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Effect of nanocrystalline mixed rare earth oxide coatings on the high temperature oxidation behavior of Fe20Cr5Al alloy

Stela M.C.Fernandes^a, Olandir V.Correa^b, Lalgudi V.Ramanathan^c

Abstract

Rare earths (RE) have been used to improve high temperature oxidation resistance of chromium dioxide and alumina forming alloys. The RE can be added to the alloy as elements or as oxide to form dispersions. It can also be applied as a RE oxide coating to the surface of the alloy. In this investigation the sol-gel technique was used to prepare sols of the RE oxides as it produces nanocrystalline oxide particles. In an effort to increase further the oxidation resistance of high temperature alloys, optimization of RE oxide additions to the alloy surface has been attempted. This paper presents the effect of nanocrystalline oxide gel coatings of CeO₂, Nd₂O₃, Pr₂O₃, CeO₂ + Nd₂O₃, CeO₂ + Pr₂O₃ and Pr₂O₃ + Nd₂O₃ on the oxidation behavior of Fe20Cr5Al alloys at 1100 °C. The individual oxides decreased oxidation rate. However, the CeO₂ + Nd₂O₃ mixture did not increase oxidation resistance of the alloy further, compared to those with either one of these two rare earth oxides. The Pr₂O₃ + CeO₂ mixture increased oxidation resistance of the alloy markedly where as the mixture Nd₂O₃ to Pr₂O₃ had no significant effect. The differences in the influence of a specific rare earth oxide or a mixture are attributable to differences in the ionic radii of the RE and the morphology as well as the crystallite sizes of the RE oxides.

Keywords: Rare earth oxides, coating, oxidation, iron-chromium-aluminum alloy.

1. Introduction

The use of rare earths (RE) to improve high temperature oxidation resistance of chromium dioxide and alumina forming alloys is well known. The improvements in oxidation resistance are in the form of reduced oxidation rates and increased oxide scale adhesion. (1,2) The RE can be added to the alloy as an element or oxide (to form a dispersion) or applied as an oxide coating to the alloy surface. (3,4) The sol-gel technique can be used to coat alloy surfaces with RE oxides. Essentially this technique is based on the use of sols, which consists of a stable dispersion in a liquid of colloidal units of hydrous RE oxides or hydroxides. The RE oxide sol is applied to the alloy surface by a suitable technique, such as dipping, spin coating or electrophoresis. On drying, (removing water from the colloidal units) the sol is transformed into a gel of RE oxide ranging in size between 2 and 100 nm. (5) Compared to adding RE elements to the alloy to improve its oxidation resistance, RE oxide coatings do not affect

^a Dra., Pesquisadora – IPEN, São Paulo, Brazil.

^b Técnico – IPEN, São Paulo, Brazil.

^c Ph.D., Pesquisador – IPEN, São Paulo, Brazil.

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. A marked increase in isothermal and cyclic oxidation resistance of Fe-Cr alloys coated with nanocrystalline RE oxides has been observed and reported. (6,7) This increase in oxidation resistance was attributed to a combination of factors that include the ionic radius of the RE and the morphology of the RE oxide. Considering the increasing demand in recent years for even higher oxidation resistance in chromium dioxide and alumina forming alloys, attempts are in progress to optimize RE oxide coatings based on specific RE oxide cost, nanocrystallite size and morphology. In this investigation, this optimization was done in the form of simultaneous addition of different RE oxides. This paper presents: (a) the effect of surface addition of nanocrystalline oxides of different REs on the oxidation behavior of Fe₂₀Cr₅Al alloy.

2. Methodology

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. Two sets of experiments were carried out. The first set of experiments was carried out to study correlations between RE oxide morphology as well as crystallite sizes on cyclic oxidation behavior of Fe₂₀Cr alloy. In this set, Fe-20Cr alloy specimens 1.0 x 1.0 x 0.5 cm were coated with (gels of La₂O₃, CeO₂, Pr₂O₃, Nd₂O₃, Sm₂O₃, Gd₂O₃, Dy₂O₃, Y₂O₃, Er₂O₃, and Yb₂O₃) and cyclically oxidized between 900 °C and room temperature. The specimens were weighed after each cycle and oxide spalling marked the end of the test. In the second set of experiments, Fe₂₀Cr₅Al alloy specimens (2 x 2 x 3 mm) were prepared by grinding to 400 mesh, rinsing and drying. Two different procedures were used in the preparation of mixed RE oxides. The first consisted of preparing separate sols of two RE oxides followed by mixing of the sols in the proportion 50:50. In the second, the RE oxides were mixed first in the same proportion and then a sol prepared. The crystallite sizes of the different RE oxides were determined by x-ray diffraction analysis. The specimens were spray coated with sols of CeO₂, Nd₂O₃, Pr₂O₃, La₂O₃, CeO₂ + La₂O₃, CeO₂ + Pr₂O₃, CeO₂ + Nd₂O₃, Pr₂O₃ + La₂O₃ and Nd₂O₃ + La₂O₃. All the coated specimens were heated to 150 °C to form a 10 μm thick surface layer of the RE oxide gel. The uncoated and coated specimens were isothermally oxidized at 1100 °C in a thermogravimetric analyzer for about 450 min. The weight gain per unit area versus time curves was plotted. The surfaces of all the specimens were 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 most of the RE oxide gels are shown in figure 1 and the main morphological features and the crystallite sizes of the RE oxides are given in Table 1. Marked differences in morphology of the oxides can be seen. The results of the first set of experiments are shown in Figure 2.

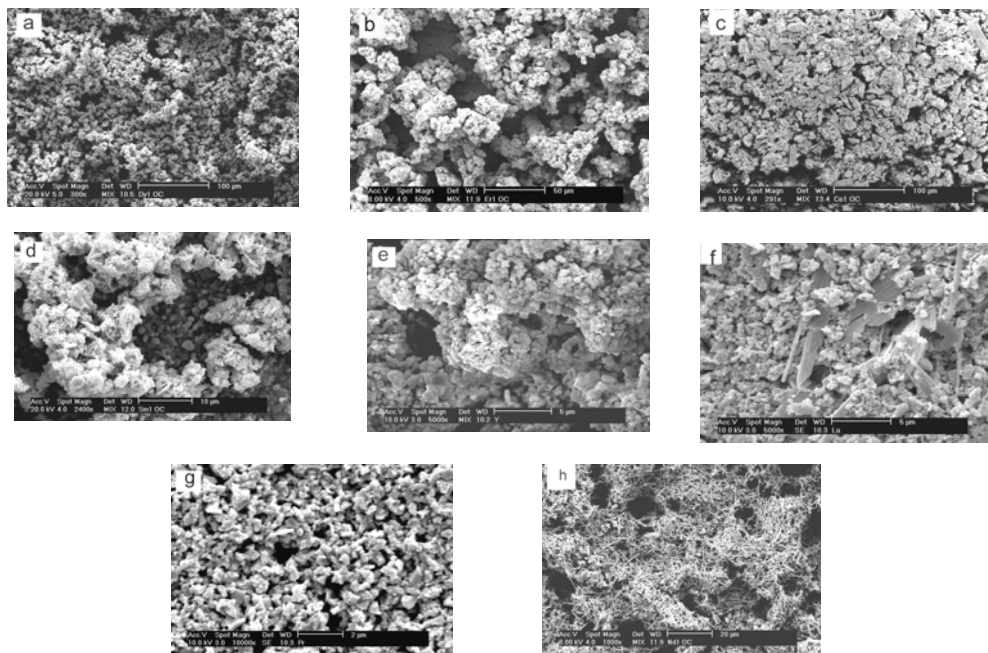


Figure 1 - Scanning electron micrographs of different RE oxides. (a) Dy, (b) Er, (c) Ce, (d) Sm, (e) Y, (f) La, (g) Pr, (h) Nd.

Table 1. Main morphological feature of the rare earth oxides and their crystallite sizes.

Rare earth oxide	Main morphological feature	Crystallite size(nm)
Lanthanum	Cubes and rods	36.4
Cerium	Cubes	58.4
Praseodymium	Cuboids	60.2
Neodymium	Fine needles, acicular	58.1
Samarium	Clusters	63.0
Gadolinium	Interlocking clusters	27.8
Dysprosium	Tiny clusters	36.6
Yttrium	Platelets	26.9
Erbium	Open clusters	36.6
Ytterbium	Clusters and disperse platelets	26.5

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 on the specimen surface. 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 $0.17 \text{ mg}\cdot\text{cm}^{-2}$. In general, spalling of the chromium dioxide layer occurred when weight gains exceeded $1.25\text{-}1.5 \text{ mg}\cdot\text{cm}^{-2}$.

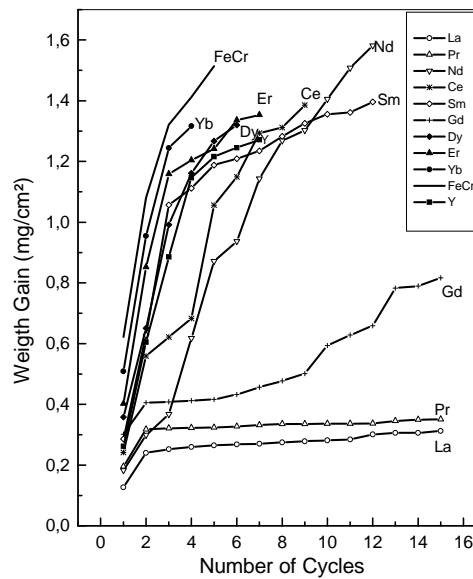


Figure 2 - Weight gain versus number of cycles of oxidation of Fe-20Cr alloy without and with surface deposited RE oxide.

This indicated that the time at temperature to reach a specific chromium dioxide layer thickness varied with the nature of RE. The COR of the Fe20Cr alloy coated with the different RE oxides is shown in Table 2. Comparison of data in Tables 1 and 2 reveals two correlations. (a) Between the morphology of the RE oxide and the COR of the specimen coated with that RE oxide. 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. (b) Between crystallite size and COR. Except for La_2O_3 , the COR of specimens coated with RE oxides (Ce, Pr, Nd, Sm) with crystallite size in the range 58-63 nm was almost double that of specimens coated with RE oxides with crystallite sizes that were almost half that of the cited RE and in the range 25-35 nm (Gd, Dy, Y, Er, Yb). That is, RE oxide with small crystallite size were not as effective as RE oxides with larger crystallite size on COR of Fe20Cr alloy.

The effect of surface additions of individual RE oxides and mixed RE oxides on oxidation behavior at 1100 °C was compared. Table 2 shows the weight gains of the Fe20Cr5Al specimens coated with the different RE oxides or mixtures. All specimens exhibited parabolic oxidation growth and due to alumina formation the oxidation rates were quite low. Hence the oxidation curves are not shown and compared but the overall weight gain as a function of specimen surface area after 450 minutes at 1100 °C.

The RE oxide gels were analyzed using x-ray diffraction analysis and Table 3 shows the results of a Ce oxide + La oxide mixture as an example.

The XRD results of the mixed RE oxides indicated oxides, nitrates and hydroxides of the respective RE. Heating the mixture of two individually prepared sols or sold of RE oxides that were mixed prior to preparing the sols revealed only oxides and hydroxides of the REs. Pr

never showed the Pr nitrate peak, where as in the as mixed sols prepared from the oxides, La, Nd and Ce showed their respective nitrate peaks.

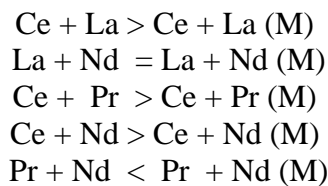
Table 2. Oxidation weight gains of RE oxide coated Fe20Cr5Al specimens after 450 min at 1100 °C.

Surface coated with oxide of	Weight gain (10^{-3} mg. mm ⁻²)
Uncoated	8.6
Ce	6.3
Nd	6.25
Pr	1.5
Ce + Nd	6.4
Ce + Pr	3.0
La + Nd	7.0
Pr + Nd	6.2
Pr + La	4.8

Table 3. Constituents in the RE oxide gels prepared by different methods and the effect of heat treatment.

Mixed RE oxide preparation procedure	Detected x-ray diffraction peaks
CeO ₂ and La ₂ O ₃ oxides were mixed and then the sol was prepared	CeO ₂ , La ₂ NO ₃ , CeNO ₃ , La(OH), Ce(OH)
The above mixed sol was heat treated at 1000 °C for 5 hours	CeO ₂ , La(OH), Ce(OH)
The CeO ₂ sol and the La ₂ O ₃ sols were prepared separately and then mixed	CeO ₂ , La ₂ O ₃ , Ce(OH), La(OH)

Abbreviating oxidation weight gain of a Fe20Cr5Al specimen coated with a sol that was prepared after the individual oxides were mixed as RE1 + RE2 and that of a specimen coated with a sol of RE1 mixed with a sol of RE2 as RE1 + RE2 (M), the following list shows which procedure to prepare RE oxide mixes was more effective in terms of increasing oxidation resistance of the alloy for a specific combination of REs.



4. General discussion

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. The crystallite size and morphology of the different RE oxide revealed marked differences. (3,7) 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, 10) When the RE ion concentration at the grain boundaries reaches a critical amount it results in the two effects. 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. 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. (11)

5. Conclusions

1. The individual RE oxides decreased oxidation rate.
2. The CeO₂ + Nd₂O₃ mixture did not increase oxidation resistance of the alloy further, compared to those with either one of these two rare earth oxides.
3. The Pr₂O₃ + CeO₂ mixture increased oxidation resistance of the alloy markedly where as the mixture Nd₂O₃ to Pr₂O₃ had no significant effect.
4. The application of mixed RE oxide sols where in the sols were prepared separately and then mixed prior to application increased oxidation resistance more than when the RE oxides were mixed and then the sol prepared.
5. The differences in the influence of a specific rare earth oxide or a mixture are attributable to differences in the ionic radii of the RE, the morphology and the crystallite sizes of the RE oxides.

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