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Influence of Alloy Content and a Cerium Surface Treatment on the Oxidation Behavior of Fe-Cr Ferritic Stainless Steels.

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The cost of solid oxide fuel cells (SOFC) can be significantly reduced by using interconnects made from ferritic stainless steels. In fact, several alloys have been developed specifically for this application (Crofer 22APU and Hitachi ZMG323). However, these steels lack environmental stability in SOFC environments, and as a result, degrade the performance of the SOFC. A steel interconnect can contribute to performance degradation through: (i) Cr poisoning of electrochemically active sites within the cathode; (ii) formation of non-conductive oxides, such as SiO_2 or Al_2O_3 from residual or minor alloying elements, at the base metal-oxide scale interface; and/or (iii) excessive oxide scale growth, which may also retard electrical conductivity. Consequently, there has been considerable attention on developing coatings to protect steel interconnects in SOFC environments and controlling trace elements during alloy production. Recently, we have reported on the development of a Cerium surface treatment that improves the oxidation behavior of a variety alloys, including Crofer 22APU [1-5]. Initial results indicated that the treatment may improve the performance of Crofer 22APU for SOFC application by: (i) retarding scale growth resulting in a thinner oxide scale; and (ii) suppressing the formation of a deleterious continuous SiO_2 layer that can form at the metal-oxide scale interface in materials with high residual Si content [5].

Crofer 22 APU contains Fe-22Cr-0.5Mn-0.1Ti (weight percent). Depending on current market prices and the purity of raw materials utilized for ingot production, Cr can contribute upwards of 90 percent of the raw materials cost. The present research was undertaken to determine the influence of Cr content and minor element additions, especially Ti, on the effectiveness of the Ce surface treatment. Particular emphasis is placed on the behavior of low Cr alloys.

Experimental

Both commercial and custom ferritic stainless steels containing between 11 and 26 weight percent (%) Cr were selected for study. Commercial alloys were procured and custom alloys were produced in house at the National Energy Technology Laboratory (NETL). Vacuum induction melting was used to produce 7 kg ingots from high purity starting elemental materials. After casting, the alloys were reduced to sheet (approximately 0.75 mm thick) by hot working and cold rolling. Table I details the compositions of both the commercial and custom alloys.

A pack cementation like surface treatment developed at the NETL was used to modify the surface of polished coupons of each of the alloy compositions. This method consists of applying a slurry mixture containing the Ce in compound form, a halide activator, and water to the surface of a material via dip coating. The slurry is dried and subsequently reacted with the alloy during a thermal treatment in a low vacuum ($1x10^{-3}$ Torr) at 900^oC for 12 hours. After treating, excess slurry is removed by simply rinsing the treated sample in water.

Prior to oxidation testing the starting weights and physicals dimensions of the coupons were measured and recorded. Oxidation tests were conducted at 800^oC in moist air. The moist air was generated by bubbling commercial purity dry air through two glass columns (each column was 2.54 cm in diameter by 120 cm in height) filled with distilled water prior to entering the furnace. This was intended to generate saturated air containing $3\%H_2O$, the maximum amount of moisture air can hold at ambient conditions. After a predetermined time interval, the coupons were removed from the furnace and the weight of each coupon was measured and recorded. The samples were then replaced into the furnace for the next cycle. Oxide scales were examined by standard X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques.

Table 1: Nominal and Measured Compositions of Alloys, in Weight Percent (values in parenthesis are nominal compositions)

Alloy	Fe	Cr	Mn	Ti	Si	Al	Other
Type 446	71.6 (bal)	26.1 (23-26)	0.6 (1.5)	0.02	0.6 (1.0)	<0.01	
Crofer 22APU	75.9 (bal)	22.8 (22)	0.45 (0.5)	0.1 (0.1)	0.3	0.1	0.08 La, 0.003 O (0.1 La)
Type 430	81.5 (bal)	16.4 (14-18)	0.5 (1.0)	0.01	0.5 (1.0)	0.01	
Type 409	86.5 (bal)	11.5 (10.5-11.75)	0.46 (1.0)	0.13 (6xC)	0.52	0.02	0.6 Ni (0.5 Ni)
F1	76.8 (bal)	22.2 (22)	0.47 (0.5)	0.1 (0.1)	0.08	0.13	0.002 C, 0.001 O
F6	76.8 (bal)	22.2 (22)	0.49 (0.5)	0.3 (0.5)	0.01	<0.01	0.02 C, 0.01 O
F9	86.2 (bal)	12.0 (12)	0.5 (0.5)	1.0 (1.0)	0.01	0.01	0.009 C, 0.001 O
F10	80.3 (bal)	17.9 (18)	0.52 (0.5)	1.0 (1.0)	0.01	0.01	0.004 C, 0.002 O
F11	77.25 (bal)	22.0 (22)	0.53 (0.5)	1.0 (1.0)	0.01	<0.01	0.01 C, 0.003 O

Alloys F1, F6, F9, F10 and F11 are custom alloys fabricated at NETL.

Results and Discussion

Figure 1 illustrates the oxidation behavior of the Fe-22Cr-0.5Mn alloys as a function of Ti content. F11 (which contained 1% Ti) has an accelerated oxidation rate compared to the other alloys. After 2000 hours of exposure, the mass gain exhibited by F11 was about 3 times greater than F1 and F6. XRD analysis of oxidized surfaces of F1 and F6 revealed primarily $(Mn,Cr)_3O_4$, Cr_2O_3 with a trace amount TiO_2 (amount of phase based on peak intensity for the phase). However, the oxide scale that formed on F11 was primarily TiO_2 with minor amounts of $Cr_{1.5}Fe_{1.5}O_3$, $CrMn_{1.5}O_4$. Most likely the formation of a significant amount of TiO_2, resulted in the accelerated oxidation behavior of F11 compared to the lower Ti containing alloys. The difference in the behavior of F1 and Crofer 22APU, both nominally Fe-22Cr-0.5Mn-0.1Ti, may be a consequence of Crofer 22APU containing La and/or slight differences in Al and Si contents, all of which can affect oxidation behavior [5].

Figure 2 shows influence of Cr content on the behavior of the Fe-Cr-1Ti-0.5Mn alloys. F9 (12%Cr) had a significantly higher oxidation rate than F10 (18%Cr) and F11 (22%Cr). The mass gains, after 2000 hours of oxidation, of the alloys were 55, 8 and 3 mg/cm^2, respectively. This difference can be correlated to the formation of Fe_2O_3 on the low Cr alloys during oxidation. Only Fe_2O_3 formed on the surface of F9 during oxidation (as determined by XRD). TiO_2, $Cr_{1.5}Fe_{1.5}O_3$, $CrMn_{1.5}O_4$, and a trace amount of Fe_2O_3 formed on the surface of F10. As mentioned above, TiO_2 and $Cr_{1.5}Fe_{1.5}O_3$, $CrMn_{1.5}O_4$ formed on the surface of F11 (no Fe_2O_3 was detected by XRD) during oxidation.

Figure 3, shows the oxidation behavior of the commercial alloys. Based on the magnitude of the mass change, it appears that the oxidation behavior of the lower Cr content alloys (Type 409 and Type 430) were superior to the higher Cr alloys (Crofer 22APU and Type 446). However, the oxide scale that formed on the both Type 409 and Type 430 spalled during testing, resulting in the apparent lower weight gain during oxidation.

Figure 4 illustrates the effectiveness of the Ce-surface treatment for improving the performance of all the alloys studied. Results are also plotted for the untreated Crofer 22APU and F11, for comparative purposes. For all the alloys, the surface treatment significantly improves oxidation resistance, as evidenced by lower mass gains during exposure. For instance the Ce-surface treatment reduced the mass gain during oxidation of Crofer 22APU by a factor of 2.5 (0.5 mg/cm^2 in the Ce treated condition compared to 1.3 mg/cm^2 in the untreated condition after 4000 hours). The treatment had a similar effect on the oxidation of Type 446 steels. Further, the treatment suppressed scale spallation during oxidation of the Type 409 and Type 430 steels. Inspection of Figures 3 and 4, reveals that Type 409 in the Ce surface treatment condition has a comparable mass gain as the untreated Type 446 and 33% lower mass gain than the untreated Crofer 22APU. In other words, an 11.5%Cr steel with the Ce surface treatment outperforms an untreated 22%Cr steel.

Figure 5 compares the oxide scales that formed on the Type 409, Type 430, Crofer 22APU in the Ce-surface treated condition, and untreated Crofer 22APU. As expected based on weight gain measurements, the scale that formed on all the treated alloys was thinner than the scale that formed on the untreated Crofer 22APU. In all cases, a continuous Cr-Mn spinel formed at the gas-oxide interface (identified as S on Fig. 5). The spinel formed on top of a Cr_2O_3 scale (identified as C). CeO_2 particles were also observed towards the outer surface of the scales (white particles at surface of scales on the Ce surface treated coupons). At the oxide scale-base metal interface, a Si-rich oxide (identified as I) was detected in all the coupons except the Ce surface treated Crofer 22APU. The Si-rich oxide subscale appeared to be nearly continuous in the untreated Crofer and 409+Ce coupons. Although not evident from the SEM cross sections shown on Fig. 5, the treatment significantly decreased the depth of internal oxidation. More extensive descriptions of the effect of the Ce surface treatment on oxide scale formation can be found elsewhere [ref 4 and 5].

The surface treatment also decreased the oxidation rates of the custom experimental alloys with high Ti content. This was especially true for F9 (12%Cr-1Ti), in which an order of magnitude decrease in oxidation rate was achieved through surface treatment (1.5 mg/cm^2 in the Ce surface treated condition compared to 55 mg/cm^2 in the untreated condition). Once again, a 12%Cr alloy subjected to the Ce surface treated condition (F9+Ce) outperforms an untreated 22Cr alloy (F11). This result is attributed to the Ce treatment, which suppresses the formation of Fe_2O_3 in this alloy. XRD detected TiO_2, $Cr_{1.5}Fe_{1.5}O_3$, $CrMn_{1.5}O_4$, and CeO_2 on the oxidized surface of the F9 in the Ce surface condition. For alloy F11, the decrease in oxidation rate was due to the surface treatment retarding scale growth, as the same oxides formed on the surface of F11 in both conditions (note: CeO_2 was also detected on the oxidized surface of F11 in the Ce treated condition).

Summary and Conclusions

The effectiveness of a Ce surface treatment on improving oxidation resistance of ferritic steels was demonstrated. In general the Ce surface treatment retarded scale growth, resulting in thinner oxide scales and consequently lower mass gains during oxidation. For low Cr commercial alloys, the surface treatment suppressed oxide scale spallation. For a custom low Cr alloy with relatively high Ti content, the treatment suppressed Fe_2O_3 formation. Significantly, low Cr alloys in the Ce-surface treated condition possessed better oxidation resistance than untreated alloys with considerably higher Cr contents.

References

1. D.E. Alman and P.D. Jabblonski, in Fuel Cell Seminar-2004, San Antonio, TX, 2004.
2 P.D. Jablonski and D.E. Alman, in Fuel Cell Seminar-2005, Palm Springs, CA 2005.
3. P.D. Jablonski, D.E. Alman and S.C. Kung, Ceram. Engr. Sci. Proc., Vol 26, ed N.Bansal, Amer. Ceram. Soc., Westerville OH, 2005. p. 193.

4. D.E. Alman, P.D. Jablonski, S.C. Kung, Ceram. Engr. Sci. Proc., Vol 27, Issue 4, ed N.Bansal, Amer. Ceram. Soc., Westerville OH, 2006, p. 253.
5. D.E. Alman and P.D. Jablonski, "Effect of Minor Elements and a Ce Surface Treatment on the Oxidation Behavior of an Fe-22Cr-0.5Mn Steel," accepted for publication in *Inter. J. Hydrogen Energy.* 2006.

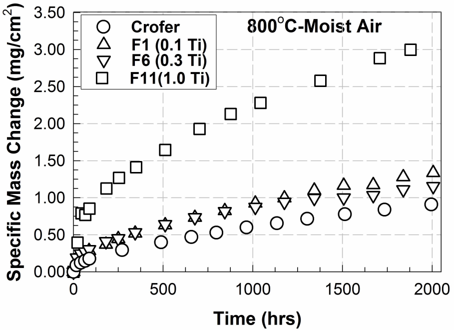

Figure 1: Influence of Ti content on the oxidation of Fe-22Cr-0.5Mn-Ti alloys.

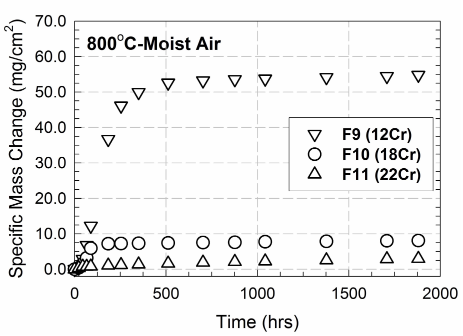

Figure 2: Influence of Cr content on the oxidation of Fe-Cr-0.5Mn-1Ti alloys.

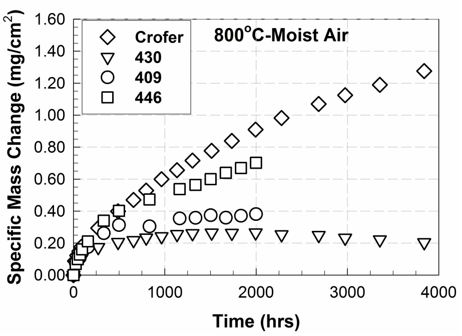

Figure 3: Oxidation of commercial ferritic stainless steels.

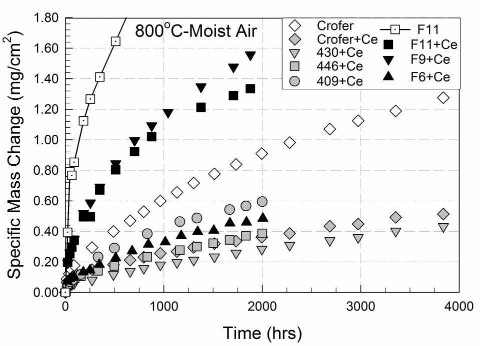

Figure 4: Effect of Ce surface treatment on the oxidation of ferritic stainless steels.

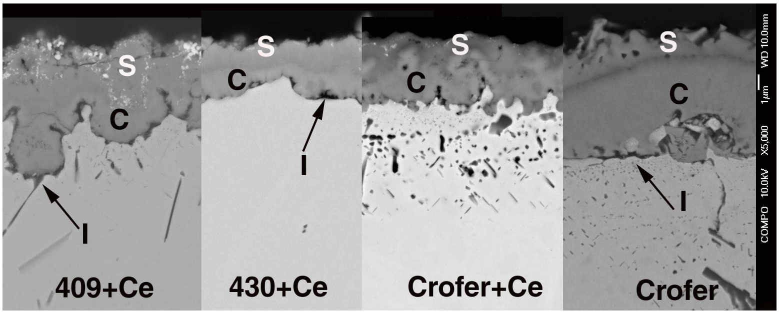

Figure 5: Cross sections of the oxide scales that formed during oxidation (after 2000 hrs). See text for details.