Nanocrystalline rare earth oxide coatings for improved H.T. oxidation resistance of chromia forming alloys

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Abstract

Rare earths (RE) have been used to improve the high temperature oxidation resistance of chromium dioxide and alumina forming alloys. The RE are added either to the alloy or are applied as a coating to the alloy's surface. In this study, the sol-gel technique, well known to produce fine grained ceramic oxides, was used to prepare nano-crystalline RE oxides of La, Ce, Pd, Nd, Sm, Gd, Dy, Y, Er, and Yb. These oxides were used to coat Fe-20Cr specimens. The cyclic oxidation resistance of the RE oxide coated specimens was determined. Marked improvements were observed in the coated specimens and the extent of improvement depended on the nature of the RE oxide, its ionic radius and other features of the coating. Extended oxidation tests were carried out with La_2O_3 and Pr_2O_3 coated Fe-20Cr alloy. In these tests the specimens were heated to different peak temperatures and cooled at rates of up to 1000C/s. The La_2O_3 coatings were more effective in increasing cyclic oxidation resistance compared to Pr_2O_3 coatings. The role of RE in increasing overall oxidation resistance of chromium dioxide forming alloys is discussed.

Key words: Rare earth oxide, coating, iron-chromium alloy, cyclic oxidation.

Introduction

Reactive elements, especially rare earths (RE), have been added to high temperature alloys to further improve their oxidation resistance. 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 an oxide to form dispersions. It can also be introduced into the surface by ion implantation or applied as an oxide coating to the alloy surface.(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 fine oxide.(5) The sol can be applied to a metallic substrate by a suitable technique, such as dipping, spin coating or electrophoresis.

This paper presents the microstructural characteristics of the different RE oxide coatings and its influence on the oxidation behavior of Fe-20Cr alloy. The mechanism by which REs improve overall oxidation resistance of chromium dioxide forming alloys is discussed.

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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. Two sets of experiments were carried out. In the first set, the effect of different RE oxide 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) with the oxide crystallites in the size range 26-60 nm, 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 indicating that the oxides of La and Pr had the most 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 to and fro using automatic controls. 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, 1000º C and 1100º C 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 scanning electron microscope (SEM) coupled to an energy dispersive spectroscopy (EDS) system. The oxide scales were also analyzed by x-ray diffraction (XRD) analysis.

Results and discussion

The morphology of the RE oxide gels are shown in figure 1 and the main morphological features are summarized in Table 1. The results of the first set of experiments are shown in Figure 2. 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. 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. On the basis of these 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 2.

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.

General discussions

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 3. 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 crystallite size and morphology of the different RE oxide revealed marked differences. (3, 7) Correlations between the morphology of the RE oxide and the COR of coated Fe-20Cr alloy have been reported. (7) Specimens coated with RE oxides with cube, rod or needle-like morphology withstood a higher number of oxidation cycles compared to those coated with RE oxides with platelet or cluster morphology. Coverage, or the extent to which the Fe-20Cr surface was covered by the different RE oxides also varied and correspondence between coverage and COR has been reported. (7)

The COR of Fe-20Cr alloy coated with RE oxide gels varied and it was shown that COR 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 it 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.

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.

Role of rare earths in improving H.T. oxidation resistance of chromia forming alloys

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.(9-15) This is shown schematically in Figure 3. Their ions segregate to the scale grain boundaries. When the RE ion concentration at the grain boundaries reaches a critical amount it results in the two effects that have been 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, 14) 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.(15) 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.(16) This results in a smaller average grain size in α-Cr_2O_3 scales and higher scale plasticity.(17) 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.

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 chromium dioxide layer thickness on the RE oxide coated Fe-20Cr alloy varied with the type of RE oxide.
3. Among the different RE oxides, La_2O_3 was the most efficient in increasing the oxidation resistance of the Fe20Cr alloy.
4. Further evidence of a direct correlation between RE ion radius and oxidation resistance of chromia forming alloys has been observed.

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Table 1. Main morphological feature of the rare earth oxides

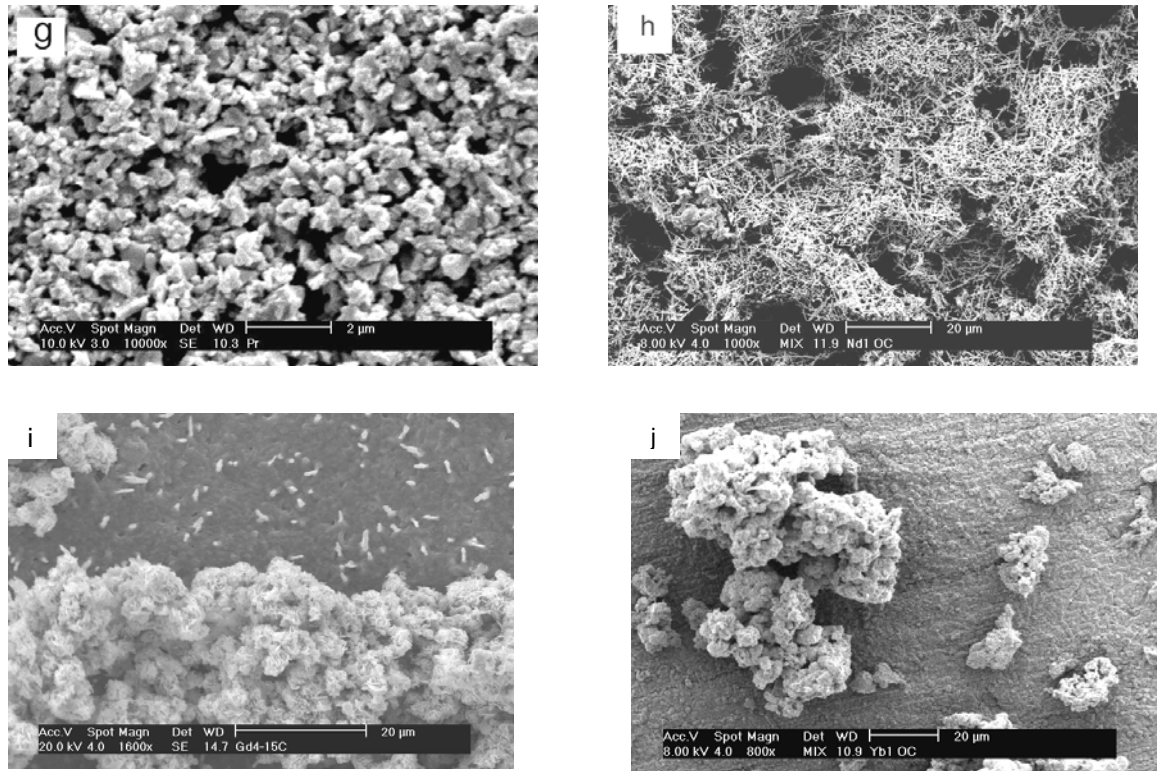| Rare earth oxide	Main morphological feature
Lanthanum	Cubes and rods
Cerium	Cubes
Praseodymium	Cuboids
Neodymium	Fine needles, acicular
Samarium	Clusters
Gadolinium	Interlocking clusters
Dysprosium	Tiny clusters
Yttrium	Platelets
Erbium	Open clusters
Ytterbium	Clusters and disperse platelets
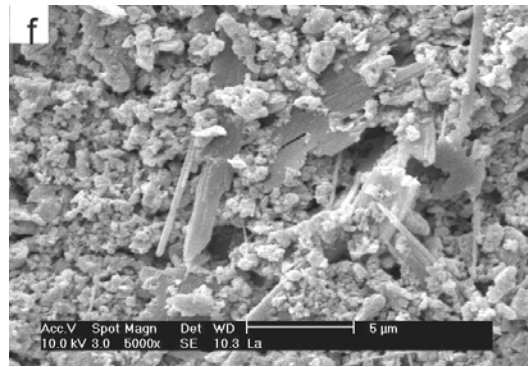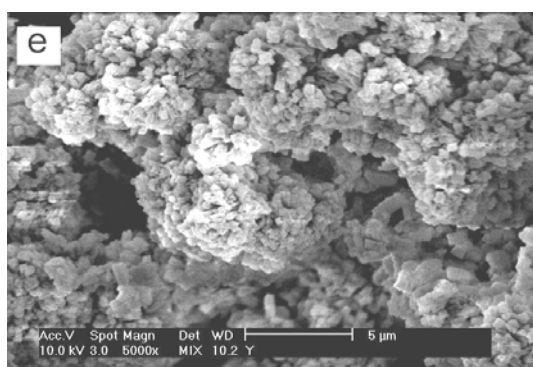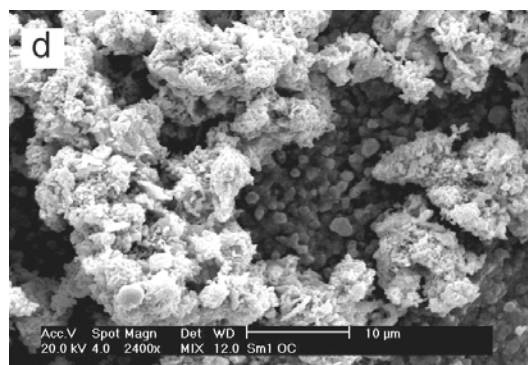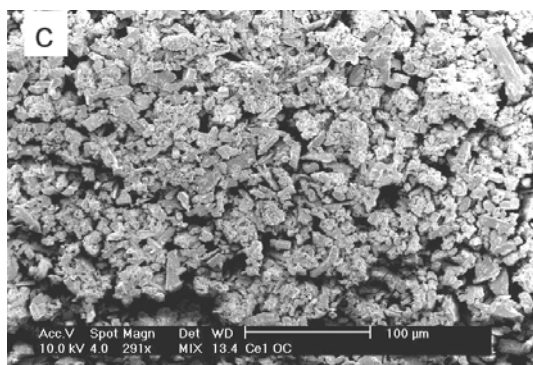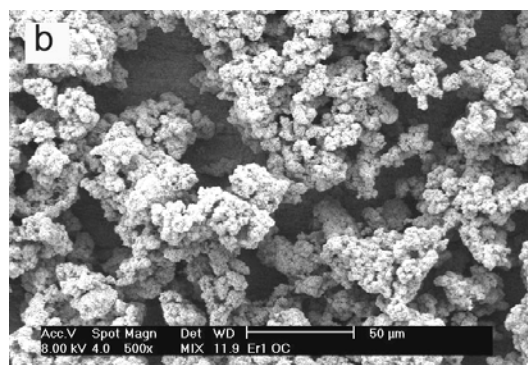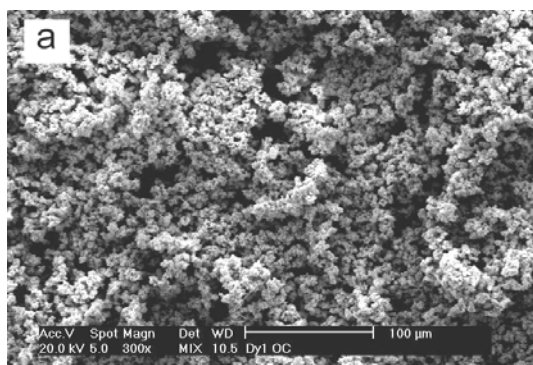
Figure 1: Scanning electron micrographs of different RE oxides. (a) Dy, (b) Er, (c) Ce, (d) Sm, (e) Y, (f) La, (g) Pr, (h) Nd, (i) Gd and (j) Yb.
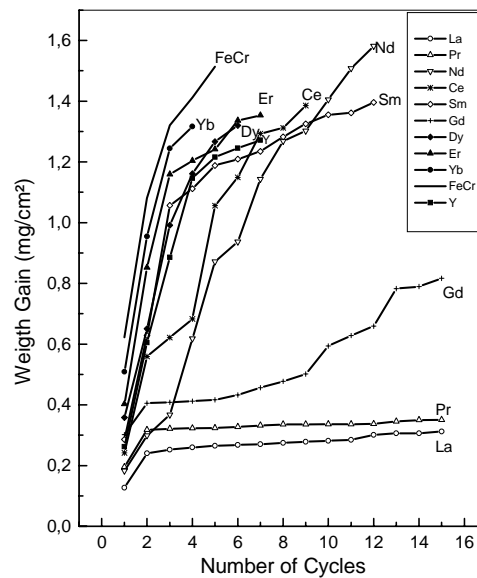

Figure 2. Weight gain versus number of cycles of oxidation of Fe-20Cr alloy without and with surface deposited RE oxide.

Table 2. 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

Table 3. The cyclic oxidation resistance (COR) (or cycles before spalling) and the ratios of the RE ion radius to the radius of chromium ion.

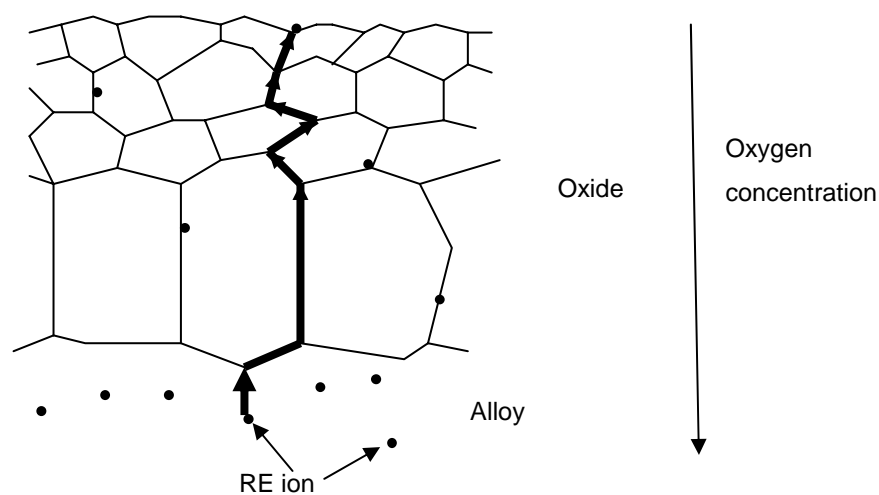| Oxide of	COR	R_{RE}/R_{Cr} ratio
Lanthanum	15+	1.64
Cerium	9	1.60
Praseodymium	15+	1.57
Neodymium	12	1.54
Samarium	12	1.50
Gadolinium	15+	1.46
Dysprosium	6	1.42
Yttrium	7	1.39
Erbium	7	1.37
Ytterbium	4	1.34

Figure 3. Schematic diagram showing RE ion diffusion along chromia scale grain boundaries.