ROLE OF RARE EARTH OXIDE COATINGS IN MITIGATING H.T. DEGRADATION OF CHROMIUM DIOXIDE FORMING ALLOYS[1]

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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. In this study the high temperature oxidation resistance of rare earth (RE) oxide coated Fe20Cr alloy was determined. Oxide gels of a number of rare earths (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), obtained by the sol-gel technique, were used to coat Fe-20Cr specimens. The cyclic oxidation resistance of the alloy increased with increase in ionic radius of the RE in the coating. Extended cyclic oxidation tests were carried out with La_2O_3 and Pr_2O_3 coated Fe20Cr alloy. In these tests the specimens were cooled from peak temperatures of 900° C, 1000° C and 1100° C at 300° C/s and 1000° C/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 chromia forming alloys is discussed.

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

PAPEL DE REVESTIMENTOS DE ÓXIDOS DE TERRAS RARAS EM REDUZIR A DEGRADAÇÃO EM TEMPERATURAS ELEVADAS DE LIGAS FORMADORAS DE DIÓXIDOS DE CROMO

Resumo

Terras raras (TR) tem sido usados para melhorar a resistência a oxidação em temperatura elevadas de ligas formadoras de óxidos de cromo e alumina. Neste estudo foram determinados a resistência a oxidação de ligas Fe-20Cr revestidos com óxidos de terras raras. Géis de diversas terras raras (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), obtidos por técnica de sol-gel, foram usados para revestir corpos de prova de Fe-20Cr. A resistência a oxidação cíclica da liga aumentou com o raio iônico da TR no revestimento. Foram realizados ensaios de oxidação cíclica prolongadas com a liga Fe-20Cr revestidos com La_2O_3 and Pr_2O_3. Nestes ensaios, as amostras foram resfriados a 300° C/s and 1000° C/s dos temperaturas de 900° C, 1000° C e 1100° C. Foi observado que revestimentos de La_2O_3 são mais eficientes em aumentar a resistência a oxidação cíclica da liga comparado com revestimento de Pr_2O_3. Neste trabalho discute-se o papel de TR em aumentar o resistência a oxidação das ligas formadoras de dióxido de cromo.

Palavras chaves: Oxido de terra rara; Revestimentos; Liga ferro-cromo; Oxidação cíclica.

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1 INTRODUCTION

Iron, nickel or cobalt based alloys are alloyed with chromium, aluminum or silicon to establish more protective oxides (scales) of chromia, alumina or silica respectively. Protective oxide scales should be non-volatile, stoichiometric, stress free at operating temperatures, adherent, and defect free. In practice, it is almost impossible to form such scales. 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 introduced into the surface by ion implantation or 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 can be applied to a metallic substrate by a suitable technique, such as dipping, spin coating or electrophoresis. Compared to adding RE to the alloy, RE oxide coatings do not affect adversely the mechanical properties of the alloy. The oxide coatings can be also used on metallic components in service and exposed to high temperature oxidizing environments. This paper presents the effect of a number of RE oxide coatings, the RE ion radius and other oxide coating features on the cyclic oxidation behavior of Fe-20Cr alloy. The mechanism by which REs improve overall oxidation resistance of chromium dioxide forming alloys is 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. Two sets of experiments were carried out. In the first set, the effect of various 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) on cyclic oxidation behavior of Fe-20Cr alloy specimens 1.0 x 1.0 x 0.5 cm was studied. These specimens were oxidized cyclically between 900°C and room temperature (RT) and each oxidation cycle consisted of 2 hours at 900°C. The cyclically oxidized specimens were weighed after each cycle and further oxidation discontinued when the scale spalled. In another set of experiments, new Fe20Cr specimens coated with La_2O_3 and Pr_2O_3 were cyclically oxidized for extended periods and a different experimental set up was used. 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.

3 RESULTS AND DISCUSSION

The morphology of the RE oxide gels varied with the nature of the RE and the main morphological features of the different RE oxides are summarized in Table 1.(6)

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

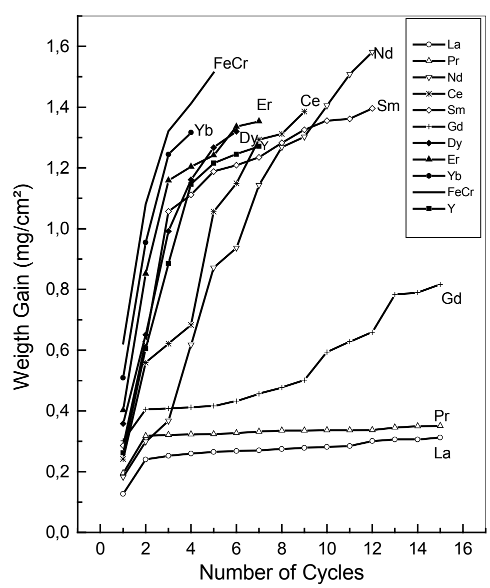

Figure 1. Weight gain versus number of cycles of oxidation of Fe-20Cr alloy without and with surface deposited RE oxide.

The results of the first set of experiments are shown in Figure 1 and Table 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 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 2. 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.

Table 2. Number of oxidation cycles withstood before spalling and the ratios of the RE ion radius to the radius of chromium ion.

Oxide of	Number of cycles at spall	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

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 $mg.cm^{-2}$. After one cycle of oxidation the weight gain of the La_2O_3 coated specimen was one quarter that of the specimen coated with Yb_2O_3. A significant part of the weight gain of specimens coated with La_2O_3 and Pr_2O_3, due to chromium dioxide growth, occurred during the first cycle of oxidation. In general, spalling of the chromium dioxide layer occurred when weight gains were above 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 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 from 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.

	Number of cycles to spalling					
Fe-20Cr specimen	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 DISCUSSIONS

The morphology of the different RE oxide gels 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.

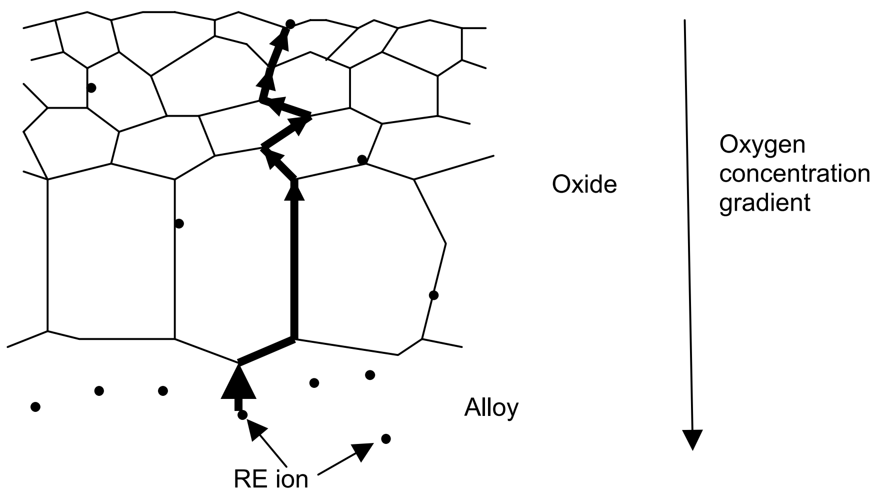

Figure 2. Schematic diagram showing RE ion diffusion along chromia scale grain boundaries.

In the case where REs are added to the alloy, the reactive elements in the alloy diffuse into the scale due to the oxygen potential gradient which extends from the gas interface into the substrate. The RE diffuses through the oxide to the gas interface. Proof of this was shown after prolonged oxidations.(8) En-route to the gas interface the RE ions first segregate to the metal-scale interface and then these RE ions follow the fastest path to the gas interface, which are the scale grain boundaries.(9-15) This is shown schematically in Figure 2. The RE oxides applied as coatings to the alloy surface is incorporated in the growing scale.(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 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 presented by Papaiacovou et. al. for 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.

5 CONCLUSIONS

1. The 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 RE oxide.
3. The COR varied with the type of RE oxide.
4. The COR of Fe-20Cr coated with La_2O_3 was significantly higher than that of the same alloy coated with Pr_2O_3.
5. The COR of La_2O_3 coated Fe-20Cr was unaffected with increase in cooling rate from 330º C/s to 1000º C/s.
6. Further evidence of a direct correlation between RE ion radius and oxidation resistance of chromia forming alloys has been observed.

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