

## **EFFECT OF SOL-GEL PREPARATION TECHNIQUE OF MIXED NANOCRYSTALLINE RARE EARTH OXIDE COATINGS ON HIGH TEMPERATURE OXIDATION BEHAVIOR OF Fe<sub>20</sub>Cr<sub>5</sub>Al ALLOY.**

S.M.C.Fernandes, O.V.Correa, L.V.Ramanathan

Instituto de Pesquisas Energéticas e Nucleares

Av. Prof. Linus Prestes 2242, Cidade Universitária, 05508-000 São Paulo.

[Lalgudi@ipen.br](mailto:Lalgudi@ipen.br)

### **ABSTRACT**

Rare earth (RE) oxide coatings improve high temperature oxidation resistance of chromium dioxide and alumina forming alloys. Further increase in oxidation resistance is considered to be possible through optimization of the RE oxide coating. This optimization was attempted by varying the sol-gel preparation route as well as the use of mixed RE oxides. Two routes were used to prepare mixed RE oxides: (1) sols of specific RE oxides were prepared first and then mixed; (2) two RE oxides were mixed first followed by preparation of the sol. This paper presents the microstructural features of the different nanocrystalline RE oxides and the isothermal oxidation behavior of uncoated and coated specimens. Mixed oxides prepared by Route-2 was more effective in increasing alloy oxidation resistance compared with those prepared using Route-1. The differences in influence of a specific rare earth oxide or a mixture is presented.

Keywords: rare earth oxides, coating, oxidation, iron-chromium-aluminium alloy.

### **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. This technique results in oxides ranging in size between 2 and 100 nm. (5) 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 prepared using two routes. The effect of surface addition of nanocrystalline oxides of different REs on the oxidation behavior of Fe<sub>20</sub>Cr<sub>5</sub>Al alloy was determined.

## **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. Specimens (2 x 2 x 3 mm) of the Fe<sub>20</sub>Cr<sub>5</sub>Al alloy were prepared by grinding to 400 mesh, rinsing and drying. Two routes were used to prepare mixed RE oxides. Route-1 consisted of preparing separate sols of two RE oxides followed by mixing of the sols in the proportion 50:50. In Route-2 the RE oxides were mixed first in the same proportion and then a sol of the mixture prepared. The crystallite sizes of the different RE oxides were determined by x-ray diffraction analysis. The specimens were spray coated with sols of CeO<sub>2</sub>, Nd<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> + La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> + Pr<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> + Nd<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub> + La<sub>2</sub>O<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub> + La<sub>2</sub>O<sub>3</sub>. 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).

## RESULTS AND DISCUSSION

The morphology 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.

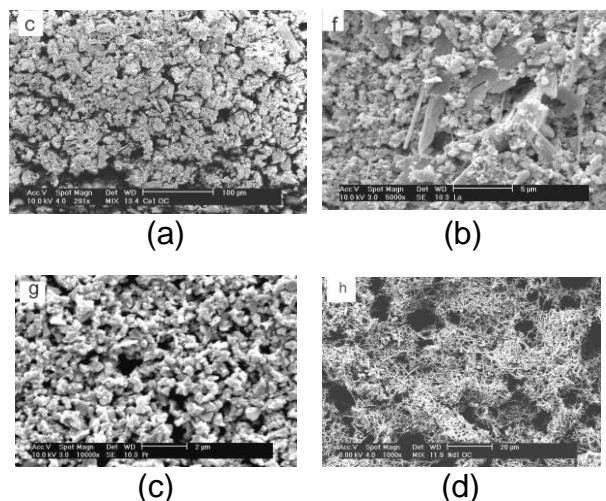


Figure 1 - Micrographs of (a)  $\text{CeO}_2$ , (b)  $\text{La}_2\text{O}_3$ , (c)  $\text{Pr}_2\text{O}_3$ , (d)  $\text{Nd}_2\text{O}_3$ .

**Table 1. Morphology and crystallite sizes of the rare earth oxides**

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

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. This table reveals that in the presence of Nd oxide, either as a single oxide or mixed with another RE oxide, the extent of oxidation did not decrease markedly. However in the presence of Pr oxide, a marked increase in oxidation resistance of the alloy was observed.

**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 <sup>-2</sup> )
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

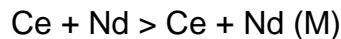
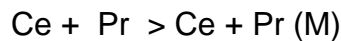
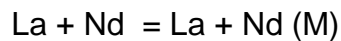
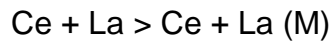
**Table 3. Constituents in mixed RE oxide gels**

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

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 sols 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. The higher oxidation resistance of the specimen coated with a Pr containing oxide could be attributed to the absence of nitrate in the sol.

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. In most of the cases, the route that involved mixing of the RE oxides followed by preparation of the sol was more effective compared mixing of sold of the individual RE oxides.



## 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)

## CONCLUSIONS

1. The individual RE oxides decreased oxidation rate.
2. The  $\text{CeO}_2 + \text{Nd}_2\text{O}_3$  mixture did not increase oxidation resistance of the alloy further, compared to those with either one of these two rare earth oxides.
3. The  $\text{Pr}_2\text{O}_3 + \text{CeO}_2$  mixture increased oxidation resistance of the alloy markedly where as the mixture  $\text{Nd}_2\text{O}_3$  to  $\text{Pr}_2\text{O}_3$  had no significant effect.
4. The application of mixed RE oxide sols where in the two RE oxides were mixed first followed by preparation of the sol was more effective in increasing the oxidation resistance of the alloy compared to when sols were prepared separately and then mixed prior to application.

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