, and it was close to the minimum spallation time for this temperature. The average spalled size was approximately 20 μm. Exposed alloy surface consisted of many voids with different shapes and sizes. With longer oxidation times, the spalled areas were much larger; an example is given in Fig. 3(b) after 170 h. On these alloy surfaces, individual voids were no longer distinguishable. Instead, the surface appeared smooth with evidence of thermal etching, which indicated that the oxide scale above these areas had detached from the alloy at the oxidation temperature. Cr₂O₃ scale is known to fail by buckling [15], where the critical stress for buckling is heavily dependent on internal defect sizes [16]. It seems that the mechanism for failure observed here is dominated by the formation of interfacial defects, which evidently started with interfacial voids and then extended into large delaminated areas.

To assess scale adhesion as a function of time at a given temperature, tensile pull test was used and the results for 800 °C are shown in Fig. 4. Included on the same figure is the fraction of exposed interfacial area, i.e., areas where the oxide scale was pulled off, thus showing metallic surfaces. The failure force at the critical time for spallation (12 h, see Fig. 1) was 26.3 lb s; it then quickly

dropped with longer oxidation times. The amount of interfacial failure concomitantly increased with time, approaching 100% for times longer than 200 h. Since failure from this type of pull test, where no pre-cracks were experimentally introduced before testing, is dominated by internal defects within the sample, results in Fig. 4 further demonstrate that scale failure is dictated by interfacial defects that develop with oxidation time.

Based on the results in Fig. 4, 458 h at 800 °C was chosen to be the test condition to evaluate the effectiveness of different surface treatments. These treatments, described in Table 1, were chosen to affect the stainless steel surface by cleaning or modifying it via chemical or mechanical means, and many of them are common commercial practices. None of these surface treatments significantly affected the oxidation process, since specimen weight gains from oxidation and the composition of oxide scales were similar. Relative adhesion of the oxide layer formed on different surfaces, compared by the average tensile failure forces of the pull test, is illustrated in Fig. 5. For the lower loads, less than 15 lb s, all of the failure took place at the scale/alloy interface. The two highest loads showed 70–80% failure at the interface.

It is seen from Fig. 5 that polishing to 600 grit led to the least adherent scales. SEM examinations showed that the interface was

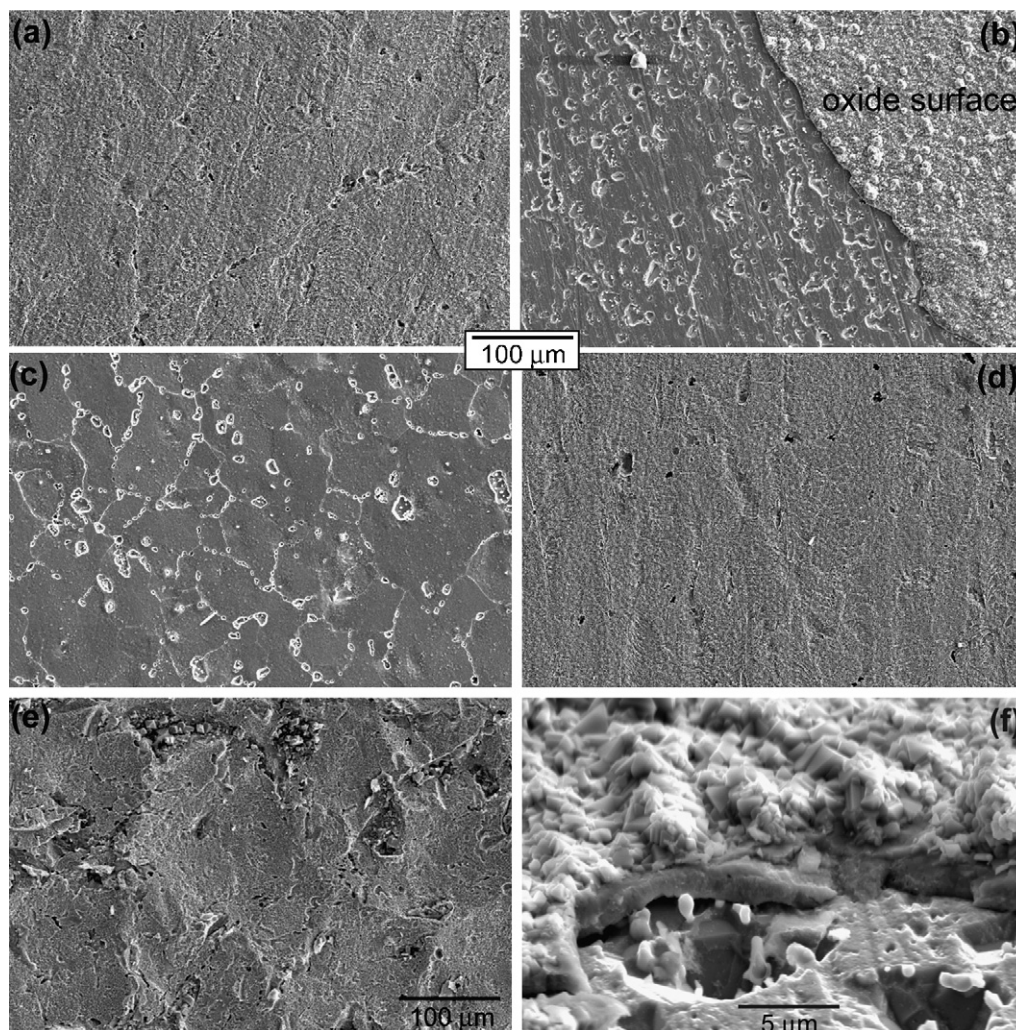


Fig. 6. SEM images of alloy surfaces after scale removal by tensile pull tests. All samples were oxidized at 800 °C in air for 458 h, but with different surface pre-treatments: (a) untreated, (b) 600-grit polished showing part of the oxide scale, (c) electropolished, (d) reduced, and (e) sandblasted. Micrographs from (a) to (e) have the same magnification; (f) is the 600-grit polished sample tilted at 60°, showing oxide buckling above an interfacial void.

heavily voided, especially along polishing marks (Fig. 6(b)). Oxides above these voids are detached and sometimes buckled (Fig. 6(f)). This many voids undoubtedly diminish scale adhesion by reducing the contact area between the oxide and the alloy and by acting as defects that assist crack initiation and propagation. Interface defects and impurities have been shown to be the most critical factors in controlling oxide scale adhesion [14,17]. The loss of contact due to void formation can also affect conductivity in a SOFC assembly. With a rougher grit, and therefore less dense polishing marks, the interfacial void density was lower, so some improvement was observed on the 240 grit polished sample, although the interface strength was still noticeably weaker than that of the untreated. Electropolishing led to preferential void formation at the alloy grain boundaries after oxidation (Fig. 6(c)), and poorer adhesion. The high density of voids may be related to preferential etching of the alloy grain boundary during the polishing process; it is also possible that the sample was slightly over-etched. Compared to the acid pickled sample, the presence of these etching voids evidently weakened interfacial strength. Acid pickling did not affect the scale adhesion much; the alloy surface after oxidation appeared similar to that of the untreated (Fig. 6(a)). All of these results again point to the detrimental effect of interfacial voids on scale adhesion. It has been demonstrated for many Al_2O_3 forming alloys [18,19] that interfacial voids preferentially nucleate along surface scratch marks, probably due to lower nucleation energies associated with the geometry of the scratch groove.

The stronger interfaces in Fig. 5 are those found on the sandblasted and the reduced surfaces, with the latter being the strongest among those tested. Note also that on these samples the percentage of area removed by the pull stub was not 100%, like the others, but between 70% and 80%. This indicates a lower failure rate at the interface, with part of the failure taking place in the oxide. These samples clearly display a higher tensile strength at the scale/alloy interface than all others. The sandblasted sample had the most tortuous interface (Fig. 6(e)) due to bombardment of the glass particles. This should have improved adhesion mechanically by making crack propagation along the interface more difficult [20]. Alloy surfaces under the pulled areas of the reduced sample appeared most uniform with the least amount of voids (Fig. 6(d)). The void density is strikingly lower compared to the polished surfaces, but only slightly less than that of the untreated. High temperature annealing in hydrogen has repeatedly been shown to improve Al_2O_3 scale adhesion [11], and for Cr_2O_3 as well [12], by removing excess sulphur in the alloy. Common surface impurities have also been shown to severely degrade Al_2O_3 scale adhesion [21]. Although reducing a sample at the current experimental condition of lower temperatures and shorter times would not be sufficient to eliminate bulk impurities, it should be able to clean the sample surface in a similar way, whereby surface non-metallic impurities are removed by reacting with hydrogen [22]. The beneficial effect observed here from the reduction treatment may therefore be related to the elimination of surface impurities, and their removal appears to be significant enough in improving scale adhesion.

Yttrium, being a reactive element, is known to improve the adhesion of Cr_2O_3 and Al_2O_3 scales [23]. Surface coatings of yttrium nitrate, after decomposition leaving a thin layer of Y_2O_3 on the sample surface, is also known to improve the oxidation resistance of Cr_2O_3 -forming alloys [10], even at temperatures relevant to SOFC operations [24,25]. For this reason, some surfaces of the 430 steel were coated with Y-nitrate and then underwent the same oxidation and pull tests. Results are shown in Fig. 7, where the combined effects of polishing, reducing and Y coating are compared. In all cases, Y coating improved the tensile strength of the interface, although the effect was very minimal on the polished sample,

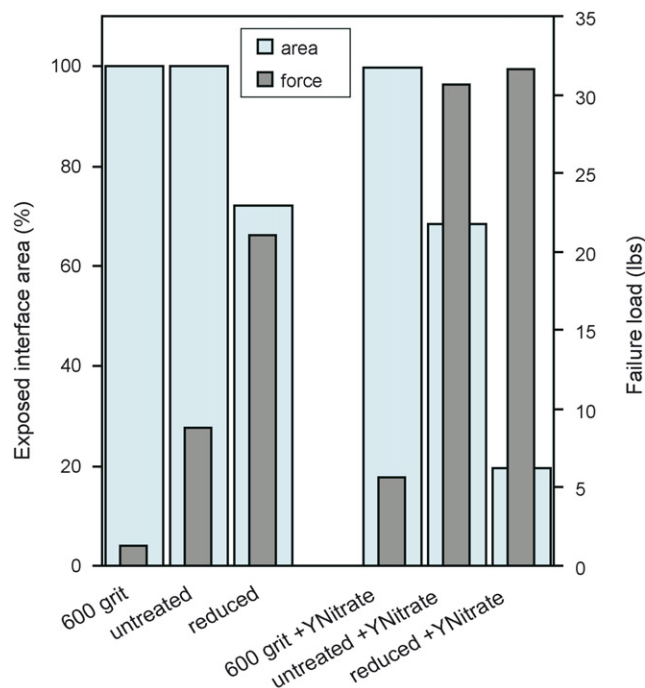


Fig. 7. Effect of Y-nitrate coating on scale adhesion for different surface-treated samples, evaluated by tensile testing after oxidation at 800°C for 458 h.

because interface porosity along scratch marks still dominated the failure. Improvements were significant on the untreated and the reduced samples, especially on the reduced one, where not only did the failure load increase, the location of failure also shifted from the interface to within the oxide. The fact that only 20% of failure took place at the interface of the reduced plus Y-nitrate treated sample indicates that this interface is the strongest tested so far. In other words, the presence of Y on the sample surface prior to oxidation enhances interfacial strength beyond the beneficial effect of surface cleaning by a H_2 -reduction treatment. Similar conclusion on the positive effect of reactive elements on scale adhesion had been made experimentally [26] and theoretically [27] for Al_2O_3 scales.

To further test the effect of combined surface reduction heat treatment and Y coating on the spallation resistance of oxide scales, different samples were oxidized at 800 and 850°C for various durations, followed by fast cooling and observation for spallation. These results are included in Fig. 2 as the “reduced + Y-nitrate” data. In accordance with the tensile pull test results shown in Fig. 7, scale adhesion was improved such that the critical time for spallation increased by over an order of magnitude. Extrapolation from the trend line indicates a time greater than 50,000 h at 700°C before the scale will show any noticeable spallation. The critical scale thickness for spallation also increased, by about a factor of two, but since Y coating reduces the oxide growth rate, with greater reduction at higher temperatures [24], the increase in critical scale thickness may diminish above 900°C .

4. Conclusion

This study has focused on determining the critical spallation thickness of chromia scale developed on 430 stainless steel and to evaluate the oxide adhesion strength after different surface treatments of the alloy. Oxidation was carried out in air between 600 and 850°C for various lengths of time. Adhesion strength was measured using a tensile test via gluing a stub onto the surface of the

oxide. The oxidation time and scale thickness at which spallation took place both increased with decreasing temperature. At 600 °C, the scale could remain adherent above 100,000 h. Primary failure mechanism in oxide spallation was the development of voids at the oxide/alloy interface. Voids formed preferentially along polishing marks or alloy grain boundaries, making polishing techniques none desirable. Sandblasting and firing in a reducing atmosphere prior to oxidation gave rise to noticeably improved scale adhesion, and both resulted in lowered interface void density. Combining the reducing treatment with a Y-nitrate surface coating further enhanced scale adhesion, shifting the failure location from the oxide/alloy interface to within the oxide.

Acknowledgement

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

References

- [1] W.J. Quadackers, J. Piron-Abellan, V. Shemet, L. Singheiser, *Mater. High Temp.* 20 (2003) 115–127.
- [2] J.W. Fergus, *Mater. Sci. Eng.* 397 (2005) 271–283.
- [3] S. Taniguchi, M. Kadowaki, H. Kawamura, T. Yasuo, Y. Akiyama, Y. Miyake, T. Saitoh, *J. Power Sources* 55 (1995) 73–79.
- [4] S.C. Paulson, V.I. Birss, *J. Electrochem. Soc.* 151 (2004) A1961–A1968.
- [5] H. Kurokawa, C.P. Jacobson, L.C. DeJonghe, S.J. Visco, *Solid State Ionics* 178 (2006) 287–296.
- [6] I. Belogolovsky, X.-D. Zhou, H. Kurokawa, P.Y. Hou, S.J. Visco, H.U. Anderson, *J. Electrochem. Soc.* 154 (2007) B976–B980.
- [7] K.P. Lillerud, P. Kofstad, *J. Electrochem. Soc.* 127 (1980) 2397–2410.
- [8] H. Hindam, D.P. Whittle, *Oxid. Met.* 18 (1982) 245–262.
- [9] D.P. Moon, M.J. Bennett, *Mater. Sci. Forum* 43 (1989) 269–298.
- [10] P.Y. Hou, J. Stringer, *Mater. Sci. Eng. A* 202 (1995) 1–10.
- [11] J.L. Smialek, D.T. Jayne, J.C. Schaeffer, W.H. Murphy, *Thin Solid Films* 235 (1994) 285–292.
- [12] P.Y. Hou, J.L. Smialek, *Scripta Met.* 33 (1995) 1409–1416.
- [13] X. Chen, P.Y. Hou, C.P. Jacobson, S.J. Visco, L.C. De Jonghe, *Solid State Ionic* 176 (2005) 425–433.
- [14] P.Y. Hou, K. Priimak, *Oxid. Met.* 63 (2005) 113–130.
- [15] P. Kofstad, A.Z. Hed, *J. Electrochem. Soc.* 116 (1969) 224–229.
- [16] A.G. Evans, G.B. Crumley, R.E. Demaray, *Oxid. Met.* 20 (1983) 193–216.
- [17] P.Y. Hou, *Mater. Sci. Forum* 369–372 (2001) 23–38.
- [18] V.K. Tolpygo, D.R. Clarke, *Mater. High Temp.* 17 (2000) 59–70.
- [19] P.Y. Hou, A.P. Paulikas, B.W. Veal, *Mater. High Temp.* 22 (2006) 373–381.
- [20] M. Schutze, in: Y. Saito, B. Onay, T. Maruyama (Eds.), *Proceeding of the Workshop on High Temperature Corrosion of Advanced Materials and Protective Coatings*, Elsevier Sci. Pub., 1992, pp. 39–49.
- [21] P.Y. Hou, C. Van Lienden, *Mater. High Temp.* 20 (2003) 357–364.
- [22] J.L. Smialek, *Oxid. Met.* 55 (2001) 75–86.
- [23] D.P. Whittle, J. Stringer, *Phil. Trans. Roy. Soc. Lond.* 295 (1980) 309–329.
- [24] K. Huang, P.Y. Hou, J.B. Goodenough, *Mater. Res. Bull.* 36 (2001) 81–95.
- [25] W. Qu, L. Jian, D.G. Ivey, J.M. Hill, *J. Power Sources* 157 (2006) 335–350.
- [26] P.Y. Hou, *Oxid. Met.* 52 (1999) 337–351.
- [27] J.R. Smith, Y. Jiang, A.G. Evans, *Int. J. Mater. Res.* 12 (2007) 1214–1221.