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Role of rare earth oxide coatings on oxidation resistance of chromia-forming alloys

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Abstract Rare earths (RE) have been used to increase high temperature oxidation resistance of chromia and alumina forming alloys. The RE can be added as elements (or oxides) to the alloys or applied as oxide coatings to the alloy surface. This paper presents the effect of different RE oxide coatings and lanthanum chromite coatings on the high temperature oxidation behavior of Fe20Cr and Fe20-Cr4Al alloys. The oxidation resistance of the Fe20Cr alloy increased with increase in ionic radius of the RE element in the coating. The RE oxides decreased chromia growth rate more than alumina growth rate. In extended cyclic oxidation tests that were carried out from peak temperatures of 900 °C, 1,000 °C and 1,100 °C to room temperature at cooling rates of 300 °C/s and 1,000 °C/s, the La_2O_3 coating increased cyclic oxidation resistance of the Fe20Cr alloy significantly more than the Pr_2O_3 coating. The role of RE in increasing overall oxidation resistance of chromia forming alloys is discussed.

Introduction

Metallic materials used in high temperature environments are usually iron, nickel or cobalt based alloys. The oxides formed on these metals are not sufficiently protective above 500 °C and are therefore 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 to maintain low ionic transport, stress free at operating high temperatures to reduce scale failure, adherent, free of defects like pores and cracks to prevent short circuit transport of reactants. In practice, it is almost impossible to form such ideal scales. The use of reactive elements, especially rare earths (RE) to improve high temperature oxidation resistance of chromia 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 have been added to the alloy bulk in the form of elements or as oxide dispersions. Addition of RE to the alloy surface by ion implantation or as oxide coatings, have the same effect on alloy oxidation resistance as bulk additions [2–5]. A variety of precursors have been used to obtain RE oxide coatings on alloy 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 removal of water from the colloidal units is known to produce oxide particles in the range 2 nm–1 μm. This sol–gel technique has been used to produce a variety of ceramic coatings [6]. To obtain coatings based on this technique, 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 the potential of being used on metallic components in service and exposed to high temperature oxidizing environments.

Lanthanum chromite has been used as interconnects in solid oxide fuel cells (SOFC) [7]. In recent years, attempts to reduce SOFC operating temperature to circumvent manufacturing problems has prompted the use of metallic

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interconnects. In this context lanthanum chromite coated Fe–Cr alloy was considered a candidate interconnect material. Formation of a mixed oxide on lanthanum oxide coated chromia forming alloys has also been reported [8]. In this context the effect of lanthanum chromite coatings on the isothermal and cyclic oxidation behavior of Fe20Cr and Fe20Cr4Al alloy specimens was studied.

This paper presents the effect of different RE oxide coatings on oxidation behavior of Fe20Cr alloy and the oxidation behavior of lanthanum chromite coated Fe20Cr and Fe20Cr4Al alloy. The influence of the RE element, its ionic radius and the RE oxide coating characteristics on chromia and alumina growth are discussed. Results of extended cyclic oxidation tests performed with La_2O_3 and Pr_2O_3 coated Fe20Cr alloy specimens are also presented as further proof of the dominant role of RE ion radius in increasing the oxidation resistance of chromia forming alloys.

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. The Fe20Cr alloy specimens (1.0 × 1.0 × 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. In preliminary experiments, the Fe20Cr specimens coated with Y_2O_3, Pr_2O_3 and Dy_2O_3 were isothermally oxidized at 1,000 °C and their oxidation behavior compared with that of the uncoated specimens [9]. Subsequently the effect of various RE oxide coatings (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 Fe20Cr specimens was studied. The latter specimens were oxidized cyclically in a muffle furnace between 900 °C and room temperature (RT) and each oxidation cycle consisted of 2 h 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 (supported on a base) was moved to and fro using automatic controls. This set up enabled the specimen dwell time (in the hot and/or cold zone) and the heating/cooling rates of the specimens to be varied, by controlling the traverse speed of the furnace. The La_2O_3 and Pr_2O_3 coated specimens were cycled from 900 °C, 1,000 °C and 1,100 °C to RT at cooling rates of 330 °C/s and 1,000 °C/s.

A suspension of a powder mixture of Cr_2O_3 and La_2O_3 was sprayed on to the alloy surfaces. The $LaCrO_3$ coating was formed 'in-situ' during the oxidation tests [8]. The average coating thickness was 10–15 μm. The isothermal tests were carried out at 1,000 °C for periods of up to 200 h. In the cyclic oxidation tests, the uncoated and $LaCrO_3$ coated specimens were cycled 15 times and each cycle consisted of holding the specimens at 1,000 °C for 7 h followed by cooling to RT.

The cyclic oxidation test specimens 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 varied with the RE. The main morphologies of the oxides were cubes, rods, cuboids, needles, clusters and platelets and these are summarized in Table 1 [10].

The weight gain versus time curves of the uncoated and RE oxide coated Fe20Cr specimens oxidized at 1,000 °C in the thermogravimetric analyzer are shown in Fig. 1. The weight gains were due mainly to chromia formation and this was detected by XRD analysis. The oxidation rate of RE oxide coated specimens was lower, as expected, than that of the uncoated specimens. The parabolic rate constants of the two types of specimens at 1,000 °C are given in Table 2 and it can be seen that the oxidation rates of the coated specimens decreased by one order of magnitude.

The results of the cyclic oxidation tests carried out with Fe20Cr specimens coated with the different RE oxides are shown in Fig. 2 and Table 3. The uncoated specimen was cycled five times before the surface oxide 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 morphology of the oxides and the extent to which the oxide covered the surface also affected COR [10]. The number of cycles to scale spalling of 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 can be seen 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. This indicates that the ionic radii of the RE influenced the rate of oxidation of the chromia forming alloy.

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

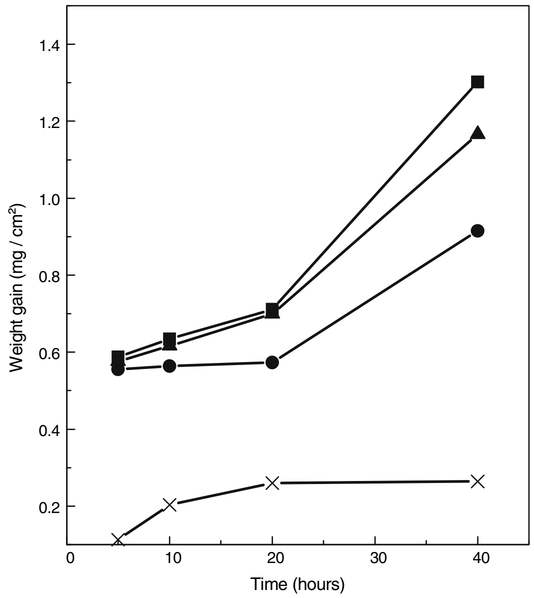

Fig. 1 Weight gain curves of uncoated and RE oxide coated Fe20Cr specimens oxidized at 1,000°C. ■ uncoated; •Y_2O_3 coated; +Pr_2O_3; ▲Dy_2O_3

Table 2 Parabolic rate constants (K_p) for chromia growth at 1,000 °C on uncoated and RE oxide coated Fe20Cr specimens

Fe20Cr specimen coated with	K_p ($mg^2\ cm^{-4}\ h^{-1}$)
–	1.84×10^{-3}
Y_2O_3	1.13×10^{-3}
Dy_2O_3	9.5×10^{-4}
Pr_2O_3	7.9×10^{-4}
CeO_2	7.6×10^{-4}
La_2O_3	7.29×10^{-4}
Nd_2O_3	7.32×10^{-4}

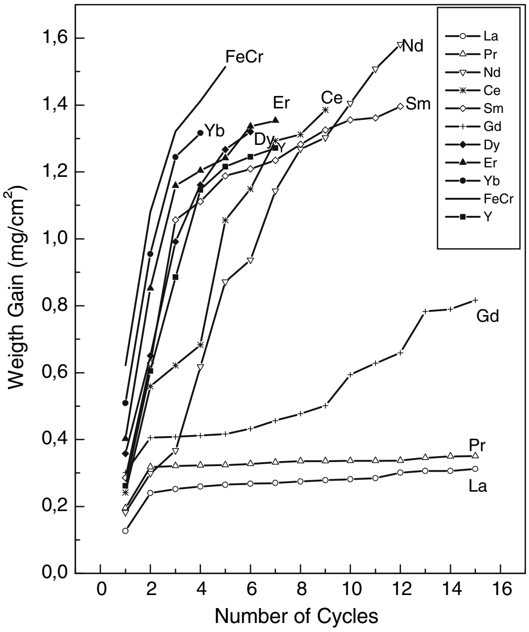

Fig. 2 Weight gain versus number of cycles of oxidation of uncoated and RE oxide coated Fe20Cr alloy specimens

The chromia 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 approximately 0.17 mg cm^{-2}, signifying that most of the weight gain due to chromia growth occurred during the first cycle of oxidation and further oxide growth during the subsequent oxidation cycles was stifled or was extremely low. In general, spalling of the chromia layer on specimens coated with the other RE oxides occurred when weight gains were above a certain value, in the range 1.25–1.5 mg cm^{-2}. This corresponds to a chromia scale thickness at which the thermal and growth stresses caused cracks in the scale or at the scale-metal interface. This also indicated that the time at temperature to reach the limiting weight gain (or scale thickness) varied with the nature of RE. To evaluate further the influence of the two most efficient RE oxides, namely La_2O_3 and Pr_2O_3, another series of extended cyclic oxidation tests were carried out. The results of these tests are shown in Table 4.

Table 3 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

Table 4 Cyclic oxidation resistance of uncoated, La_2O_3 coated and Pr_2O_3 coated Fe20Cr specimens

Fe20Cr specimen	Number of cycles to spalling					
	Low cooling rate (330 °C/s)			High cooling rate (1000 °C/s)		
	900 °C	1,000 °C	1,100 °C	900 °C	1,000 °C	1,100 °C
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

The COR of both the uncoated and La_2O_3 or Pr_2O_3 coated specimens decreased with increase in the peak temperature. This is due to higher oxidation rates at the higher temperature. Consequently, the limiting scale thickness was attained in less time at the higher temperature. This behavior did not change with cooling rate. The La_2O_3 coated specimens that were cooled at the low and high cooling rates from 900 °C could be cycled for over 100 and 47 cycles respectively. The Pr_2O_3 coated specimens could be cycled for only 15 and 11 cycles under identical conditions, indicating significantly lower COR. Increase in peak temperature from 900 °C to 1,000 °C decreased the COR of La_2O_3 coated specimens by approximately 33%. A further increase in peak temperature to 1,100 °C decreased COR of the La_2O_3 coated specimens by a further 33%. This is due mainly to the higher rate of chromia scale formation at the higher temperature. The overall COR of La_2O_3 coated Fe20Cr did not alter with increase in cooling rate from 330 °C/s to 1,000 °C/s. This indicated that the thermal stresses generated in the scale during cooling from the two temperatures, even though different, along with the scale growth stresses were well within the stress value necessary to cause scale spallation.

The weight gain curves of uncoated and $LaCrO_3$ coated Fe20Cr and Fe20Cr4Al alloys exposed for 200 h at 1,000 °C are shown in Fig. 3. The oxides formed on these two alloys were mainly chromia and alumina respectively, as determined by XRD [8]. The curves in this figure also reveal that the effect of RE coating on the chromia forming Fe20Cr alloy was significantly more than on alumina forming Fe20Cr4Al alloy. The scales formed on both the isothermally and cyclically oxidized specimens did not spall.

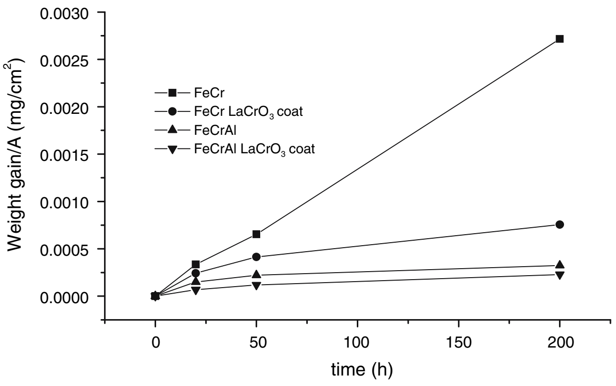

Fig. 3 Oxidation curves of uncoated and $LaCrO_3$ coated Fe20Cr and Fe20Cr4Al alloy specimens

The cross sections of $LaCrO_3$ coated Fe20Cr and Fe20Cr4Al specimens oxidized for 200 h at 1,000 °C are shown in Figs. 4a and b respectively. The EDS and XRD measurements revealed the grey oxide layers on Fe20Cr and Fe20Cr4Al to be Cr_2O_3 and α-Al_2O_3 respectively [8]. The Cr_2O_3 layer was about 3.5 μm thick and revealed embedded particles from the coating. The α-Al_2O_3 layer was much thinner than the chromia layer on Fe20Cr alloy formed under identical conditions and was <1 μm. This further indicated the marked influence of La_2O_3 on chromia growth compared to alumina growth.

General discussion

In cyclic oxidation, the oxide layer formation during the first cycle is identical to that during isothermal oxidation. In the initial or transient stage of oxidation, metastable oxides of the base metals, such as iron oxide, form on the alloy surface. The effects of RE on scale growth are not evident at this stage. The effect is noticeable only after this stage. Published literature shows enough evidence that the overall effect of RE additions on chromia and alumina growth are the same, independent of the nature of addition, be it to the alloy or the surface of the alloy [8, 11]. Consequently, many of the reasons that have been put forth to explain the reactive element effect when the RE is added to the alloy are valid when the alloy surface is doped with RE. In the case of RE addition to the alloy the RE diffuses into the scale due to the oxygen potential gradient which extends from the gas interface into the substrate. The RE has been shown to diffuse as RE ions through the oxide scale to the gas interface after prolonged oxidations [11]. It has also been shown that en-route to the gas interface, the RE ions first segregate to the metal-scale interface and then

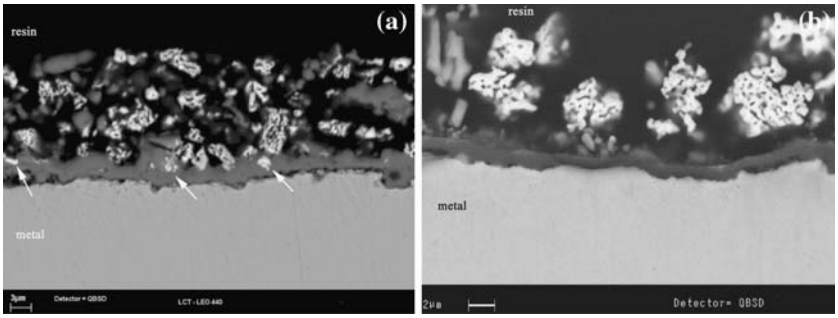

Fig. 4 Cross sections of $LaCrO_3$ coated specimens after 200 h at 1,000 °C. (**a**) Fe20Cr; (**b**) Fe20Cr4Al

these RE ions follow the fastest path to the gas interface, which are the scale grain boundaries [12–17]. This process is shown schematically in Fig. 5. In the case of RE oxide coatings to alloy substrates, some of the RE oxide gets incorporated in the growing scale as observed in this study. Once incorporated in the chromia or alumina scale the RE ions segregate to grain boundaries in the oxide scale due to driving forces acquired by it as a result of its larger ionic radius [8]. The presence of the RE ion at the oxide scale grain boundaries results in 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 slow diffusion of the large RE ions. The slow moving RE ions block or impede the movement of chromium or aluminium ions along the grain boundaries in chromia and alumina forming alloys respectively [9, 11]. The higher oxidation resistance of La_2O_3 coated Fe20Cr compared with the Pr_2O_3 coated or with any other RE oxide Fe20Cr alloy lends proof to the effect of the RE ion size. That is, larger the RE ion, slower is its diffusion along the oxide grain boundaries. It is well known that oxide growth on metallic surfaces is due to transport of anions, such as oxygen, to the M/MO interface and alloy cations to the MO/O interface. The fact that Cr ion movement along grain boundaries is blocked or decreased markedly by the slower moving RE ion, also along the scale grain boundaries, results in the oxygen ion transport becoming the new rate limiting step. The time taken to form the limiting chromia layer thickness on the Fe20Cr alloy coated with RE oxide with large RE ions is significantly longer. During this period the scale formed is thin, more plastic, more adherent to the alloy and therefore more capable of withstanding thermal and scale growth stresses. Similar observations were presented by Papaiacovou et al. for scale growth on cerium oxide coated Fe–Cr alloys [18]. Inhibition of the outward transport of alloy cations also results in a reduction in the parabolic rate constant as observed in this study and elsewhere [8, 11].

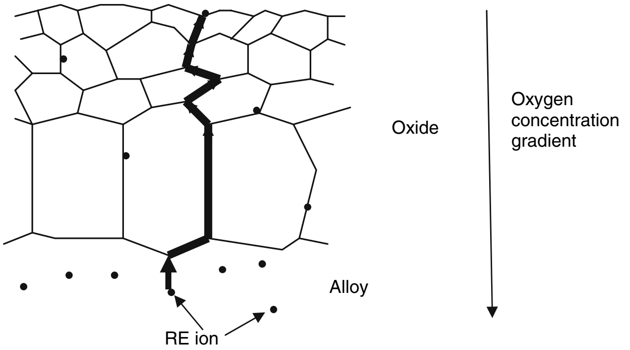

Fig. 5 Schematic diagram showing RE ion diffusion along chromia scale grain boundaries [11]

The second effect is reduction in oxide scale grain growth and this is due to a solute-drag effect of the RE ions that are at the scale grain boundaries [19]. This has been observed as small grained oxides on RE oxide coated alloy compared with that formed on the uncoated alloy. This is considered to also result in higher scale plasticity [20].

Conclusions

1. The cyclic oxidation resistance (COR) of RE oxide coated Fe20Cr alloy was significantly higher than that of the uncoated alloy.
2. The thickness of the chromia layer on RE oxide coated Fe20Cr alloy varied with the RE oxide.
3. Spalling of the chromia scale occurred when mass gain due to scale formation reached a limiting value of 1.25–1.5 mg cm^{-2}.
4. The COR of Fe20Cr coated with La_2O_3 was significantly higher than the Pr_2O_3 coated alloy and this was unaffected by increase in cooling rate from 330 °C/s to 1,000 °C/s.
5. Evidence of a direct correlation between RE ion radius and oxidation resistance of RE oxide coated Fe-20Cr alloy has been observed.
6. The RE oxide coatings decreased chromia growth rate more than alumina growth rate.

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