Rare Earth Element Effect on Oxidation Behavior Of Chromia Forming Alloys.

Lalgudi V. Ramanathan,
Comissao Nacional de Energia Nuclear,
Instituto de Pesquisas Energeticas e Nucleares,
C.P. 11049, Cidade Universitaria,
Sao Paulo 05422-970,
Brazil.

ABSTRACT

The addition of rare earth (RE) elements favorably influences the oxidation behavior of high temperature alloys. Various explanations have been put forth to account for the reduction in scale growth rates and scale failures. Some have been verified for specific systems. This paper presents the influence of superficial application of RE oxides and alloying additions of RE elements and oxides on the oxidation behavior of chromia forming alloys. The role of RE elements on chromia scale growth has also been discussed. Superficial application of RE oxides and concentrates of Y and Ce improved isothermal and cyclic oxidation resistance of the relatively low Cr steel (AISI 304)but not that of the high Cr steel (AISI 310). The oxides of Y, Ce, Nd, La, Sm and Gd influenced oxidation resistance in decreasing order. Alloying additions of CeO_2, Y_2O_3, Ce and Y enhanced oxidation resistance of the Fe-Cr alloy in increasing order. In the presence of Y, Ce or their oxides, the scale was thin, fine grained and adherent chromia. The main stages by which oxidation resistance is enhanced are probably incorporation of the RE element in the oxide scale followed by their segregation to scale grain boundaries and consequent modification in ionic transport properties.

Key Terms : Rare earth elements, oxidation, stainless steels, chromia.

Introduction

Alloys or metallic coatings used in high temperature oxidative environments rely for their protection on a continuous and slow growing oxide scale. Ideally, these scales should be non volatile, adherent, coherent, stress free, pore free, crack free and have low defect concentrations for the transport of species. Commonly, three oxides have such capabilities, Cr_2O_3, Al_2O_3, and SiO_2. All three are used in practice and the former two, Cr_2O_3 and Al_2O_3, to a much greater extent than the latter.

The addition of small quantities (1%) of certain oxygen reactive elements to high temperature alloys is well known to reduce oxidation rates and increase scale adhesion. Several mechanisms have been proposed to account for the beneficial effects of adding the reactive elements. These include: (a) mechanical keying through formation of oxide pegs into the alloy (1), (b) promotion of preferential anionic diffusion rather than cationic diffusion in the scale, and thus oxide growth at a different interface (2-5), (c) formation of graded oxide or interlayers containing the reactive element (6), (d) reduction in accumulation of voids at the alloy/scale interface (7,8), (e) enhancement of scale plasticity by modification of the structure (9), and (f) inhibition of segregation of sulphur to the alloy/scale interface (10). Some of these explanations have been verified for specific alloys to which specific reactive elements have been added under specific conditions.

In most of the investigations, the rare earth (RE) elements were added either in metallic form or as oxide dispersions to the alloy (11,12). In some investigations, RE elements were introduced into the surface by ion implantation techniques and in others applied as oxides to the surface by various techniques (2-5,13-19). The application of RE elements to alloy substrates has the advantage of not affecting adversely the mechanical properties of the substrate alloy.

In this paper the influence of (a) superficial application of RE oxides, (b) alloying additions of RE elements, (c) additions of RE oxide dispersions to FeCrNi alloys and (d) superficial application of RE oxides to Si containing FeCrNi alloys has been studied, to extend the data available and address the effect of RE element addition on high temperature oxidation behavior of chromia forming alloys.

Methods and Materials

Commercial grade AISI 304 (Fe-18Cr-8Ni) and 310 (Fe-25Cr-20Ni) sheet specimens 1x1x0.3 cm were ground to 400 grit, degreased, rinsed and dried prior to applying the RE oxide. The RE oxide was applied by heating the specimen to 200 C followed by immersion in saturated RE nitrate solutions and drying at 200° C for 10 min (20). Oxides of Ce, La, Gd, Nd, Sm and Y as well as oxide concentrates rich in Ce and Y (as shown in table I) were applied. The specimens were isothermally oxidized in air at 900° C and 1000° C for up to 100h. AISI 304 and 310 specimens covered with RE oxides of Nd, La, Ce and Y were also tested for cyclic oxidation resistance.Each cycle consisted of 6h at 1000° C followed by cooling in air outside the furnace to room temperature.

The conjoint influence of Si as an alloying element and superficially applied RE oxide on the oxidation behavior of FeCrNi alloys was studied. In these tests CeO_2 was applied to Fe-18Cr-8Ni alloys containing 0.6 to 4.7 wt% Si and the oxidation behavior at 1000° C in air for 20h was investigated.

The effect of alloying additions of elemental RE and RE oxide dispersions to Fe-Cr alloys on oxidation behavior has also been studied. Fe-20Cr alloys containing (a) 0.1wt% Ce or Y prepared by vacuum induction melting and (b) 1wt% CeO_2 or Y_2O_3 dispersoids prepared by cold compaction from elemental powders and sintered. The alloys were subsequently homogenized in vacuum at 1000° C for 20h, 2mm thick specimens were cut, ground, rinsed, dried and oxidized in air at 1000°C for 20h.

In all experiments, the weight gain measurements were made either in a thermogravimetric balance or with a precision balance followed by examinations of the surface morphology of the oxidized specimens in a SEM coupled to a quantitative energy dispersive (EDS) system.

Results

Surface Addition of RE Oxides

The thickness of the deposited RE oxide was typically 2-4μm and its structure depending on the composition of the oxide and condition of the substrate,consisted of either separate, closely packed grains or fractured platelets. Similar observations were made elsewhere (16). The Ce and Y oxides were found as closely packed grains.

The oxidation behavior of AISI 304 covered with RE oxides and Ce and Y concentrates at 1000°C is shown in figure 1. Straight lines have been used to join the points, since the measurements were discontinuous. Superficial application of RE oxides reduced the extent of oxidation, with Y and Ce oxides resulting in the 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. The isothermal oxidation behavior of RE oxide covered AISI 304 at 900°C in air is shown in figure 2. Superficial addition of any of the RE oxides results in significant reduction in the extent and rate of oxidation of AISI 304. Y and Ce and their concentrates exercise greater influence than the other two oxides and La_2O_3 had greater influence than Nd_2O_3. Figure 3 shows the isothermal oxidation curves of AISI 310 at 900°C. All the curves lie within a narrow band, indicating limited influence, if any, of the surface deposited oxides on oxidation behavior.

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.

The influence of the conjoint presence of Si and CeO_2 on the extent of oxidation is shown in figure 4. It can be seen that at 1000°C the extent of oxidation did not vary significantly with Si content. 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 oxidative weight gains. The increase in oxidation resistance with increasing Si is probably due to formation of both Cr_2O_3 and SiO_2.

Alloy Additions of Rare Earths to Fe-20Cr.

The effect of RE element addition or RE oxide dispersoids to Fe-20Cr on oxidation at 1000°C is shown in figure 5. The addition of Ce or Y in elemental form has a greater influence on reducing the oxidation rate of the alloys than the addition of ceria or yttria dispersoids. In either form, Y reduced the oxidation rate more than Ce.

Oxide Morphology

Optical and scanning electron microscopic studies on oxidized specimens were carried out. The outer oxide surface on RE free AISI 304 oxidized for 20 h at 1000°C revealed spikes of iron rich oxide (figure 6a), whereas close to the alloy/scale interface a fine grained structure was seen. SEM/EDAX measurements on sections of scale formed on AISI 304 showed a duplex scale consisting of a mixed oxide above a chromia layer. After oxidation, surface deposited RE oxides were observed at the oxide/gas interface, indicating that the deposited oxide was pushed outwards as the scale grew (figure 6b). The RE oxide particles on the scale surface were 5-25μm in size and randomly distributed. The marked improvement in the overall oxidation behavior upon addition of Y, Ce, La or Nd, is due to the formation of fine grained Cr_2O_3 as shown in figure 6c.

The addition of RE oxide to AISI 310 did not alter the oxide morphology. Fine grained Cr_2O_3 similar to that shown in figure 6c was observed on both the RE oxide covered and RE free AISI 310 oxidized for 20h at 1000°C.

The surface of oxidized AISI 304 covered with Ce or Y concentrate revealed on different regions of the surface either spike like iron oxide, rounded fine grained chromia or a mixture of both. The mixed morphology of the scale is due to the presence of RE elements with varying influence on scale growth.

General Discussion

Superficial application of RE oxides to AISI 304 improves the overall oxidation resistance. The RE elements 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 RE oxide covered alloys, mostly chromia with increasing amounts of iron oxide. The morphology and thickness of the scales on both RE oxide covered as well as RE oxide free AISI 310 (Fe25Cr20Ni) were similar and consisted of fine grained Cr_2O_3. Thus superficial application of RE oxide exercised greater influence on the oxidation behavior of low Cr alloy, which normally forms discontinuous chromia scales. Hou and Stringer also observed that in the presence of surface deposited RE oxide continuous and adherent chromia scales form on alloys which normally form discontinuous scales (16).

Even though a significant part of the superficially applied RE oxide on AISI 304 was found at the scale/gas interface, the formation of fine grained chromia on specimens covered with CeO_2 or Y_2O_3 and not on specimens free from RE oxides could be attributed to the presence of the RE oxides. These RE oxides may be acting as scale nucleation sites. The presence of RE oxide in the growing scale has been reported (16,21). The surface applied RE oxide probably influenced scale growth in a manner similar to when RE elements were added to the alloy. In this study, the extent to which RE elements influence oxidation resistance, was found to be highest when present as an alloying element. It is well known that the RE elements added to the alloy become incorporated into the chromia scale as an oxide (16). It has been suggested that the RE oxide in the scale forms spinels (depending on their solubility) followed by dissociation to the RE ion, and segregation to grain boundaries where they slow the outward Cr ion movement (3). Even though direct evidence of these phenomenon are yet to be confirmed in this investigation, the observed variations in the extent of influence of the different RE elements on oxidation behavior could be attributed to their diffusion behavior in the scale.

The addition of RE oxides as dispersoids to chromia forming alloys also improves oxidation resistance. This has been observed in this investigation and elsewhere (22). The improvement in oxidation behavior is possibly brought on by the dispersoids acting as cation vacancy sinks (remote from alloy/scale interface)(23). The improvement may also be attributable to the dispersed RE oxide particles in the alloy acting as heterogenous nucleation sites (8). Thus the time required for subsequent lateral growth processes to link nucleii and form a complete protective layer is less.

In this investigation no peg formation was observed.However,based on the observed differences in scale morphologies and grain size between the RE containing and RE free alloys the improved adhesion may be attributed to increase in scale plasticity.

Conclusions

1. Superficial application of RE oxides and concentrates of Y and Ce to AISI 304 increases oxidation resistance.

2. Cerium and yttrium oxides resulted in highest isothermal and cyclic oxidation resistance. They promoted the formation of fine grained chromia on AISI 304.

3. The oxidation behavior of Si containing Fe-18Cr-8Ni alloys was not affected by superficially applied ceria.

4. The addition of 0.1wt% Ce or Y or 1wt% of their oxides as dispersions to Fe-20Cr improved their oxidation resistance.

References

1. C.S. Giggins, B.H. Kearn, F.S. Petit and J.K. Tien, Metall. Trans., 5, (1974), p.1685.
2. K. Przybylski, A.J. Garratt-Reed and G.J. Yurek, J. Electrochem Soc., 135,2,(1988),p.509.
3. K. Przybylski and G.J. Yurek, J. Electrochem Soc., 135,2, (1988), p.517.
4. C.M. Cottell, G.J. Yurek R.J. Hussey, D.F. Mitchell and M.J. Graham, Oxid. Met., 34,314, (1990), p.173.
5. C.M. Cottell, G.J. Yurek, R. J. Hussey, D.F. Mitchell and M.J. Graham, Oxid. Met., 34, 314, (1990), p.201.
6. F.A. Golightly, F.H. Stott, and G.C. Wood, Oxid Met., 10, (1976), p.163.
7. J.D. Kuenzley and D.L. Douglass, Oxid Met., 8, (1974), p.139.
8. J.Stringer, B.A. Wilcox and R.I. Jaffee, Oxid. Met., 5, (1972) p.11.
9. J.E. Antill and R. A. Paskall, J.Iron Steel Inst., London, (1967),p.1136.
10. R.W. Funkenbusch, J.G. Smeggil and N.S. Bornstein, Metall. Trans., 16A, (1985), p.1164.
11. H. Nagai, Mat.Sci. Forum, 43, (1989), p.75.
12. T.N. Rhys-Jones and H.J. Grabke, Mat. Sci. and Tech., 5,4, (1988), p.446.
13. J.E. Antill, J.J. Bennet, R.f. A. Bernsley, F.H. Fern, P.H. Goode, B.L.Myatt, J.F. Furner and J.B. Warburton, Corros. Sci., 16, (1976), p.729.
14. M. Landkof, A.V. Levy, D.H. Boone, R. Gray and E. Yanif., Corrosion, 41, (1985), p.344.
15. Y. Saito and T. Maruyama, Mat.Sci and Eng., 87, (1987) p.275.
16. P.Y. Hou and J.Stringer, Mat. Sci and Eng., 87, (1987) p.295.
17. T. Fransen, M.A. de Jough, M.M.A. Perik and P.J. Gellings, Proc.9th Int. Cong. Met. Corr., Canada, V-4, (1984), p.311.
18. R.J. Hussey, P. Papaiacovou, J. Shen, D.F. Mitchell and M.J. Graham, Mat. Sci and Eng., A120, (1989) p.147.
19. M.J. Bennet, J. Vac. Sci. Tech. B2(4), (1984), p.800.
20. L.V. Ramanathan, Proc. 9 Bras. Mat. Sci Conf., Aguas de Sao Pedro, Brazil, (1990).
21. J. Stringer, Mat. Sci and Eng., A120, (1989), p.129.

22. D. Caplan, Met. Trans A, 12A, 12, (1981), p.2135.
23. D.P. Moon, Mat. Sci and Tech., 8, 5, (1989), p.754.

Table I. Composition of oxide concentrates

Element	Y concentrate (wt%)	Ce concentrate (wt%)
Y	78	2.5
Dy	14	1.2
Gd	2	10.0
Ho	2	-
Tb	1.5	-
La	-	14.5
Ce	-	37.5
Nd	-	23.0
Sm	-	11.3
Eu	-	0.25

Table II. Cyclic oxidation resistance of RE oxide coated AISI 304. Each cycle consisted of 20h at 1000°C. S - Spalling, NS - No Spalling

Rare Earth Oxide	Specimen after cycle					
	1	2	3	4	5	6
Y_2O_3	NS	NS	NS	NS	S	S
CeO_2	NS	NS	NS	S	S	S
La_2O_3	NS	S	S	S	S	S
Nd_2O_3	S	S	S	S	S	S

Figure 1. Isothermal oxidation behavior of AISI 304 with surface deposited RE oxides at 1000°C.

Figure 2. Isothermal oxidation behavior of AISI 304 with surface deposited RE oxides at 900°C.

Figure 3. Isothermal oxidation behavior of AISI 310 with surface deposited RE oxides at 900°C.

Figure 4. Isothermal oxidation behavior of Si containing Fe-18Cr-8Ni superficially coated with CeO_2.

Figure 5. Isothermal oxidation behavior of Fe-20Cr at 1000°C with and without additions of 0.1wt% RE elements and 1wt% RE oxides.

Figure 6. Scanning electron micrographs of outer oxide surface on AISI 304 specimens oxidized at 1000°C.
(a) RE oxide free
(b) Nd_2O_3 deposited
(c) CeO_2 deposited

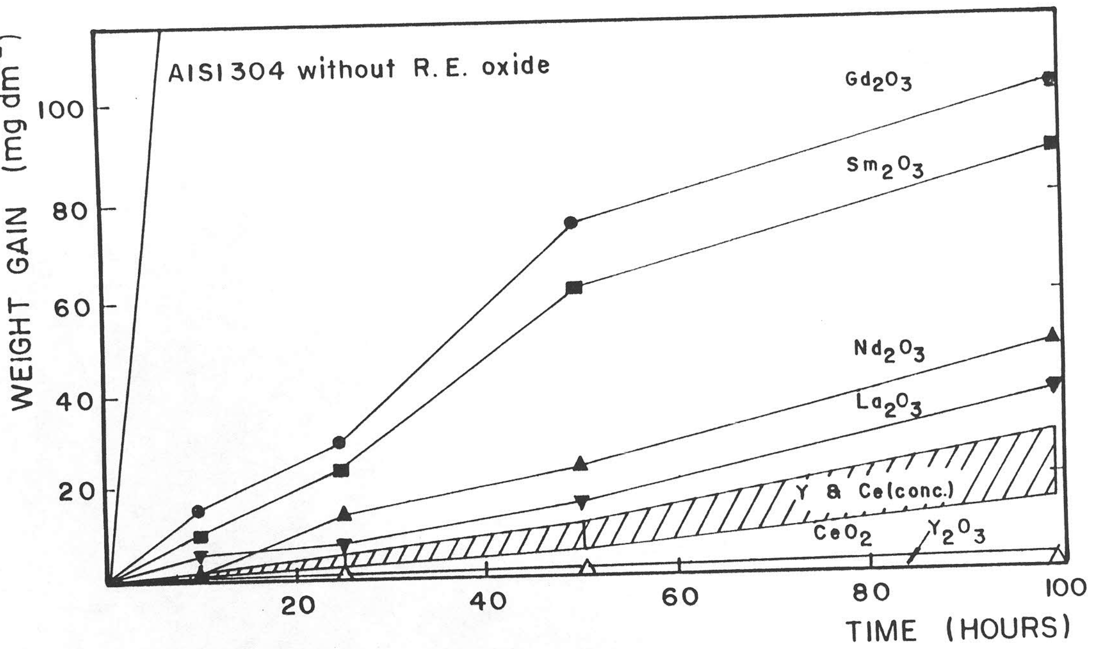


Figure 1

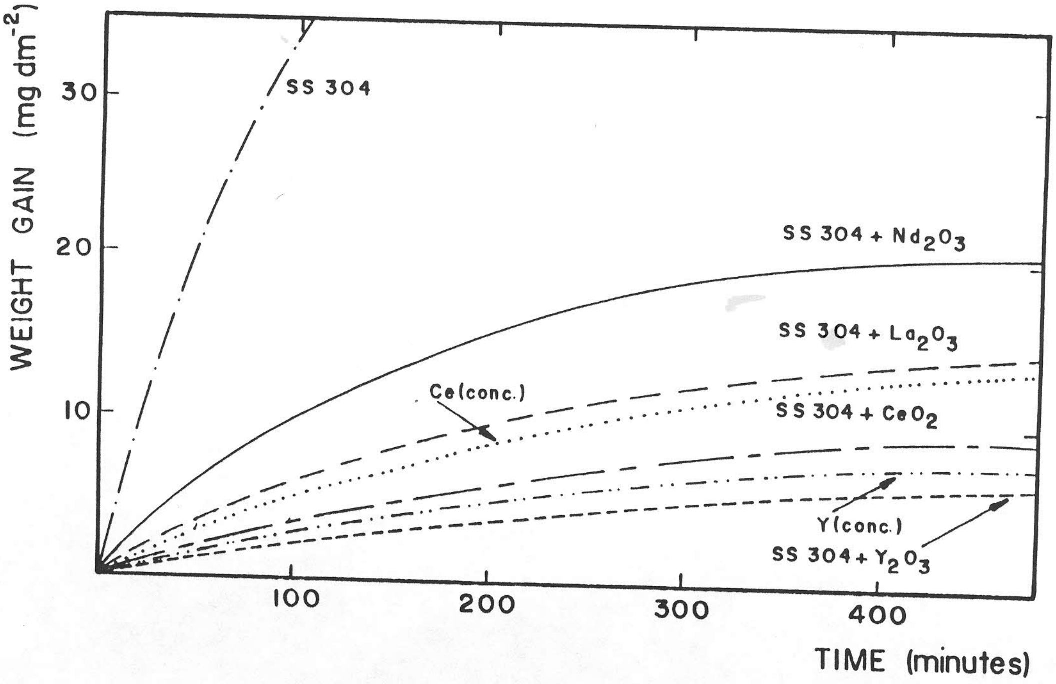


Figure 2

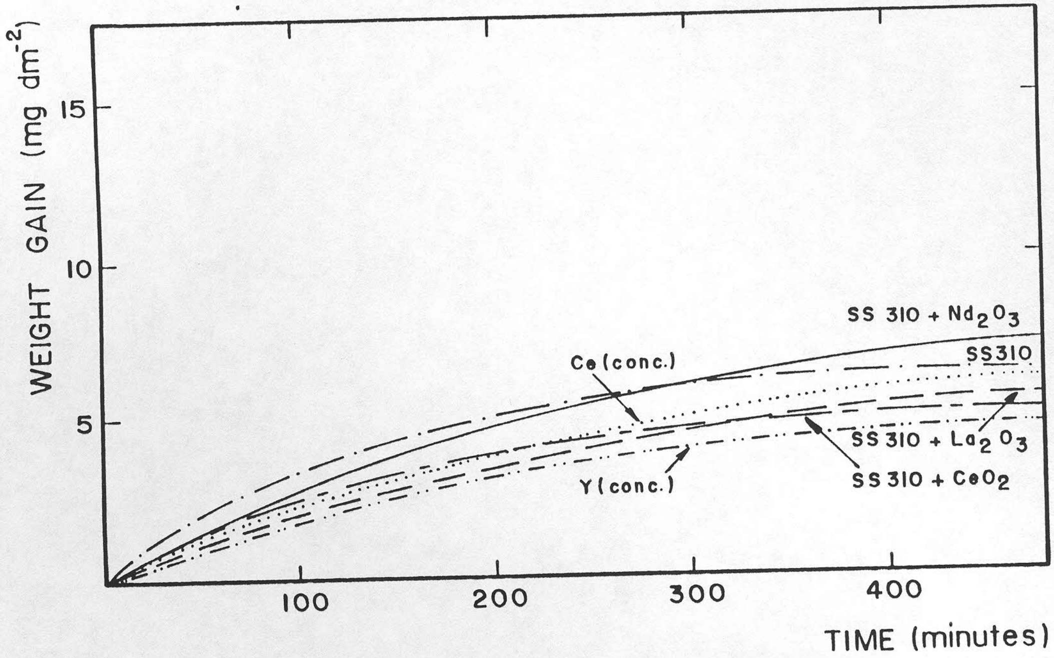
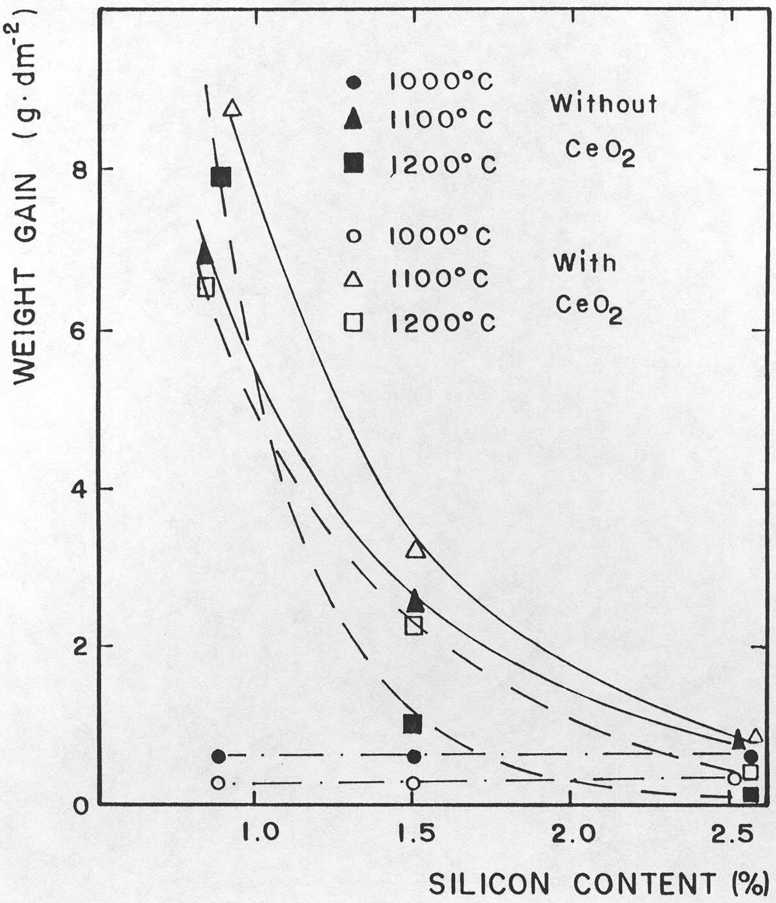
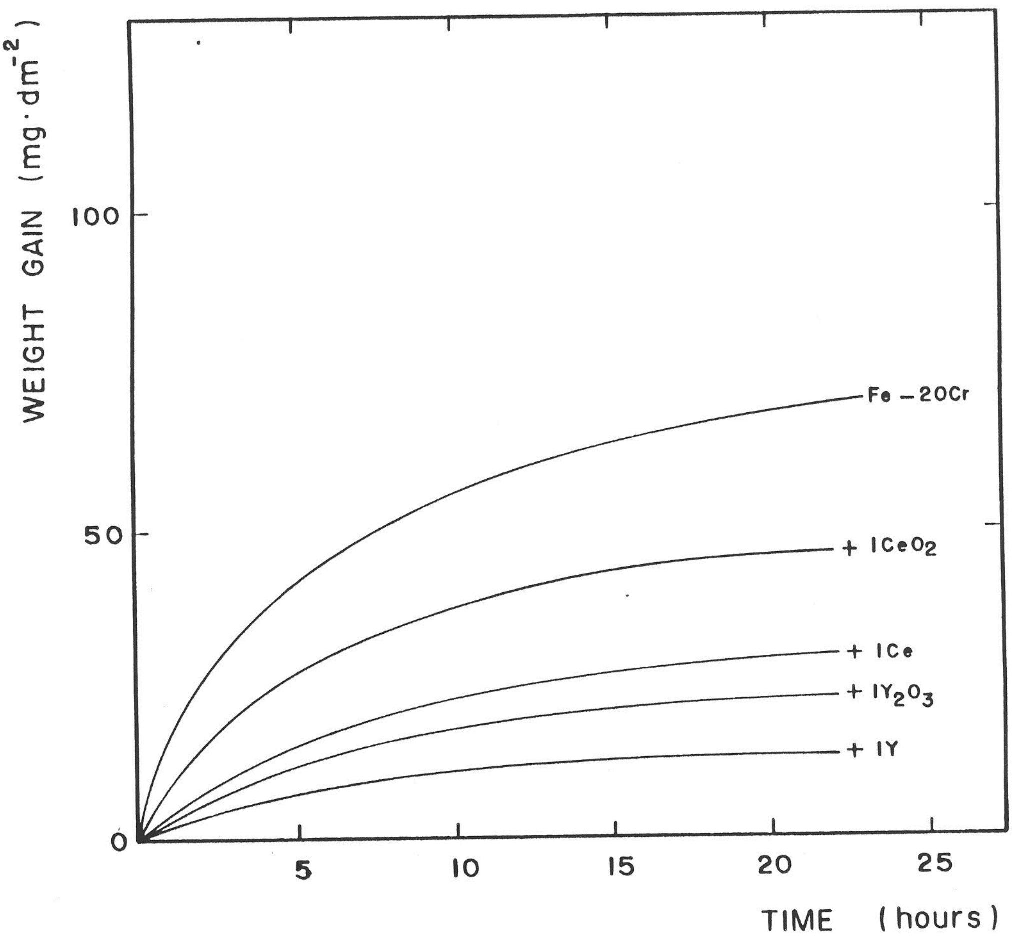

WEIGHT GAIN (mg dm^{-2})
15
10
5
100
200
300
400
TIME (minutes)
SS 310 + Nd$_2$O$_3$
SS310
Ce (conc.)
SS 310 + La$_2$O$_3$
SS 310 + CeO$_2$
Y (conc.)

Figure 3



● 1000°C
▲ 1100°C
■ 1200°C
Without CeO2
○ 1000°C
△ 1100°C
□ 1200°C
With CeO2
WEIGHT GAIN (g·dm⁻²)
0
2
4
6
8
1.0
1.5
2.0
2.5
SILICON CONTENT (%)

figure 4


WEIGHT GAIN ($mg \cdot dm^{-2}$)
100
50
0
5
10
15
20
25
TIME (hours)
Fe – 20Cr
+ 1CeO$_2$
+ 1Ce
+ 1Y$_2$O$_3$
+ 1Y

Cr

Fe rich oxide

(a)

Nd2O3

Cr2O3

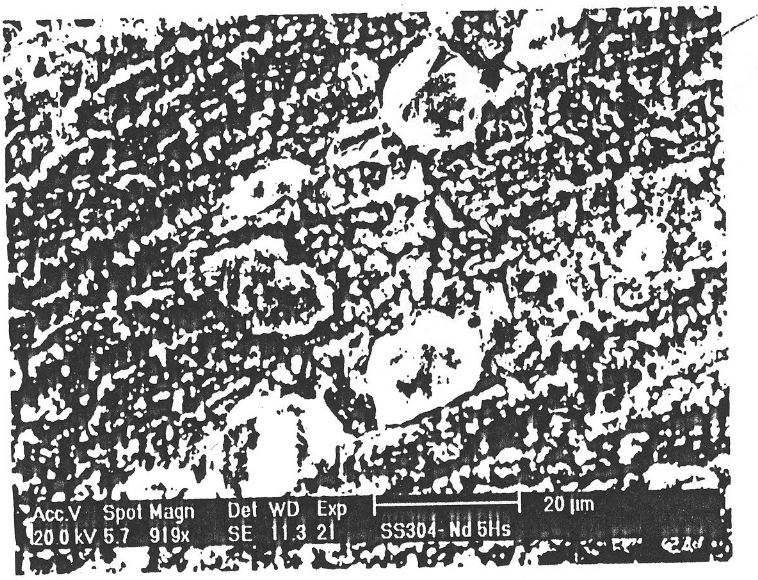
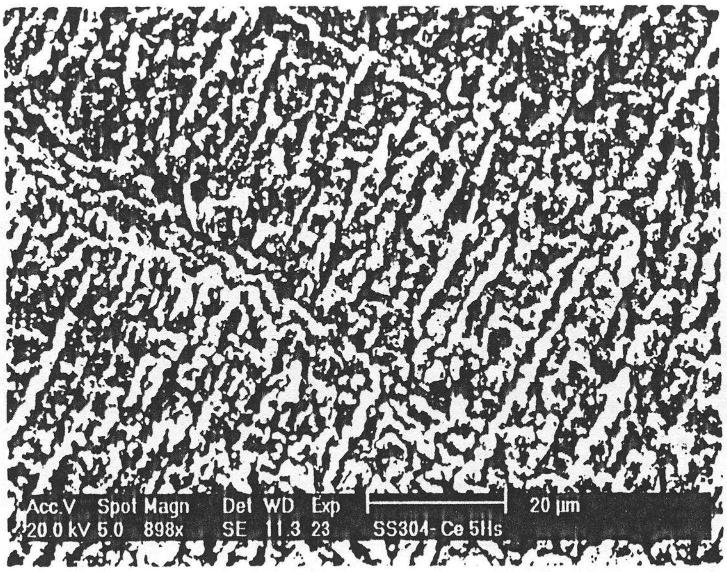


figure 6

(b)



(c)

Are grain where the