

ROLE OF RARE-EARTH ELEMENTS ON HIGH TEMPERATURE OXIDATION BEHAVIOR OF Fe–Cr, Ni–Cr and Ni–Cr–Al ALLOYS

L. V. RAMANATHAN

Comissao Nacional de Energia Nuclear, Instituto de Pesquisas Energeticas e Nucleares, C.P. 11049, Cidade Universitaria, 05508 Sao Paulo, Brazil

Abstract—The influence of rare-earth elements (REEs) on oxidation behavior of Fe–Cr–Ni, Fe–Cr and Ni–Cr alloys has been studied and the role of REEs on oxidation behavior of chromia forming alloys discussed. The REEs were (a) applied superficially to Fe–18Cr–8Ni (AISI 304) and Fe–25Cr–20Ni (AISI 310) alloys, and (b) added as alloying additions or as oxide dispersions to Fe–20Cr and Ni–20Cr alloys. Superficial application of rare-earth oxides (REOs) and concentrates of Y and Ce improved the isothermal and cyclic oxidation resistance of the low Cr alloys, but not that of the high Cr alloy. The oxides of Y, Ce, Nd, La, Sm and Gd influenced oxidation resistance in decreasing order. The addition of 0.1% Ce and Y as well as 1% CeO₂ or Y₂O₃ as dispersoids to Fe–Cr and Ni–Cr alloys improved their oxidation resistance and the alloy with Al and Y was found to be the most resistant. In the presence of Y or Ce (as alloying addition or as oxide on the surface) the oxide formed on the surface was convoluted and fine grained chromia. The increase in oxidation resistance of chromia forming alloys in the presence of REEs is due to changes in the cation diffusion process. This is brought about by segregation of REEs to the grain boundaries of the scale, and consequent variations in ionic defect concentrations.

INTRODUCTION

THE ADDITION of low levels (0.1%) of certain oxygen reactive elements such as rare-earths to alloys used in high temperature oxidative atmospheres, has been known to reduce oxidation rates and increase scale adhesion. Various explanations have been put forth to account for the beneficial effects of active metal addition. These include: (a) mechanical keying through formation of oxide pegs into the alloy;^{1–4} (b) promotion of preferential cationic or anionic diffusion in the scale and thus inducing the formation of oxide at one preferential interface;^{5–10} (c) formation of graded oxide or interlayers containing the reactive element;^{11,12} (d) reduction in accumulation of voids at the alloy/scale interface;^{3,13–16} (e) enhancement of scale plasticity by modification of the structure^{17,18} and (f) inhibition of segregation of sulphur to the alloy/scale interface.¹⁹ Some of these explanations have been verified for specific alloys doped under specific conditions. In most of the investigations the rare-earth elements (REEs) have been added either in metallic form or as oxides to the alloy.^{20,21} In some investigations REEs have been introduced into the surface by ion implantation techniques or applied to the surface using various techniques.^{7–10,22–27} Application of REEs as oxides to alloy substrates has the advantage of not altering the microstructure of the substrate. This paper presents the main results of an investigation where the superficial application of various rare-earth oxides (REOs) to Fe–Cr–Ni alloys and addition of rare-earths in metallic form or as oxides to Fe–Cr and Ni–Cr alloys on oxidation behavior has been studied, and discusses the role of REEs on oxidation behavior of chromia forming alloys.

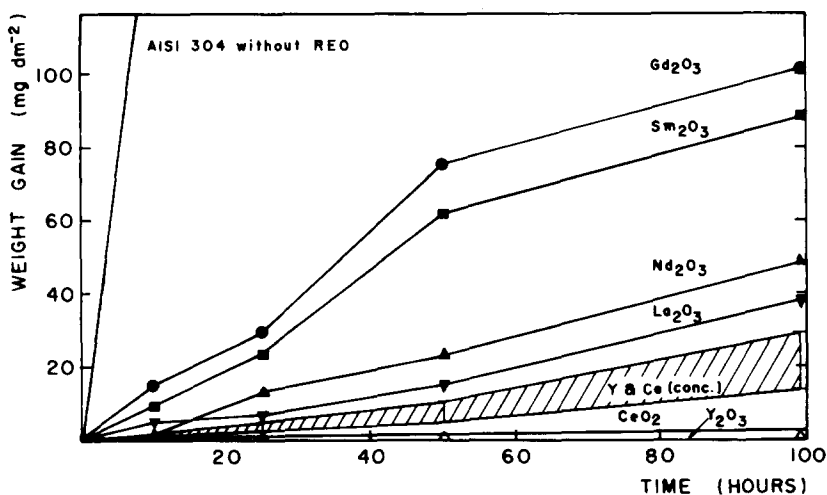


Fig. 1. Isothermal oxidation behavior of Fe-18Cr-8Ni (AISI 304) with superficially applied rare-earth oxides at 1000°C.

EXPERIMENTAL METHOD

Preliminary experiments were carried out to establish (a) the method for applying rare-earth oxides to metallic substrates and (b) the substrate preparation procedure.²⁸ On the basis of these tests, specimen preparation procedure consisted of grinding to 400 grit followed by rinsing, degreasing and drying. The REO was applied by heating the specimen to 200°C followed by immersion in saturated rare-earth nitrate solutions and drying at 200°C for 10 min. A number of sets of experiments were carried out.

(1) Oxides of Ce, La, Gd, Nd, Sm and Y as well as concentrates of Ce (40%) and Y (80%) were applied to surfaces of specimens 10 × 10 × 3 mm of Fe-18Cr-8Ni (AISI 304) and Fe-25Cr-20Ni (AISI 310) alloys. These specimens were isothermally oxidized in air at 900 and 1000°C for up to 100 h.

(2) Specimens covered with oxides of Nd, La, Ce and Y were tested for cyclic oxidation resistance. Each cycle consists of 6 h at 1000°C followed by cooling to 25°C.

(3) The conjoint influence of Si and REO on oxidation behavior of Fe-Cr-Ni alloy was studied. In this test, CeO₂ was superficially applied to Fe-18Cr-8Ni alloys containing 0.6 to 4.7 wt% Si, and the oxidation behavior at 1000°C in air for 20 h verified.

(4) The effect of REE and REO addition to various alloys on oxidation behavior was also studied. Alloys of Fe-20Cr, Ni-20Cr and Ni-20Cr-2Al containing (a) 0.1% Ce and Y were prepared by vacuum induction melting and (b) 1% CeO₂ and Y₂O₃ dispersoids were prepared by cold compaction from elemental powders and sintered. The alloys were subsequently homogenized in vacuum at 1000°C for 20 h, 2 mm thick specimens cut, ground, rinsed, dried and oxidized in air at 1000°C for 20 h.

In all experiments, oxidation kinetics were determined by weight gain measurements. The surface morphology of the oxidized specimens was examined by SEM coupled to a quantitative EDS system.

EXPERIMENTAL RESULTS AND DISCUSSION

Superficial addition of rare-earth oxides

The oxidation behavior of Fe-18Cr-8Ni covered with REO and Ce and Y concentrates at 1000°C are shown in Fig. 1. Straight lines have been used to join the points as the measurements were discontinuous. Superficial application of REO reduced the extent of oxidation and Y and Ce oxides resulted in highest overall oxidation resistance. The Y and Ce concentrates also reduced the extent of oxidation. The reduced influence of the concentrates is due to the presence and distribution of the other RE elements with reduced and/or detrimental influence on alloy oxidation. The oxides of La, Nd, Sm and Gd influenced oxidation rates to lesser

extents and in decreasing order. From the isothermal oxidation curves of the REO covered Fe–18Cr–8Ni and Fe–25Cr–20Ni, it was observed that the influence of REO on oxidation of AISI 304 is quite marked whereas that of AISI 310 is influenced very little. This difference in behavior is attributable to the formation of a fine grained and continuous layer of Cr_2O_3 on the REO free and REO covered AISI 310.

The cyclic oxidation behavior of AISI 304 covered with oxides of Y, Ce, Nd and La is summarized in Table 1. In the presence of Y or Ce oxides, the scale is more resistant to spalling and is due mainly to the formation of thin fine grained Cr_2O_3 on the surface.

In the presence of Si, the oxidation behavior of AISI 304 at 1000°C did not vary appreciably. However, at higher temperatures, the oxidation rate decreased with increasing silicon. The superficial application of CeO_2 to these alloys did not result in any notable change in weight gains. The increase in oxidation resistance with increasing Si can be considered to be due to the presence of increasing amounts of the ferrite phase in the alloy. Since the ferrite phase is richer in Cr, it promotes the formation of a more continuous and defect free film of either Cr_2O_3 or Cr_2O_3 and SiO_2 .

Alloy addition of rare-earths

The effect of REEs and REO dispersoids in Fe–20Cr and Ni–20Cr on oxidation at 1000°C are shown in Figs 2 and 3. Ce or Y has greater influence on reducing the oxidation rate of the alloys as compared to CeO_2 or Y_2O_3 dispersoids. In either form (elemental or as oxides) Y influenced oxidation rate more than Ce. In the presence of 2% Al and 0.1% Y the alloy Ni–20Cr exhibited the highest overall oxidation resistance. Similar results were reported by Nagai *et al.*²¹

Oxide morphology

The outer oxide surface on RE free Fe–18Cr–8Ni oxidized for 20 h at 1000°C revealed spikes of iron rich oxide (Fig. 4a), whereas close to the M/MO interface a fine grained structure was seen. Often the REO added to the alloy surface was observed on the outer oxide surface indicating that they were pushed outwards by the growing scale. The marked improvement in the overall oxidation behavior upon addition of Y, Ce or Nd is due to the formation of fine convoluted and relatively thin Cr_2O_3 on the alloy surface as shown in Fig. 4(b). On Fe–25Cr–20Ni similar convoluted Cr_2O_3 was observed even in the absence of REE. The oxide formed on

TABLE 1. CYCLIC OXIDATION RESISTANCE OF RARE-EARTH OXIDE COATED Fe–18Cr–8Ni (AISI 304). EACH CYCLE CONSISTED OF 20 h AT 1000°C. S—SPALLING; NS—NO SPALLING

Rare-earth oxide	Specimen after cycle					
	1	2	3	4	5	6
Y	NS	NS	NS	NS	S	S
Ce	NS	NS	NS	S	S	S
La	NS	S	S	S	S	S
Nd	S	S	S	S	S	S

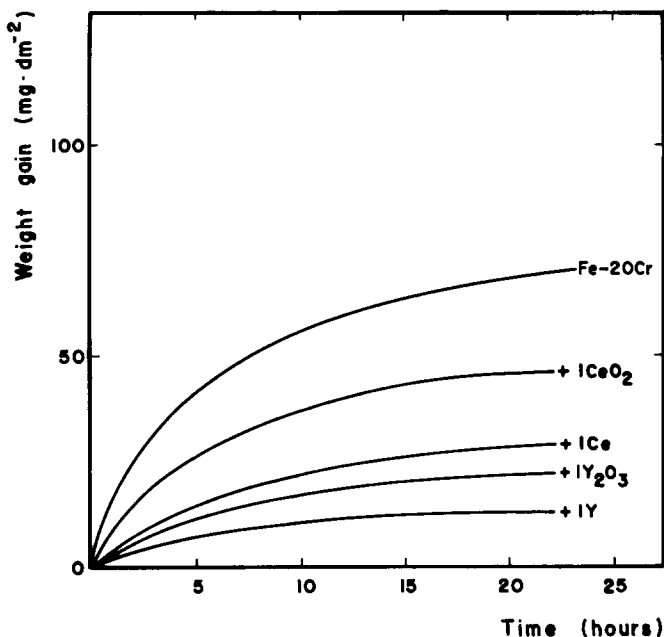


FIG. 2. Isothermal oxidation curves of Fe-20Cr at 1000°C with and without alloy additions of rare-earth elements and oxides.

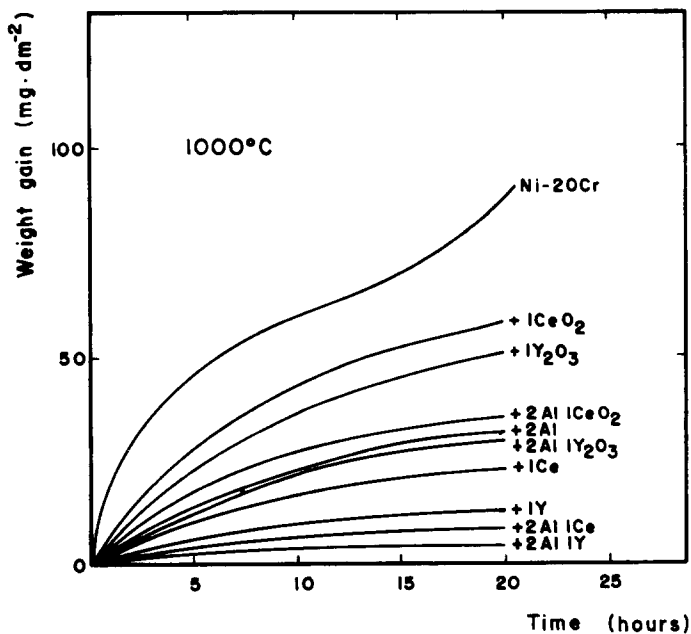


FIG. 3. Isothermal oxidation curves of Ni-20Cr at 1000°C with and without alloy additions of rare-earth elements and oxides.



FIG. 4. Scanning electron micrographs of AISI 304 specimens oxidized at 1000°C for 20 h: (a) outer oxide surface on REO free specimen, (b) convoluted oxide on Nd_2O_3 covered specimen, (c) outer oxide on cerium concentrate covered specimen.

alloys covered with Y and Ce concentrates revealed both iron oxide spikes and rounded Cr oxides as shown in Fig. 4(c). This is due to the presence of other REEs in the concentrate which have varying influence on oxide growth rate and morphology. Scanning electron microscopy of metal/oxide sections revealed oxide intrusions into the alloy and internal oxides. The improved adhesion of the surface scales to the substrate in the presence of REE may be attributed to formation of intrusions, convolutes and finer grain size. In Si containing alloys an inner Si rich layer was observed. Similar results were observed for the Al containing Ni–20Cr alloys. The morphology of the surface oxide on Ni–20Cr alloys with and without REE was fine grained Cr_2O_3 , especially on specimens oxidized for sufficiently long times.

GENERAL DISCUSSION

Superficial application of REOs to Fe–18Cr–8Ni alloy improves the overall oxidation resistance. The REEs in increasing order of influence on the oxidation behavior are Gd, Sm, Nd, La, Ce and Y. The scale formed on (a) the Y_2O_3 covered alloy consisted of a thin layer of fine grained chromia, (b) the CeO_2 covered alloy, predominantly chromia with some iron oxide and (c) the other REO covered alloys, mostly chromia with increasing amounts of iron oxide. The morphology and thickness of the scales on both REO covered as well as REO free Fe–25Cr–20Ni were similar. Hence, superficial application of REO exercised greater influence on the oxidation behavior of low Cr alloy. Although a significant part of the superficially applied REO was found at the scale/gas interface, the modifications in the scale characteristics can be attributed to the REOs. These not only acted as the scale nucleation sites, as evidenced by the fine grained scale, but were also found in the growing chromia scale.²⁷ The surface applied REO entrapped in the scale influences scale growth in the same manner as when REO dispersoids or REEs were added to the alloy. The REOs in the scale have been shown to form spinels (depending on their solubility) followed by dissociation to the RE ion and its segregation to the scale grain boundaries (g.b.s).⁸ The segregated RE ions alter outward cation movement and cause changes in the oxidation behavior of chromia and possibly alumina forming alloys.^{6,7,29} On Y implanted Cr and Co–Cr alloys, the accumulation of Y at the scale g.b. has been shown to reduce the outward diffusion of Cr ions along g.b., even to the extent of making the inward diffusion of O^{2-} ions the predominant process.^{7–10} The exact mechanism by which Cr ion diffusion is hindered by REE at g.b.s is as yet not clear. The formation of segregant–defect pairs near g.b.s and consequent increase in the activation energy for cation diffusion is a probable mechanism.⁷ The reduced influence of certain REOs like Gd_2O_3 and Sm_2O_3 on chromia scale formation can be attributed to limited segregation of Gd/Sm ions to the scale g.b.s and availability of sufficient cation defects near g.b.s for scale growth. The morphology of the scale formed on Ce and Y concentrate covered Fe–18Cr–8Ni alloy varied from one region to another. This behavior can be explained to be due to the incorporation of different REO from the concentrate into the scale, and consequent differences in the segregated RE ions at the scale g.b. This in turn results in different cation defect concentration from one region of the scale to another. Hence, the manner in which REEs affect chromia scale growth is by segregation to g.b.s followed by alteration of the defect concentration near g.b.s for chromium ion diffusion.

Increased adhesion of the scale is probably due to a combination of effects which

include (a) mechanical keying at the troughs of the convolutes, and by the oxide intrusions into the alloy and (b) reduced oxide grain size and thereby increased plasticity.

CONCLUSIONS

(1) Superficial application of REO and concentrates of Y and Ce to AISI 304 stainless steel improves oxidation resistance.

(2) Cerium and yttrium oxides resulted in highest isothermal and cyclic oxidation resistance. They promote the formation of convoluted and fine grained chromium oxide on AISI 304 SS surface.

(3) The oxidation behavior of Si containing Fe-18Cr-8Ni alloy was not affected by superficially applied CeO₂.

(4) The addition of 0.1% Ce or Y or 1% of their oxides as dispersions to Fe-20Cr and Ni-20Cr alloys improved the oxidation resistance of these alloys. The Ni-20Cr alloy containing both Al and Y exhibited the highest overall resistance.

(5) The increase in oxidation resistance of chromia forming alloys in the presence of REEs, either in the alloy or on the surface, is brought about by segregation of REEs to the scale grain boundaries, and consequent reduction in chromium ion diffusion along grain boundary cation defects.

REFERENCES

1. J. M. FRANCIS and W. H. WHITLOW, *Corros. Sci.* **5**, 701 (1965).
2. I. KVERNES, *Oxid. Metals* **6**, 45 (1973).
3. C. S. GIGGINS, B. H. KEARN, F. S. PETIT and J. K. TIEN, *Metall. Trans.* **5**, 1685 (1974).
4. G. C. WOOD, J. A. RICHARDSON, M. G. HOBBY and J. BONSTEAD, *Corros. Sci.* **9**, 659 (1969).
5. J. G. SMEGGIL, *Mater. Sci. Engng* **87**, 261 (1987).
6. G. J. YUREK, K. PRZYBYLSKI and A. J. GARRATT-REED, *J. electrochem Soc.* **134**, 2643 (1987).
7. K. PRZYBYLSKI, A. J. GARRETT-REED and G. J. YUREK, *J. electrochem Soc.* **135**, 509 (1988).
8. K. PRZYBYLSKI and G. J. YUREK, *J. electrochem Soc.* **135**, 517 (1988).
9. C. M. COTELL, G. J. YUREK, R. J. HUSSEY, D. F. MITCHELL and M. J. GRAHAM, *Oxid. Metals* **34**, 173 (1990).
10. C. M. COTELL, G. J. YUREK, R. J. HUSSEY, D. F. MITCHELL and M. J. GRAHAM, *Oxid. Metals* **34**, 201 (1990).
11. F. A. GOLIGHTLY, F. H. STOTT and G. C. WOOD, *Oxid. Metals* **10**, 163 (1976).
12. M. PFEIFFER, *Werkst. Korros.* **8**, 574 (1957).
13. J. E. McDONALD and J. E. EBERHART, *Metall. Trans.* **233**, 512 (1965).
14. J. D. KUENZLEY and D. L. DOUGLASS, *Oxid. Metals* **8**, 139 (1974).
15. J. STRINGER, *Metall. Rev.* **11**, 113 (1966).
16. J. STRINGER, B. A. WILCOX and R. I. JAFFEE, *Oxid. Metals* **5**, 11 (1972).
17. J. E. ANTILL and K. A. PAEKALL, *J. Iron Steel Inst., Lond.* **205**, 1136 (1967).
18. J. M. FRANCIS and J. A. JUTSON, *Corros. Sci.* **8**, 445 (1968).
19. R. W. FUNKENBUSCH, J. G. SMEGGIL and N. S. BORNSTEIN, *Metall. Trans.* **16A**, 1164 (1985).
20. H. NAGAI, Y. TAKABAYASHI and H. MITANI, *Metall. Trans.* **12A**, 435 (1981).
21. H. NAGAI, *Mater. Sci. Forum* **43**, 75 (1989).
22. J. E. ANTILL, J. J. BENNET, R. F. A. BERNSELY, F. H. FERN, P. H. GOODE, B. L. MYATT, J. F. FURNER and J. B. WARBURTON, *Corros. Sci.* **16**, 729 (1976).
23. M. LANDKOF, A. V. LEVY, D. H. BOONE, R. GRAY and E. YANIF, *Corrosion* **41**, 344 (1985).
24. G. M. ECER, R. B. SINGH and G. H. MEIER, *Oxid. Metals* **18**, 55 (1982).
25. Y. SAITO and T. MARUYAMA, *Mater. Sci. Engng* **87**, 275 (1987).
26. G. AGUILAR, H. BAUSCAIL, J. C. COLSON and J. P. LARPIN, *Proc. 29th CIM Conf.; Hamilton, Int. Symp H. T. Oxid. Proc.* (August 1990).
27. P. Y. HOU and J. STRINGER, *Mater. Sci. Engng* **87**, 295 (1987).
28. L. V. RAMANATHAN, *Proc. 9th Bras. Mater. Sci. Conf., Aguas de Sao Pedro, Brazil* (1990).
29. A. M. HUNTZ, *Mater. Sci. Engng* **87**, 251 (1987).