

EFFECT OF MIXED RARE EARTH OXIDE COATINGS ON HIGH TEMPERATURE OXIDATION OF Fe-20Cr ALLOY

S. M. C. Fernandes, O. V. Correa and L. V. Ramanathan
Instituto de Pesquisas Energéticas e Nucleares – IPEN-CNEN/SP
Av. Prof. Lineu Prestes 2242, Cidade Universitária,
05508-000 São Paulo. S.P.
lalgudi@ipen.br

ABSTRACT

Reactive elements in the form of rare earths (RE) have been used to improve high temperature oxidation resistance of chromium dioxide and alumina forming alloys. Increasing demand for alloys with even higher oxidation resistance have lead to attempts at optimizing RE additions, mainly in the form of conjoint addition of two different RE oxides. This paper presents the influence of surface additions of CeO₂, CeO₂ + La₂O₃ and CeO₂ + Pr₂O₃ on the isothermal oxidation behavior of Fe20Cr (and to a lesser extent Fe20Cr5Al) alloys at 1000° C. The oxidation resistance of specimens coated with two RE oxides was significantly higher than those coated with either one of the two oxides. The marked increase in the oxidation resistance of the alloys coated with two RE oxides is due to optimization of RE ion radius and RE oxide grain size/shape.

Key words: Iron-chromium alloy, iron-chromium-aluminum alloy, oxidation, rare earth oxide.

INTRODUCTION

Reactive elements, especially rare earths (RE) have been used to improve high temperature oxidation resistance of chromium dioxide and alumina forming alloys. The improvements are in the form of reduced oxidation rates and increased scale adhesion ^(1, 2). The RE can be added to the alloy as elements or as oxide to form dispersions. It can also be applied as an oxide coating to the surface of the alloy ⁽²⁻⁴⁾. A variety of precursors have been used to obtain RE oxide coatings on metallic surfaces. The use of sols, followed by its transformation to gel is referred to as the sol-gel technique and it produces oxide particles in the range 2 nm to 1 µm ⁽⁵⁾. The

sol is applied to a metallic substrate by a suitable technique, such as dipping, spin coating or electrophoresis.

Marked improvements in isothermal and cyclic oxidation behavior of RE oxide coated Fe-Cr alloys have been observed and reported ^(6,7). Nevertheless, increasing demand in recent years for even higher oxidation resistant chromium dioxide and alumina forming alloys has lead to attempts at optimizing RE additions. This paper presents the effect of surface addition of oxide gels of cerium, lanthanum and praseodymium, both as single oxide and as mixed oxides on the oxidation behavior of Fe20Cr, and to lesser extent, on Fe20Cr5Al alloys. The mechanism by which these REs improve overall oxidation resistance of the alloys is also discussed.

METHODS AND MATERIALS

Sols of La_2O_3 , CeO_2 , Pr_2O_3 , $\text{CeO}_2 + \text{La}_2\text{O}_3$ and $\text{CeO}_2 + \text{Pr}_2\text{O}_3$ were prepared as aqueous dispersions with a nitric acid and non-ionic surfactant mix, heated to 80°C for 1 h to form a sol. The RE oxide sol was then sprayed on 2 x 2 x 3 mm specimens of the two alloys, namely Fe20Cr and Fe20Cr5Al, to form a coat and the specimens were heated to 150°C to form a 10 µm thick surface layer of the RE oxide gel. These specimens were isothermally oxidized at 1000° C for about 400 minutes in a thermogravimetric balance to determine weight change as a function of time. The specimen surfaces, both prior to and after the oxidation tests, were examined in a scanning electron microscope (SEM) coupled to an energy dispersive spectroscopy (EDS) system.

RESULTS AND DISCUSSION

Scanning electron micrographs of the three RE oxide gels are shown in Fig.1. and marked differences in morphology of the oxides can be seen.

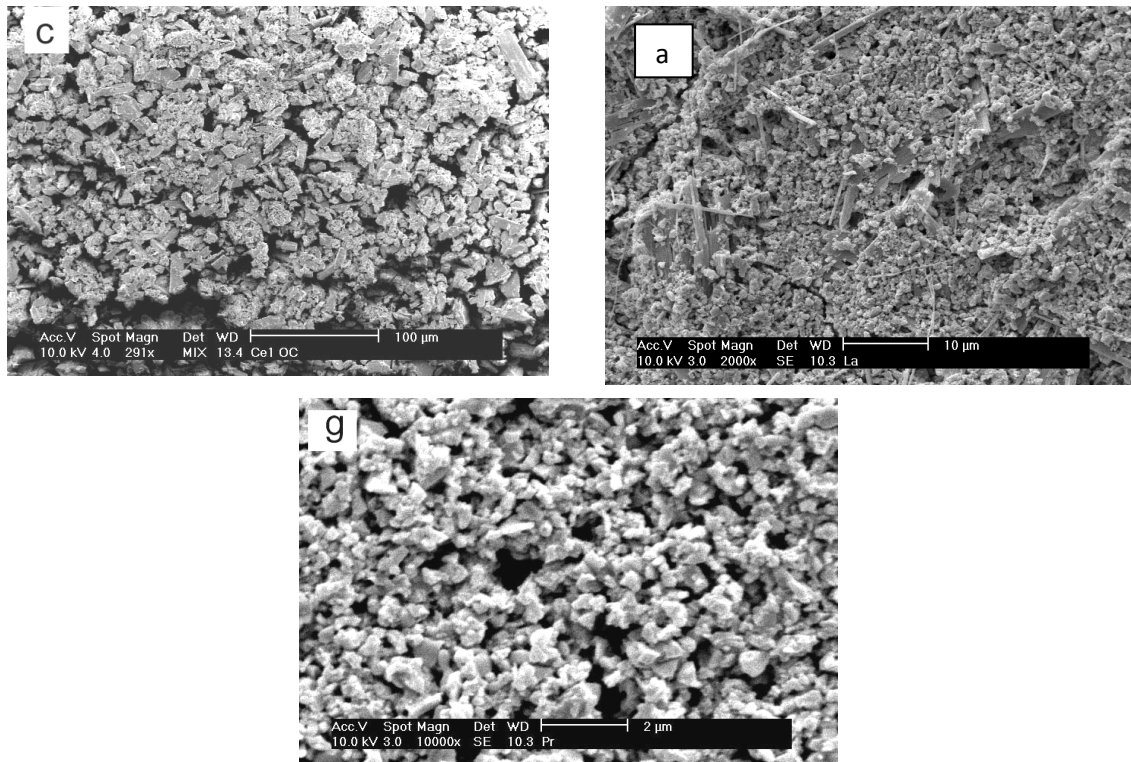


Fig. 1. Scanning electron micrographs of CeO_2 (c) and La_2O_3 (a) and Pr_2O_3 (g).

The isothermal oxidation curves of uncoated and RE oxide coated specimens are shown in Figs. 2 and 3. The weight gains of the uncoated and RE oxide coated Fe20Cr and Fe20Cr5Al specimens during oxidation are due to formation of Cr_2O_3 and Al_2O_3 respectively on the specimen surfaces ^(6, 7). Fig. 2. shows the oxidation curves of uncoated Fe20Cr, CeO_2 coated Fe20Cr, La_2O_3 coated Fe20Cr, $\text{CeO}_2 + \text{La}_2\text{O}_3$ coated Fe20Cr and $\text{CeO}_2 + \text{La}_2\text{O}_3$ coated Fe20Cr5Al specimens. The chromium dioxide layer on both the uncoated and RE oxide coated Fe20Cr specimens as well as the alumina layer on the Fe20Cr5Al specimens did not spall. All the specimens revealed parabolic oxidation behavior. The effect of rare earth oxide addition to the surface of the Fe20Cr alloy was clearly evident upon comparison of the curves of

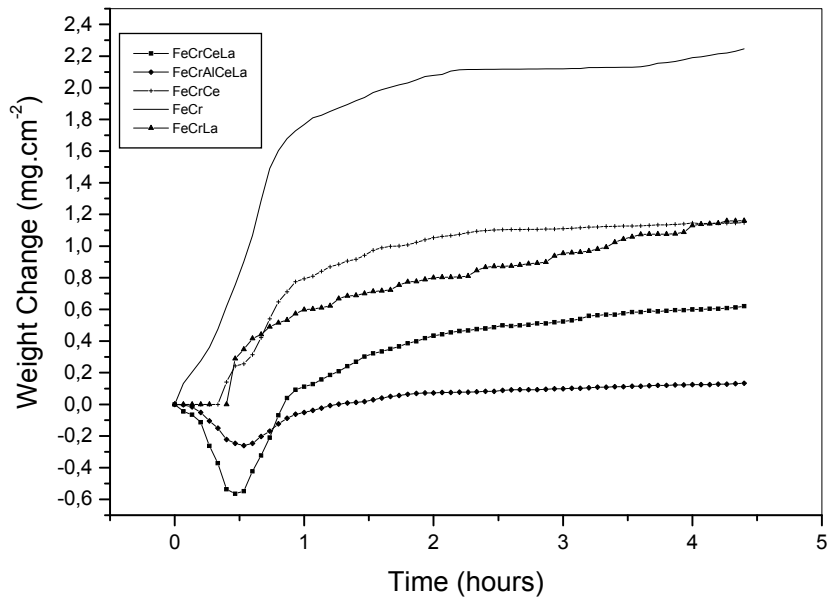


Fig. 2. Isothermal oxidation curves of uncoated, CeO_2 , La_2O_3 and $\text{CeO}_2 + \text{La}_2\text{O}_3$ coated Fe20Cr as well as $\text{CeO}_2 + \text{La}_2\text{O}_3$ coated Fe20Cr5Al at 1000 °C.

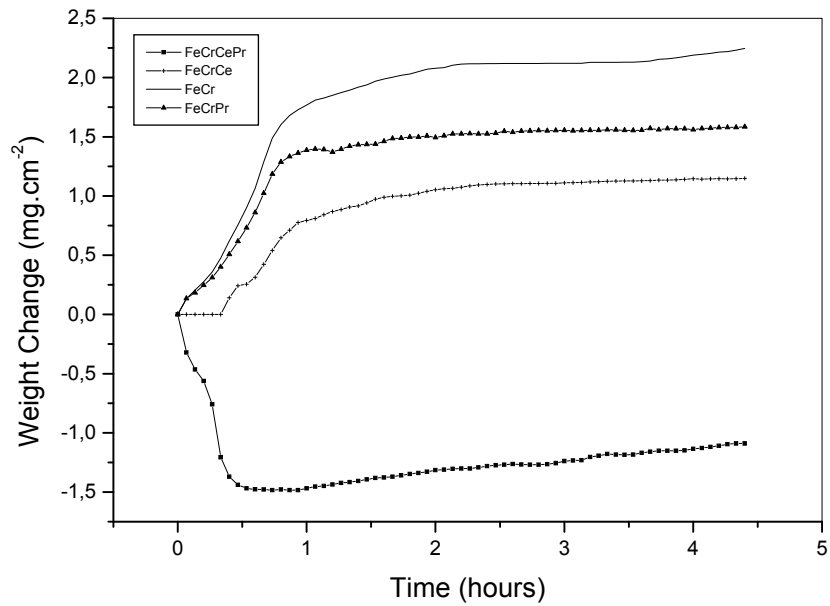


Fig. 3. Isothermal oxidation curves of uncoated, CeO_2 , Pr_2O_3 and $\text{CeO}_2 + \text{Pr}_2\text{O}_3$ coated Fe20Cr at 1000 °C.

Fe₂₀Cr and the other RE oxide covered Fe₂₀Cr specimens. Substitution of CeO₂ with La₂O₃ showed some improvement in oxidation behavior. However, when the two oxides CeO₂ and La₂O₃ were jointly present on the surface, the improvement in oxidation resistance was significant. The curve of the Fe₂₀Cr5Al specimen indicated even higher oxidation resistance. This could be attributed to the joint effect of the low oxidation rate of alumina forming alloys and the effect of the rare earth ion on alumina formation. Work is ongoing to separate these two effects. Fig. 3. shows the curves of uncoated Fe₂₀Cr, CeO₂ coated Fe₂₀Cr, Pr₂O₃ coated Fe₂₀Cr and CeO₂ + Pr₂O₃ coated Fe₂₀Cr specimens. Observations similar to those made earlier about the influence of La₂O₃ additions can be also made for Pr₂O₃ additions.

GENERAL DISCUSSION

Marked variations in the extent to which different RE oxides affect oxidation rate of chromium dioxide forming alloys was attributed to differences in RE ion radius, RE oxide morphology and coverage. The effect on alumina growth rate was similar, but to a lower extent ⁽⁷⁾.

Tab. 1: Morphology, coverage and cyclic oxidation resistance of Fe₂₀Cr alloy coated with different RE oxides ⁽⁷⁾.

Oxide of	Main morphological feature	Coverage (ranking)	R _{RE} /R _{Cr} ratio	Oxidation resistance (cycles)
La	Cubes / rods	1	1.64	15
Ce	Cubes	6	1.60	9
Pr	Cuboids	2	1.57	15
Nd	Needles / acicular	3	1.54	12
Sa	Clusters	4	1.50	12
Gd	Locked clusters	8	1.46	15
Dy	Tiny clusters	5	1.42	6
Y	Platelets	7	1.39	7
Er	Open clusters	9	1.37	7
Yb	Clusters / platelets	10	1.34	4

Table 1 summarizes this information obtained in prior studies and the oxides of La, Ce and Pr, which markedly increased oxidation resistance of chromium dioxide forming alloys, were selected to study the effect of conjoint additions. The coverage of a mixture of Ce plus La oxide or Ce plus Pr oxide can is considered to be high.

In the initial or transient stage of oxidation, metastable oxides of base metals such as iron oxide form on the alloy surface. The effects of RE on scale growth are not evident at this stage. Some of the REs exercise greater influence than others ⁽⁷⁾. In the absence of RE in the alloy or on the surface, the new oxide scale grows at the oxide /oxygen interface and in the presence of RE it grows at the metal/oxide interface. The RE oxide coating on the alloy surface gets incorporated in the growing scale and the RE ions segregate to the grain boundaries in the scale ^(6, 9-15). The RE ions at the scale grain boundaries then diffuse through the oxide scale to the gas interface. Proof of this was shown after prolonged oxidations ⁽⁸⁾. When the RE ion concentration at the grain boundaries in the scale reaches a critical amount, it results in two effects. The first is inhibition of normal outward transport of alloy cations along the scale grain boundaries due to the slower diffusion of the large RE ions along the same grain boundaries. It is also probable that large RE ions diffuse slower than small RE ions. Consequently, large RE ions probably slow down alloy cation diffusion in the oxide scale even more than small RE ions, resulting in reduced scale growth ^(8,14). The second effect is reduction in scale grain growth and this is due a solute-drag effect of the RE ions at the scale grain boundaries ⁽¹⁶⁾. This leads to smaller average grain size of α -Cr₂O₃ scales and higher scale plasticity ⁽¹⁷⁾. Spalling usually occurs when scale thickness, reflected as mass gains per unit area in oxidation measurements, is above a certain value. This was found to be 1.25-1.5 mg.cm⁻² for chromia growth in this study. This indicated that the time at temperature to reach a specific chromia layer thickness varied with the nature of RE. This mechanism is also valid for alumina scale forming alloys, but to a lesser extent.

There is evidence that RE-based spinel oxides form in the growing scale, depleting the RE ion at the scale boundaries to block outward base metal ion diffusion to the oxide/oxygen interface. It is believed that in the presence of two different RE oxides on the alloy surface these get incorporated into the scale and segregate to the scale grain boundaries. Spinel formation if energetically favored at some specific place in the scale would cause depletion locally of just one of the two

RE oxide ions, leaving behind the other RE ion to hinder Cr or Al ion diffusion to the gas interface for scale growth.

CONCLUSIONS

1. The oxidation resistance of RE oxide coated Fe20Cr alloy was significantly higher than that of the uncoated alloy.
2. The oxidation resistance of Fe-20Cr coated with La₂O₃ was significantly higher than that of the same alloy coated with CeO₂.
3. The oxidation resistance of Fe-20Cr coated with CeO₂ and La₂O₃ was even higher than that of the same alloy coated with either RE oxide.
4. The oxidation resistance of the Al containing alloy coated with CeO₂ and La₂O₃ exhibited the highest resistance compared to the coated Fe20Cr alloy.
5. The marked increase in the oxidation resistance of the two alloys coated with the two RE oxides compared to that coated with either oxide has been attributed to optimization in RE oxide grain size and shape, consequent increase in coverage and also to optimization in the chemical potentials of two RE oxides with ionic radii very close to one another.

REFERENCES

1. STOTT, F.H. Influence of alloy additions on oxidation. **Materials Science and Technology**, v.5, p.734-740, 1989.
2. STRINGER, J. The reactive elements effect in high temperature corrosion. **Materials Science and Engineering**, v. A120, p.129-137, 1989.
3. HOU, P.Y.; STRINGER, J. The effect of surface applied reactive metal oxide on the high temperature oxidation of alloys. **Materials Science and Engineering**. v. 87, p. 295-302, 1987.
4. RAMANATHAN, L.V. Role of rare earth elements on high temperature oxidation behavior of Fe-Cr, Ni-Cr and Ni-Cr-Al alloys. **Corrosion Science**, v 35 (5-8), p. 871-878, 1993.
5. BENNET, M.J. New coatings for high temperature materials protection. **Journal of Vacuum Science and Technology**, v. B2 (4), p.800-805, 1984.

6. FERNANDES, S.M.C.; RAMANATHAN, L.V. Influence of rare earth oxide coatings on oxidation behavior of Fe-20Cr alloys. **Surface Engineering**, v.16 (4) p. 327-332, 2000.
7. FERNANDES, S.M.C.; RAMANATHAN, L.V. Effect of surface deposited rare earth oxide gel characteristics on cyclic oxidation behavior of Fe20-Cr alloys. **Materials Research**, v. 9, 2, p.199-203, 2006.
8. PINT, B. Experimental observations in support of the dynamic-segregation theory to explain the reactive-element effect. **Oxidation of Metals**, v. 45, p. 1, 1996.
9. COTELL, C.M.; YUREK, G.J.; HUSSEY, R.J.; MITCHELL, D.F.; GRAHAM, M.J. The influence of grain boundary segregation of yttrium in chromium dioxide on the oxidation of chromium metal. **Oxidation of Metals**, v. 34, p.173-200, p. 201-216, 1990.
10. VERSACI, R.A.; CLEMENS, D.; QUADAKKERS, W.J.; HUSSEY, R. Distribution and transport of yttrium in alumina scales on iron-base ODS alloys. **Solid State Ionics**, v. 59, p.235-242, 1993.
11. PINT, B.; MARTIN, J.R.; HOBBS, L.W. ¹⁸O/ SIMS Characterization of the growth mechanism of doped and undoped α - Al₂O₃. **Oxidation of Metals**, v. 39, p.167, 1993.
12. PINT, B.; HOBBS, L.W. The formation of α -Al₂O₃ scales at 1500° C, **Oxidation of Metals**, v. 41, p.203-233, 1994.
13. PINT, B.; HOBBS, L.W. Limitations on the use of ion implantation for the study of the reactive element effect in β -NiAl, **Journal of Electrochemical Society**, v. 141, p.2443, 1994.
14. PINT, B.; GARRATT-REED, A.J.; HOBBS, L.W. The reactive element effect in ODS FeCrAl alloys, **Materials at High temperatures**, v. 13, p.3-16, 1995,
15. PAPAIOCOVOU, P.; HUSSEY, R.J. The effect of CeO₂ coatings on the oxidation behavior of Fe-20Cr alloys in O₂ at 1173K. **Corrosion Science**, v. 30(4/5), p.451-460, 1990.
16. KINGERY, W.D.; BOWEN, H.K.; UHLMANN, D.R. **Introduction to ceramics**, Wiley, New York, 1976.
17. RAMANARAYANAN, T.A.; RAGHAVAN, M.; PETKOVIC-LUTON, R. The Characteristics of alumina scales formed on Fe-based yttria-dispersed alloys, **Journal of Electrochemical Society**, v.131, p.923, 1984.