

Effect of Rare Earth Oxide Coating in Improving the Cyclic Oxidation Resistance of Chromia Forming Alloys

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Abstract

The use of rare earths to increase high temperature oxidation resistance of chromium dioxide and alumina forming alloys is well known. The rare earths can be added as elements (or oxides) to the alloys or applied as an oxide coating to the alloy surface. The sol-gel technique is very efficient to apply fine oxide particle coatings. The influence of various rare earth oxide gels such as 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 (RT-900°C) of Fe20Cr alloy has been studied. The morphology and coverage of the rare earth oxide gels varied with the type of rare earth. The cyclic oxidation resistance increased with increasing rare earth ion radius, increasing coverage and gel crystallites in the form of cuboids or needles.

Introduction

Alloys used in high temperature oxygen containing environments rely on the formation of a continuous and slow growing oxide scale for their protection. Alloys that form chromium dioxide and alumina are often used. Reactive elements such as zirconium and rare earths (REs) have been added to these alloys, to further improve oxidation resistance. The improvements are in the form of reduced oxidation rates and increased scale adhesion. [1, 2] The REs 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] Application of RE oxides to metallic surfaces can be achieved by immersion in aqueous RE nitrate solutions followed by thermal decomposition of the solid nitrate to oxide. Other precursors for RE oxide coatings can be molten nitrate salts, oxide slurries, or colloidal dispersions of a hydrous oxide (sol). The sol gel technique has been shown to generate the smallest oxide particles. [5] This technique has been used to produce a range of ceramic coatings. Essentially, it is based on the use of sols, which consists of a stable dispersion in a liquid of colloidal units of hydrous oxides or hydroxides ranging in size between 2 nm to 1 μm . The sol is applied to a metallic substrate by a suitable technique, such as dipping, spin coating or electrophoresis. On drying, (removing water from the colloidal units) the sol is transformed to a gel. [5]

The use of RE oxide coatings has the advantage of not affecting adversely the mechanical properties of the alloy and has also the potential of being used on surfaces of metallic components in service and exposed to high temperature oxidizing environments. In a study of the influence of praseodymium, dysprosium and yttrium oxide gel coatings on isothermal oxidation behavior of Fe20Cr alloys, the morphology of the RE oxide gel was reported to vary with the type of RE.[6] This study also reported a direct correlation between the RE ion radius and the extent of influence on chromium dioxide growth rate.[6].

The present paper considers the influence of lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, dysprosium, yttrium, erbium and ytterbium oxide gels on the cyclic oxidation behavior of Fe20Cr alloys. Correlations have been made between the RE oxide gel morphology and RE ion radius on the cyclic oxidation resistance of the chromium dioxide forming alloy.

Methods and materials

Sols of La₂O₃, CeO₂, Pr₂O₃, Nd₂O₃, Sm₂O₃, Gd₂O₃, Dy₂O₃, Y₂O₃, Er₂O₃, and Yb₂O₃, were prepared as aqueous dispersions of the respective rare earth 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. Fe-20Cr alloy specimens 1.0 x 1.0 x 0.5 cm were ground to 400 mesh, rinsed and dried. The RE oxide sol was sprayed on the specimen to form a coat. The specimens were then heated to 150°C to form a surface layer of RE oxide gel. The specimens were oxidized for 2 hours at 900°C and cooled to room temperature. This consisted of one oxidation cycle. The specimens were weighed after each cycle and further oxidation of the specimens was discontinued when oxide spalling was observed. The surfaces of the specimens were examined before, between oxidation cycles and after the last oxidation cycle in an optical microscope coupled to an image analysis system and in a scanning electron microscopic coupled to an energy dispersive spectroscopic system.

Results and discussion

The cyclic oxidation behavior of uncoated and RE oxide coated specimens is shown in figure 1. The weight gain during oxidation is due to formation of Cr₂O₃. [6] The uncoated specimen was cycled five times before surface oxide spalling occurred. The RE oxide coated specimens were cycled many more times and the cyclic oxidation resistance varied with the RE oxide. Table I presents the total number of cycles of oxidation of specimens coated with the different RE oxides. The table also lists the ratio of the radius of the rare earth ion to the radius of the chromium ion (R_{RE}/R_{Cr}). It is evident that specimens coated with oxides of RE with R_{RE}/R_{Cr} ratios lower than 1.45 could be cycled for only half as many cycles as those coated with RE oxides that had R_{RE}/R_{Cr} ratios higher than 1.45.

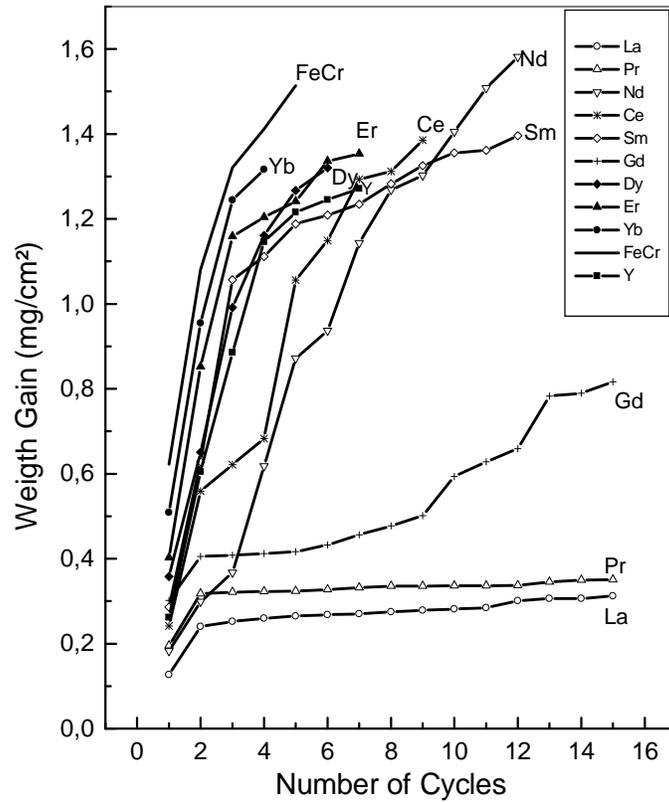


Figure 1: Weight gain versus number of cycles of oxidation of Fe-20Cr alloy without and with surface deposited RE oxide.

Table I: Total number of cycles withstood by Fe20Cr specimens coated with oxides of different rare earths and the ratios of the rare earth ion radius to the radius of chromium ion.

Rare earth element	Number of cycles	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

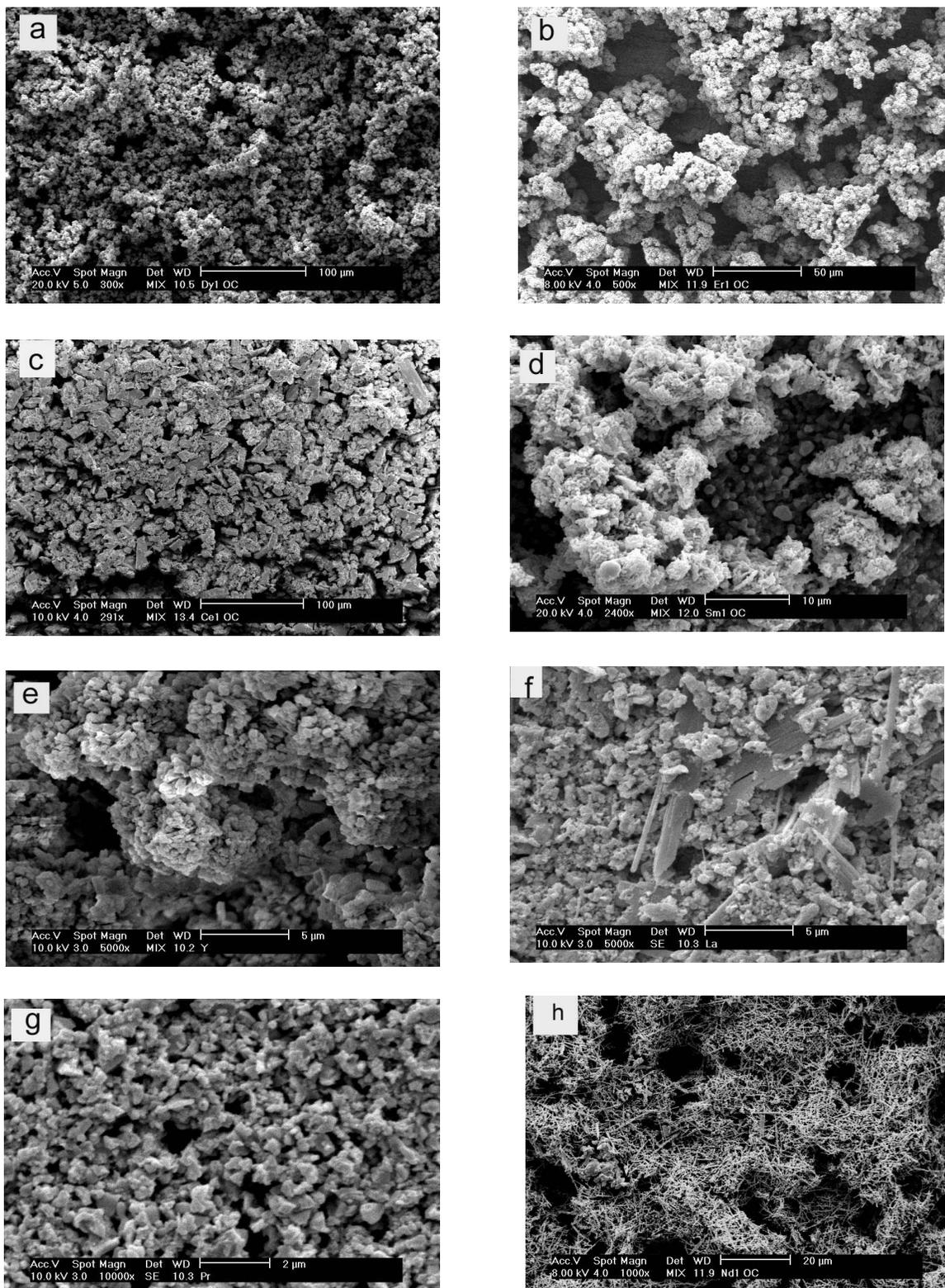


Figure 2: Scanning electron micrographs of different RE oxide gels. (a) Dy, (b) Er, (c) Ce, (d) Sm, (e) Y, (f) La, (g) Pr and (h) Nd.

Table II: Weight gain per unit area of the Fe20Cr specimens without and with RE oxide coats after 5 cycles.

Specimen coated with oxide of	Weight gain per unit area after 5 cycles
Lanthanum	0.26
Cerium	1.05
Praseodymium	0.32
Neodymium	0.87
Samarium	1.13
Gadolinium	0.41
Dysprosium	1.28
Yttrium	1.21
Erbium	1.24
Ytterbium	1.37
Uncoated	1.52

Table II presents the weight gains of the uncoated and coated specimens after 5 cycles. The overall weight gains varied quite significantly. Data from tables I and II indicate that specimens coated with certain RE oxides like Nd and Sm oxides, withstood many cycles of oxidation in spite of significant weight gains. This is contrary to expectations where in specimens that withstand a higher number of cycles of oxidation, have relatively lower weight gains. This observation suggested that increase in cyclic oxidation resistance of the Fe20Cr alloy, a chromium dioxide forming alloy, is not just dependent on the ionic radius of the rare earth in the coat.

Table III: 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

Scanning electron micrographs of the different RE oxide gels are shown in figure 2. Marked differences in the morphology of the oxides can be seen. Similar observations, with respect to morphological variations, have been reported by other authors [3]. Table III summarizes the morphological characteristics of the oxides. Comparison of data in tables III and I indicates a correlation between the morphology of the RE oxide and the cyclic oxidation resistance of the specimen coated with that RE oxide. Specimens coated 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. In the optical microscopic examinations of coated specimen surfaces, the nature of coverage was evaluated using the image analyzer. Figures 3a and 3b show the micrographs of the alloy surface covered with La_2O_3 and Yb_2O_3 . The area fractions, or coverage, of these two oxides and the other oxides were determined from image analysis

measurements. The coverage of the different oxide gels is summarized in table IV. The cyclic oxidation resistance of the alloy coated with the different RE oxides is also shown in table IV, to help correlate the two parameters. This table clearly indicates the correspondence between the extent of coverage and the cyclic oxidation resistance. The exceptions are cerium and gadolinium oxides. The influence of cerium oxide can be attributed to its valence. Cerium oxide has the formula CeO_2 where as the other rare earth oxides have the general formula RE_2O_3 .

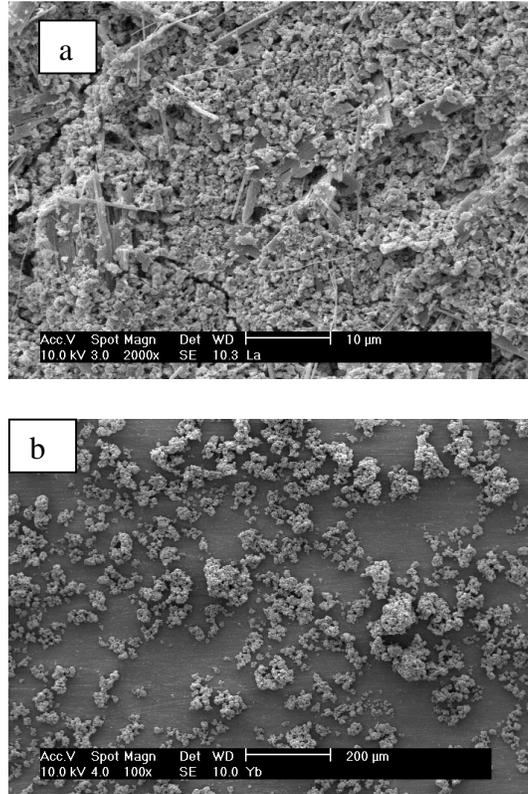


Figure 3: Alloy surface coated with (a) La_2O_3 and (b) Yb_2O_3 .

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

Rare earth element	Magnification in micrograph (microns)	Bit plane % of covered surface	Ranking of RE oxide coverage	Number of cycles
Lanthanum	2000	77.04	1	15
Cerium	200	68.60	6	9
Praseodymium	2500	72.03	2	15
Neodymium	200	97.12	3	12
Samarium	200	73.80	4	12
Gadolinium	125	71.30	8	15
Dysprosium	200	72.00	5	6
Yttrium	250	68.10	7	7
Erbium	100	55.20	9	7
Ytterbium	100	22.80	10	4

The morphology of the deposited RE oxide 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 is defined during the conversion from sol (dispersion) to gel (solid) and is maintained during subsequent oxidation.

The data presented indicate that the cyclic oxidation behavior of RE oxide coated specimens depends on the radius of the rare earth ion, the shape/size of the crystallite and the extent of coverage. Coverage in turn depends on the size and shape of the RE oxide crystallite.

Growth of chromium dioxide in RE free Fe-Cr alloys is cation driven, and the oxide scale growth takes place at the oxide/oxygen interface, due mainly to the higher mobility of Cr ions compared to the oxygen ions.[7,8] The reduced chromium dioxide growth rate in the presence of rare earths is directly linked to reduction in chromium ion mobility. Since grain boundaries are the preferred paths for ion transport in compact scales, the reduced chromium dioxide growth rate in the presence of rare earths is due to reduction in chromium ion movement along grain boundaries, caused by the presence of barriers. These barriers are the rare earth ions. Proof of this was reported earlier. [6] Similar observations were presented by Papaioacovou et. al. for scale growth on ceria coated Fe-Cr alloys.[9]

In cyclic oxidation, the Cr₂O₃ layer formed during the first cycle is influenced by the RE, in the same manner as in isothermal oxidation. The thickness of the Cr₂O₃ layer formed varies with the RE. The Cr₂O₃ and the RE oxide coat remain adherent during the first few cycles. The Cr₂O₃ layer thickness increase and RE oxide coat loss happen simultaneously. The extent of RE oxide coat loss depends on its morphology. Increase in Cr₂O₃ layer thickness is determined by the RE.

The RE ions are significantly larger than Fe or Cr ions, and their ionic radii are 1.3 to 1.65 times that of Cr. The extents to which RE elements affect oxidation rates have been found to be proportional to their sizes. [6] The larger the rare earth ion, greater its influence. It is therefore possible that fewer RE ions are needed at the oxide grain boundaries to block chromium ion movement. Direct correlation between RE ion radius and cyclic oxidation resistance has been found. This lends further proof to the mechanism by which REs influence chromium dioxide scale growth, that is, the presence of RE ions at the oxide grain boundaries effectively blocks Cr ion movement and makes thereby, anion (oxygen ion) movement predominant. Furthermore, in the case of cyclic oxidation, morphology of the RE oxide and coverage exercise marked influence.

Conclusions

1. The cyclic oxidation resistance of rare earth oxide coated Fe-20Cr alloy was significantly higher than that of the uncoated alloy.
2. The RE oxides in decreasing order of influence on cyclic oxidation of Fe20Cr alloy are: La₂O₃, CeO₂, Pr₂O₃, Nd₂O₃, Sm₂O₃, Gd₂O₃, Dy₂O₃, Y₂O₃, Er₂O₃, and Yb₂O₃.
3. The morphology of the rare earth oxide coating on the Fe-20Cr alloy surface varied with the rare earth and influenced cyclic oxidation resistance.
4. The coverage of RE oxide gel coats varied with the RE and this in turn influenced cyclic oxidation resistance.
5. Direct correlation between rare earth ion radius and cyclic oxidation resistance of Fe20Cr alloy has been observed.

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