EFFECT OF RARE EARTH OXIDE GEL CHARACTERISTICS ON HIGH TEMPERATURE OXIDATION BEHAVIOR OF IRON-CHROMIUM ALLOYS[1]

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Abstract

The influence of various rare earth (RE) oxide gels - La_2O_3, CeO_2, Pr_2O_3, Nd_2O_3, Sm_2O_3, Gd_2O_3, Dy_2O_3, Y_2O_3, Er_2O_3, and Yb_2O_3 - on cyclic oxidation behavior in the range RT- 900ºC of Fe20Cr alloys has been studied. This paper presents the effect of rare earth oxide gel characteristics such as morphology, coverage and crystallite size on oxidation behavior of the alloy. These characteristics varied with the type of rare earth. Overall, the oxidation resistance increased with increase in time at temperature required to reach a specific chromium dioxide layer thickness and this was influenced by both the rare earth ion radius as well as the oxide gel characteristics. The latter affected the adhesion and resistance to thermal and growth stresses in the chromium dioxide layer.

Key words: Rare earth oxide; Coating; Iron-chromium alloy; Cyclic oxidation.

EFEITO DAS CARACTERISTICAS DOS GEIS DE ÓXIDOS DE TERRAS RARAS SOBRE O COMPORTAMENTO DE OXIDAÇÃO EM TEMPERATURAS ELEVADAS DE LIGA FERRO-CROMO

Resumo

Tem sido estudada a influência dos geis de óxidos de terras raras (TR) - La_2O_3, CeO_2, Pr_2O_3, Nd_2O_3, Sm_2O_3, Gd_2O_3, Dy_2O_3, Y_2O_3, Er_2O_3, e Yb_2O_3 - sobre o comportamento de oxidação cíclica na faixa 25 - 900ºC da liga Fe-20Cr. Este trabalho apresenta os efeitos das caracteristicas dos geis de óxidos de TR como morfologia, tamanho dos cristalitos e grau de recobrimento sobre o comportamento de oxidação da liga. Estas caracteristicas variaram com o tipo de TR. Em geral, a resistência a oxidação aumenta com o aumento do tempo à temperatura necessária para atingir uma espessura específica da camada do dióxido de cromo. Esta, por sua vez, é influenciada tanto pelo tamanho do raio iônico da TR, como pelas caracteristicas dos geis de óxidos de TR. O último influencia a adesão e a resistência às tensões térmicas e ao crescimento da camada de dióxido de cromo.

Palavras-chave: Óxido de terra rara; Revestimento; Liga ferro-cromo; Oxidação.

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[1] *Technical contribution to 64th ABM Annual Congress, July, 13th to 17th, 2009, Belo Horizonte, MG, Brazil.*

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1 INTRODUCTION

Materials for use in high temperature environments are usually iron, nickel or cobalt based alloys. The oxides formed on these metals are not protective above 500ºC and are therefore alloyed with chromium, aluminum or silicon to establish more protective oxides (scales) of chromia, alumina or silica respectively. The use of reactive elements, like rare earths (RE) to improve high temperature oxidation resistance of chromium dioxide and alumina forming alloys is well known. The improvements are in the form of reduced oxidation rates and increased scale adhesion.(1,2) The RE can be added in elemental form or as oxide dispersions. It can also be applied as an oxide coating to the surface of the alloy. (2-4) Various precursors have been used to obtain RE oxide coatings on metallic surfaces and include aqueous nitrate solutions, molten nitrate salts, oxide slurries, or colloidal dispersions of a hydrous oxide (sol). The use of sols, followed by its transformation to gel upon removing water from the colloidal units is known to produce oxide particles (the gel) in the range 2 nm to 1 µm. The technique based on the use of sols, and referred to as the sol-gel technique, has been used to produce a variety of ceramic coatings.(5) The sol is applied to a metallic substrate by a suitable technique, such as dipping, spin coating or electrophoresis.

RE oxide gel coatings have the advantage of not affecting adversely the mechanical properties of the alloy and have also the potential of being used on surfaces of metallic components exposed to high temperature oxidizing service environments. Previous studies reported the effect of praseodymium, dysprosium and yttrium oxide gel coatings on isothermal oxidation behavior of Fe20Cr alloys.(6) The morphology of these RE oxide coatings varied with the type of RE and the RE ion radius had an effect on the extent of chromium dioxide growth.(6) The effect of other RE oxides or RE oxide concentrates on oxidation behavior of chromium dioxide and alumina forming alloys was more on the former than on alumina growth.(7,8) A direct correlation between the RE ion radius and the extent of protection of chromium dioxide forming alloys at temperatures up to 900º C has been reported.(9) Certain RE oxide coating characteristics also had an effect on oxidation behavior of iron-chromium alloys.(9)

This paper presents different RE oxide gel coating characteristics such as morphology, coverage and crystallite size and their influence on the oxidation behavior of a Fe-20Cr alloy. The mechanism by which REs improve overall oxidation resistance of chromium dioxide forming alloys is also discussed.

2 METHODS AND MATERIALS

RE oxide sols were prepared as aqueous dispersions of the respective RE oxides with nitric acid, and a non-ionic surfactant. The solution was heated to 80°C under constant agitation for an hour and the sol formed as sediment. Fe20Cr alloy specimens (1.0 x 1.0 x 0.5 cm) were ground to 400 mesh, rinsed, dried and spray coated with the different RE oxide sols. The specimens were then heated to 150°C to form a 10 µm thick surface layer of the RE oxide gel. The oxide gel coated specimens were examined in a scanning electron microscope (SEM) coupled to an energy dispersive system (EDS) to study the morphology. An image analyzer was used to evaluate coverage, or the extent to which the surface was covered by the gel. X-ray diffraction (XRD) analysis was used to determine the crystallite size of oxide gels. The Scherrer equation (1) was used to determine the crystallite size.(10,11) This relates crystallite size (D) and the full-width at half-maximum (FWHM), referred to as Δ (2θ) of XRD reflections.

$$D = 0.9\lambda / \Delta\,(2\theta) \cos\theta \qquad (1)$$

Where λ is the wavelength (in the case of a Cu target, λ = 0.15406) and θ is the diffraction angle. The use of this equation is based on the physical origin of broadening of the XRD reflections being associated with the small grain size only. The true peak broadening Δ (2θ) can be obtained using the equation (2):

$$\Delta\,(2\theta) = [(\Delta(2\theta)_h)^2 - (\Delta(2\theta)_g)^2]^{1/2} \qquad (2)$$

where $\Delta(2\theta)_h$ is the FWHM of the measured profile and $\Delta(2\theta)_g$ is the FWHM of the profile from the standard sample for the same reflection. The grain size thus obtained is volume averaged in a direction perpendicular to the diffraction plane.

Two sets of oxidation tests were carried out. In the first set, the effect of different RE oxide gel coats (La_2O_3, CeO_2, Pr_2O_3, Nd_2O_3, Sm_2O_3, Gd_2O_3, Dy_2O_3, Y_2O_3, Er_2O_3, and Yb_2O_3) on cyclic oxidation behavior of Fe-20Cr alloy specimens 1.0 x 1.0 x 0.5 cm was studied. Each oxidation cycle consisted of 2 hours at 900°C. The specimens were weighed after each cycle and oxide spalling marked the end of the test. Based on results which indicated that the oxides of La and Pr had the highest effect in reducing oxidation rates of Fe20Cr alloy, another set of experiments were carried out. New Fe20Cr specimens coated with La_2O_3 and Pr_2O_3 were cyclically oxidized for extended periods in a different experimental set up. A quartz glass tube containing the specimens was held in a fixed position and the tubular furnace around the quartz tube which was supported on a base was moved using automatic controls to heat and cool the specimens. This set up permitted the specimen dwell time (in the hot and cold zones) to be varied and the heating/cooling rates of the specimens, by controlling the speed of movement of the furnace. The La_2O_3 and Pr_2O_3 coated specimens were cycled from 900º C, 1.000ºC and 1.100ºC to RT at cooling rates of 330º C/s and 1000º C/s
All the specimens in the different tests were weighed after each cycle and their surfaces examined in a SEM.

3 RESULTS AND DISCUSSION

The results of the first set of oxidation tests are shown in Figure 1. The weight gain of the uncoated and RE oxide coated specimens during oxidation is due to formation of Cr_2O_3 on the specimen surfaces.(6,7) The uncoated specimen was cycled five times before the oxide scale spalled. The RE oxide coated specimens were cycled many more times, indicating increased cyclic oxidation resistance (COR) and this varied with the RE oxide.

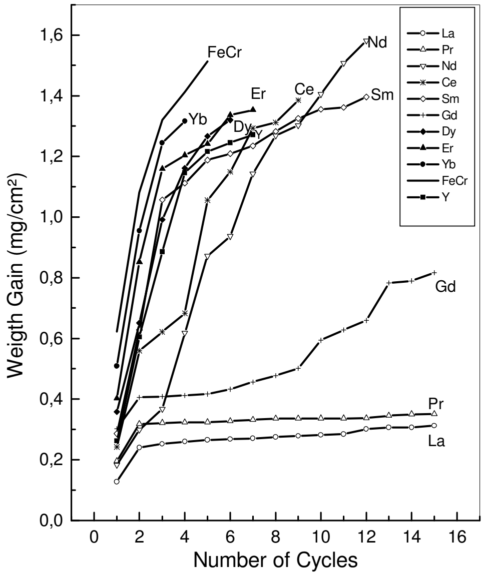
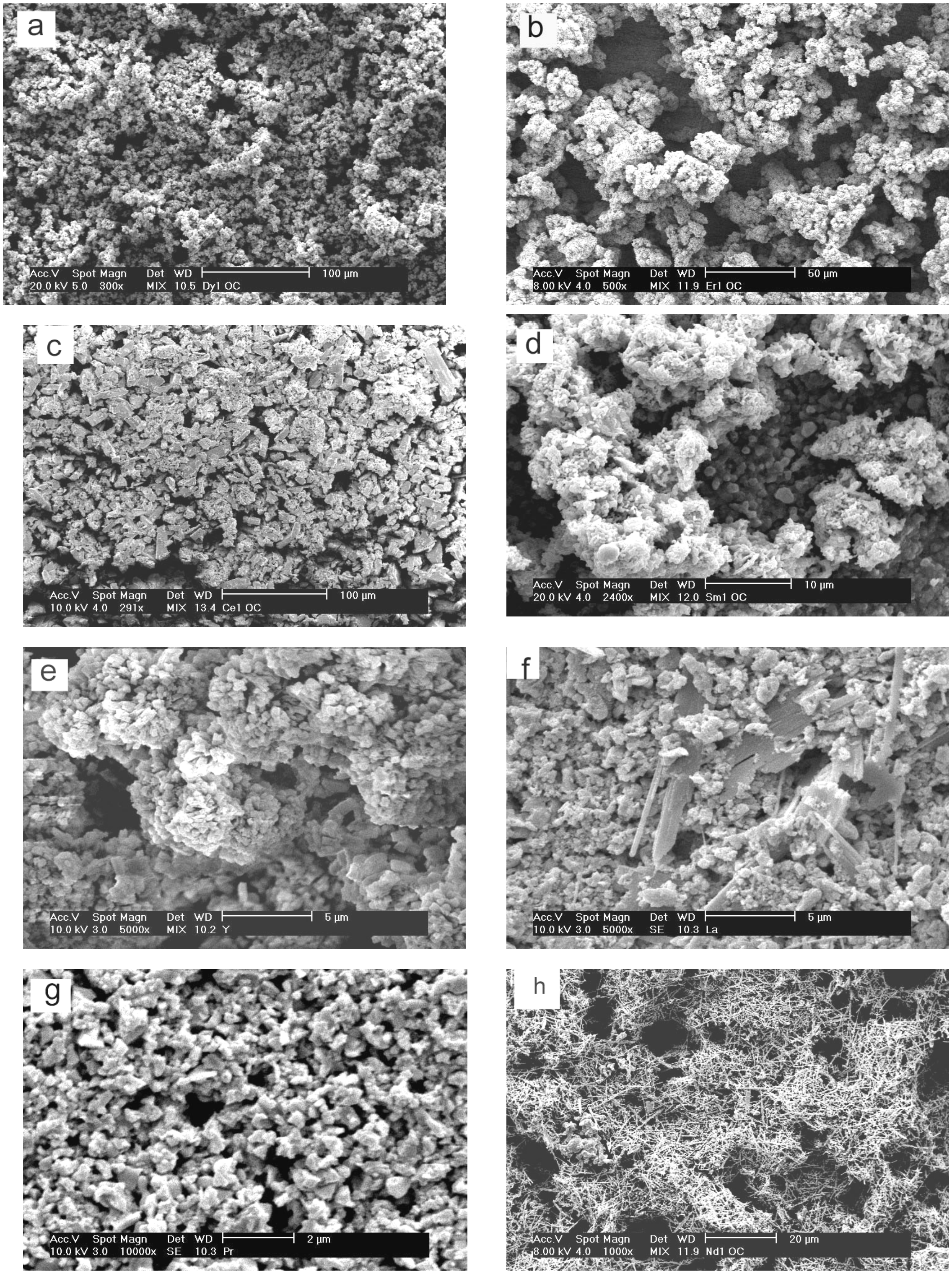


Figure 1. Weight gain versus number of cycles of oxidation of Fe-20Cr alloy without and with surface deposited RE oxide.

Table 1. The cyclic oxidation resistance (COR), ratio of radii of RE ion to Cr ion, crystallite size and the main morphological features of the RE oxide gels.

Oxides of	COR (cycles)	R_{RE}/R_{Cr} ratio	Main morphological features	Crystallite size (nm)
La	15+	1.64	Cubes and rods	36.4
Ce	9	1.60	Cubes	58.4
Pr	15+	1.57	Cuboids	60.2
Nd	12	1.54	Fine needles, acicular	58.1
Sm	12	1.50	Clusters	63.0
Gd	15+	1.46	Interlocking clusters	27.8
Dy	6	1.42	Tiny clusters	36.6
Y	7	1.39	Platelets	26.9
Er	7	1.37	Open clusters	36.6
Yb	4	1.34	Clusters and disperse platelets	26.5

The number of cycles to spalling of the scale on specimens coated with the various RE oxides and the ratio of the radius of the RE ion to the radius of the chromium ion (R_{RE}/R_{Cr}) are shown in Table 1. It is evident that specimens coated with RE oxides that had R_{RE}/R_{Cr} ratios lower than 1.45 withstood only half as many cycles compared with those coated with RE oxides that had R_{RE}/R_{Cr} ratios higher than 1.45. The chromium dioxide layer on specimens coated with La and Pr oxides did not spall even after 15 cycles. The weight gains of these specimens after one cycle and after 15 cycles were low and about 0.17 mg.cm^{-2}. In general, spalling of the chromium dioxide layer occurred when weight gains exceeded 1.25-1.5 mg.cm^{-2}. This indicates that the time at temperature to reach a specific chromium dioxide layer thickness varied with the nature of RE.


a
Acc.V Spot Magn Det WD 100 µm
20.0 kV 5.0 300x MIX 10.5 Dy1 OC
b
Acc.V Spot Magn Det WD 50 µm
8.00 kV 4.0 500x MIX 11.9 Er1 OC
c
Acc.V Spot Magn Det WD 100 µm
10.0 kV 4.0 291x MIX 13.4 Ce1 OC
d
Acc.V Spot Magn Det WD 10 µm
20.0 kV 4.0 2400x MIX 12.0 Sm1 OC
e
Acc.V Spot Magn Det WD 5 µm
10.0 kV 3.0 5000x MIX 10.2 Y
f
Acc.V Spot Magn Det WD 5 µm
10.0 kV 3.0 5000x SE 10.3 La
g
Acc.V Spot Magn Det WD 2 µm
10.0 kV 3.0 10000x SE 10.3 Pr
h
Acc.V Spot Magn Det WD 20 µm
8.00 kV 4.0 1000x MIX 11.9 Nd1 OC

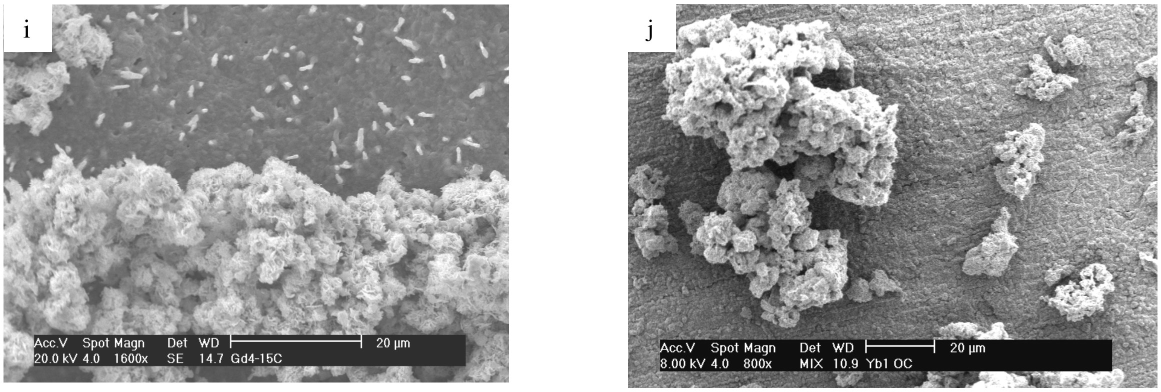


Figure 2: Scanning electron micrographs of different RE oxides. (a) Dy, (b) Er, (c) Ce, (d) Sm, (e) Y, (f) La, (g) Pr, (h) Nd, (i) Gd and (j) Yb.

The morphology of the RE oxide gels are shown in Figure 2 and the main morphological features summarized in Table 1.

Table 2: Correlation between coverage of RE oxide coat and cyclic oxidation resistance.

RE oxide	R_{RE}/R_{Cr} ratio	Cyclic oxidation resistance (cycles)	Magnification of micrograph (µm)	Covered surface (%)	Ranking of RE oxide coverage
La	1.64	15	2000	77.04	1
Ce	1.60	9	200	68.60	6
Pr	1.57	15	2500	72.03	2
Nd	1.54	12	200	97.12	3
Sm	1.50	12	200	73.80	4
Gd	1.46	15	125	71.30	8
Dy	1.42	6	200	72.00	5
Y	1.39	7	250	68.10	7
Er	1.37	7	100	55.20	9
Yb	1.34	4	100	22.80	10

The area fractions, or coverage, of the oxides were determined from micrographs taken at various magnifications using image analysis and these are summarized in Table 2. The RE oxides have been listed in decreasing order of the ratio of ionic radii of RE ion to Cr ion. Table 2 reveals a correspondence between the extent of coverage and the cyclic oxidation resistance. The exceptions are cerium and gadolinium oxides. The influence of the former can be attributed to its valence and the latter due probably to Gd_2O_3 spalling, caused by its morphology. The morphology of the RE oxide coating before and after oxidation at 1000°C were compared and found to remain unchanged. This lent further proof to the fact that the RE oxide particle shape and size are defined during the sol (dispersion) to gel (solid) conversion stage and are maintained during subsequent oxidation.

The XRD data revealed significant differences in the average crystallite size of the different RE oxide gels, as shown in Table 1. In general the RE oxides that increased COR had higher crystallite size. The exceptions were La and Pr oxides.

On the basis of the above data, the oxides of Pr and La were selected for the second set of experiments to determine their influence on oxidation behavior of Fe-20Cr alloys in extended cyclic oxidation tests with varying cooling rates. The results of these tests are shown in Table 3. The COR of both the uncoated and RE oxide coated specimens decreased with increase in the peak temperature. This behavior did not change with cooling rate. At low and high cooling rates from 900º C the La_2O_3 coated specimens could be cycled for over 100 and 47 cycles respectively. This was significantly higher than the COR of the Pr_2O_3 coated specimens under identical conditions. In the case of the La_2O_3 coated specimens, increase in peak temperature from 900º C to 1000º C decreased the COR by approximately 33%. A further increase in peak temperature to 1100º C decreased COR by a further 33%. Even though the high cooling rate tests of La_2O_3 coated specimens from 900º C were discontinued, the overall COR of La_2O_3 coated Fe20Cr did not alter with increase in cooling rate from 330º C/s to 1000º C/s. This indicates that the thermal stresses generated upon cooling from the two temperatures, even though different, were well within the limiting stress value that is necessary in combination with the growth stress to cause the oxide to spall.

Table 3. Cyclic oxidation resistance of uncoated, La_2O_3 coated and Pr_2O_3 coated Fe-20Cr specimens.

Fe-20Cr specimen	Number of cycles to spalling					
	Low cooling rate (330º C/s)			High cooling rate (1000º C/s)		
	900ºC	1000ºC	1100ºC	900ºC	1000ºC	1100ºC
Uncoated	11	7	3	5	5	3
Pr_2O_3 coated	15	12	6	11	11	5
La_2O_3 coated	102	32	11	> 47	30	11

4 GENERAL DISCUSSION

The crystallite size and morphology of the different RE oxide revealed marked differences.(3,7) Specimens coated with RE oxides with cube, rod or needle-like and closed-cluster morphology withstood a higher number of oxidation cycles compared to those coated with RE oxides with platelet or open-cluster morphology. Coverage of the different RE oxides varied and correspondence between coverage and COR has been found. The COR of Fe-20Cr alloy coated with RE oxide gels varied and depends on the thickness of the chromium dioxide layer formed on the alloy surface. In the presence of an RE oxide coating the chromium dioxide layer formed after the first cycle of oxidation is thinner than that on surfaces without a RE oxide coating and this varied with RE oxide. Spalling of the chromium dioxide layer, which marks the breakdown of COR, occurs when its thickness reaches a critical value. Hence, the longer it takes to reach this critical oxide scale thickness, higher the COR. Characteristics of the RE oxide coating that affect the time required to reach this critical oxide scale thickness are the ionic radii of the RE, the shape and size of the RE oxide crystallites and the coverage.

4.1 Role of Rare Earths on Chromium Dioxide Growth on Fe-Cr alloys

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.

During oxidation of RE containing alloys the RE diffuse into the scale due to the oxygen potential gradient which extends from the gas interface into the substrate. In the case of the RE oxide coated alloys, the coating gets incorporated in the growing scale.(6) Both in the RE element containing alloy's surface oxide and RE oxide coated alloy's oxide the RE diffuses through the oxide to the gas interface. Proof of this was shown after prolonged oxidations.(8) The RE ions first segregate to the metal-scale interface and then follow the fastest path to the gas interface, which are the scale grain boundaries.(9-6) Their ions segregate to the scale grain boundaries. When the RE ion concentration at the grain boundaries reaches a critical amount it results in two effects observed in this study.

The first effect is inhibition of normal outward short-circuit transport of alloy cations along the scale grain boundaries due to the slower diffusion of the large RE ions. It is also probable that RE with higher ionic radius diffuse slower along the grain boundaries compared with the RE ion with a smaller radius. Hence, bigger the RE ion, higher is the inhibition of alloy cation transport.(8,16) The higher COR of Fe20Cr coated with La_2O_3, compared with that coated with Pr_2O_3, or any other RE oxide is further proof of the effect of the RE ion size. In this case the time taken to form the critical chromia layer thickness is significantly longer. During much of this period, the scale formed is thin, more plastic, more adherent to the alloy and therefore capable of withstanding stresses associated with scale growth and temperature cycling. Similar observations were reported with respect to scale growth on ceria coated Fe-Cr alloys.(17) Direct correlation between RE ion radius and cyclic oxidation resistance has been found. As a result, the new rate-limiting step is the inward transport of O^- ions along the scale grain boundaries.

The second effect is reduction in scale grain growth and this is due a solute-drag effect of the RE ions on the scale grain boundaries.(19) This results in a smaller average grain size in α-Cr_2O_3 scales and higher scale plasticity.(20) In general, spalling 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.

5 CONCLUSIONS

1. The cyclic oxidation resistance (COR) of RE oxide coated Fe-20Cr alloy was significantly higher than that of the uncoated alloy.
2. The morphology, coverage and average crystallite size of the RE oxides varied with the nature of RE.
3. The chromium dioxide layer thickness on the RE oxide coated Fe-20Cr alloy varied with the type of RE oxide.
4. Correlations were found between cyclic oxidation resistance, coverage and RE oxide crystallite size.
5. Among the different RE oxides, La_2O_3 was the most efficient in increasing the oxidation resistance of the Fe20Cr alloy.
6. Further evidence of a direct correlation between RE ion radius and oxidation resistance of chromium dioxide forming alloys has been observed.

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