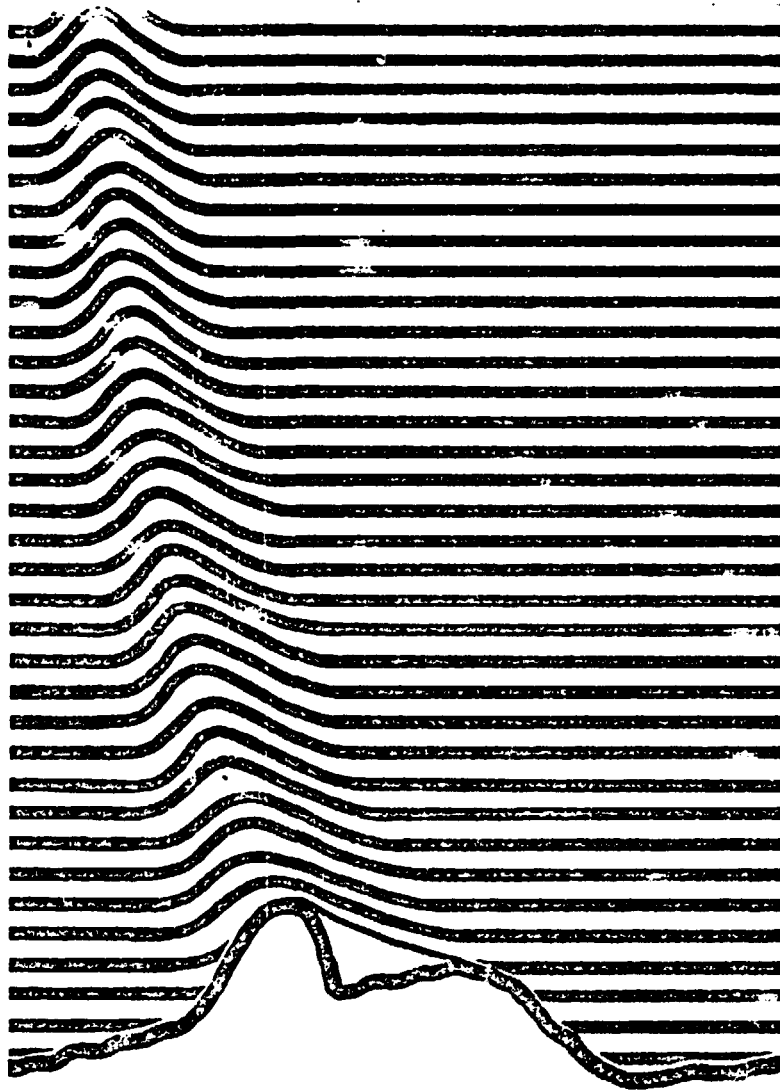


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INFLUENCE OF RARE EARTH OXIDES ON THE OXIDATION OF CHROMIA FORMING ALLOYS

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ABSTRACT

The influence of superficial application of rare earth oxides such as CeO_2 , La_2O_3 , Nd_2O_3 , Sm_2O_3 , and Gd_2O_3 to AISI 304 and 310 stainless steels, on their isothermal oxidation behavior at 900° and 1000°C, and cyclic oxidation behavior between 20° and 1000°C has been studied. The application of rare earth oxides (REO) has been found to increase the oxidation resistance of AISI 304. No significant improvements in oxidation resistance of AISI 310 were noted. The oxidation resistance of AISI 304 was highest in the presence of CeO_2 on its surface. The other REO in decreasing order of influence on oxidation resistance are La_2O_3 , Nd_2O_3 , Sm_2O_3 , and Gd_2O_3 . SEM investigations of the oxide scale morphology revealed that the improved resistance is probably due to the formation of a thin layer of fine grained compact Cr_2O_3 and the higher adhesion of the scale to its increased plasticity.

KEY WORDS: Rare earth oxides; austenitic stainless steels; high temperature oxidation; oxide scale.

INTRODUCTION

The influence of adding small quantities of certain oxygen reactive elements such as Y, Hf, Zr and others to high temperature alloys on improvements in oxidation rate and oxide scale adhesion is well documented. (1-7) Significant improvements in terms of reduced rates of oxidation and increased adhesion of both chromia and alumina films to their alloy substrates have been reported. (8,9) Several explanations have been proposed to account for the improvements in the oxide adhesion and include: (a) anchoring of the scale to the substrate due to formation of oxide pegs, (1,10); (b) elimination of pore formation at the metal/metal oxide interface by vacancy coalescence effects (11); (c) reduced growth stresses in the scale because of reduced oxidation rates (8); (d) increased plasticity of the fine grained scale (12) and (e) the formation of interlayers containing the reactive element. (2,13)

So far, most of the effort has concentrated on adding the RE element, either in metallic form or as oxides to the substrate alloy. Recently data has been reported where the elements were implanted into the surface using ion implantation techniques. (14) Direct superficial application of reactive element oxides to heat resistant alloy surfaces by immersion in aqueous or non-aqueous solutions has also been reported and found to be effective in improving the oxidation behavior. (9,15-17) Superficial application of reactive elements has many obvious advantages; the alloy structure remains unaltered and the process is simple as well as economical. This method of application of REO has been used on AISI 304 (9) and NiCrAl alloys (17).

As part of an ongoing project to study the different uses of RE elements, an investigation was undertaken to extend the work of others and inform

about the influence of various REO, applied superficially on the oxidation behavior of chromia and alumina forming alloys. In this paper the influence of Ce, Nd, La, Sm and Gd oxides on the isothermal and cyclic oxidation behavior of AISI 304 and 310 stainless steels has been reported.

EXPERIMENTAL PROCEDURE

Commercial grade AISI 304 and 310 sheet of nominal composition (shown in table I) were used to prepare specimens 1x1x0.3 cm and 1x1.5x0.4cm respectively. The specimens were ground to 600 mesh, degreased in ethanol and dried prior to applying REO. Oxides of Ce, La, Nd, Gd and Sm with a purity of >99% were used.

Table I. Nominal composition of stainless steels.

AISI	ELEMENTS										
	C	S	P	Mn	Si	Cr	Ni	N	Co	Mo	Ti
310	0.045	0.015	0.019	1.74	0.32	24.31	19.3	0.020	0.04	-	-
304	0.068	0.008	0.033	1.38	0.62	18.23	8.16	524ppm	-	0.04	0.002

Preliminary experiments were carried out to establish the most efficient method of applying REO to the stainless steel (SS) surfaces. In these, CeO₂ was applied to SS 304 surfaces using four different methods listed in Table II. The morphologies and distribution of the CeO₂ on the SS surface resulting from the four methods were compared along with the oxidation behavior of the specimens at 1000°C in air for 20 hours. Method 4 gave the most consistent results and was used henceforth to apply the different REO on the SS surfaces.

Table II. Influence of method of applying cerium oxide to AISI 304 on oxidation behavior in air at 1000°C for 20 hours.

Method of applying	weight gain mgdm ²
1 Heat specimen to 500°C, immerse in cerium nitrate solution and heat to 500°C.	10.94
2 Immerse specimen into nitrate solution at RT and dry at RT.	9.06
3 Immerse in an alcohol suspension of CeO ₂ at RT and dry at RT.	8.4
4 Immerse in nitrate solution at RT and dry directly at test temperature.	3.43

Isothermal oxidation of the REO coated SS 304 and SS 310 specimens were carried out for over 400 minutes in air at 900°C in a thermogravimetric analyzer. Isothermal oxidation tests were also carried out at 1000°C for 5, 10, 25, 50 and 100 hours. The cyclic oxidation tests consisted of six cycles of, 20 hours at 1000°C per cycle. All the tests were carried out in quadruplicate. The oxidized specimens were examined using standard metallographic techniques, a scanning electron microscope and a microprobe analyzer.

RESULTS AND DISCUSSION

Application of rare earth oxides (REO)

REO applied by immersion in the nitrate solution followed by a single shake was found to give more consistent results in terms of CeO_2 weight gains and adherence, as compared to immersion in an alcohol suspension, a method used elsewhere. (17) Among the different methods of applying CeO_2 by immersion in the nitrate solution, method 4 consisting of a room temperature dip followed by oxidation at the test temperature gave overall lower weight gains as shown in Table II. In this investigation, both the pre and post immersion heating (method 1) have not been found to be necessary. A clean and degreased surface containing air formed film has been found to be adequate for wetting by the nitrate solution (solution prepared by dissolving REO upto solubility limit in 1N HNO_3). Direct heating at 1000°C was also found to be adequate. The oxides of Ce, La, Nd and Sm were found to be more uniformly distributed on the steel surface. Gd_2O_3 had very low solubility in nitric acid, hence application from a suspension resulted in nonuniform distribution.

Oxidation measurements

The isothermal oxidation behavior of REO covered SS 304 at 1000°C is shown in figure 1. The points have been joined by straight lines as the measurements were made discontinuously. It can be observed that superficial application of CeO_2 resulted in highest overall oxidation resistance. The other REO influenced oxidation resistance to lesser extents. In decreasing order

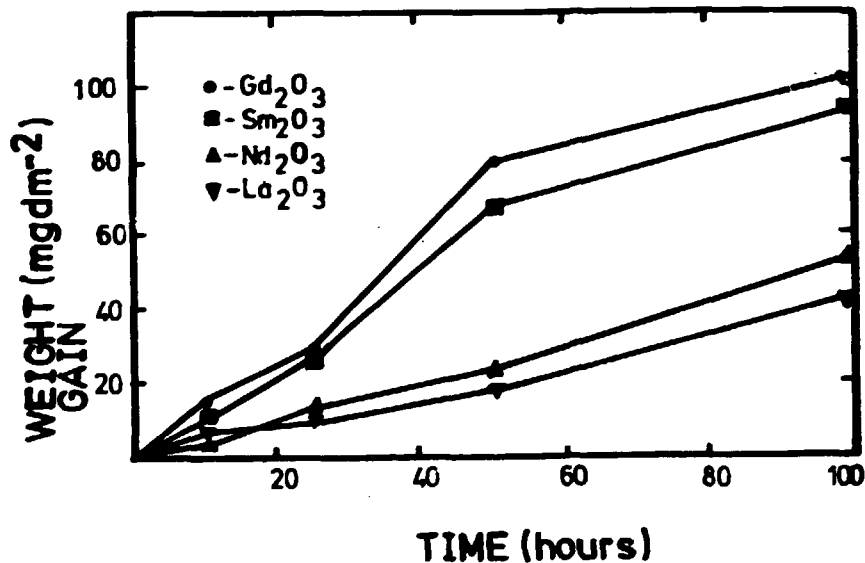


Figure 1. Isothermal oxidation curves of REO covered AISI 304 at 1000°C .

of influence on oxidation resistance, the RE elements are La, Nd, Sm and Gd. The latter two, Sm and Gd had very little influence on the overall oxidation resistance. Based on these results, the REO that were considered in subsequent oxidation measurements were CeO_2 , La_2O_3 and Nd_2O_3 . The results of the isothermal oxidation behavior of REO covered SS 304 and 310 at 900°C in air are shown in figures 2 and 3 respectively. Superficial addition of Ce, La and Nd oxides to SS 304 results in a drastic reduction in the extent and rate of

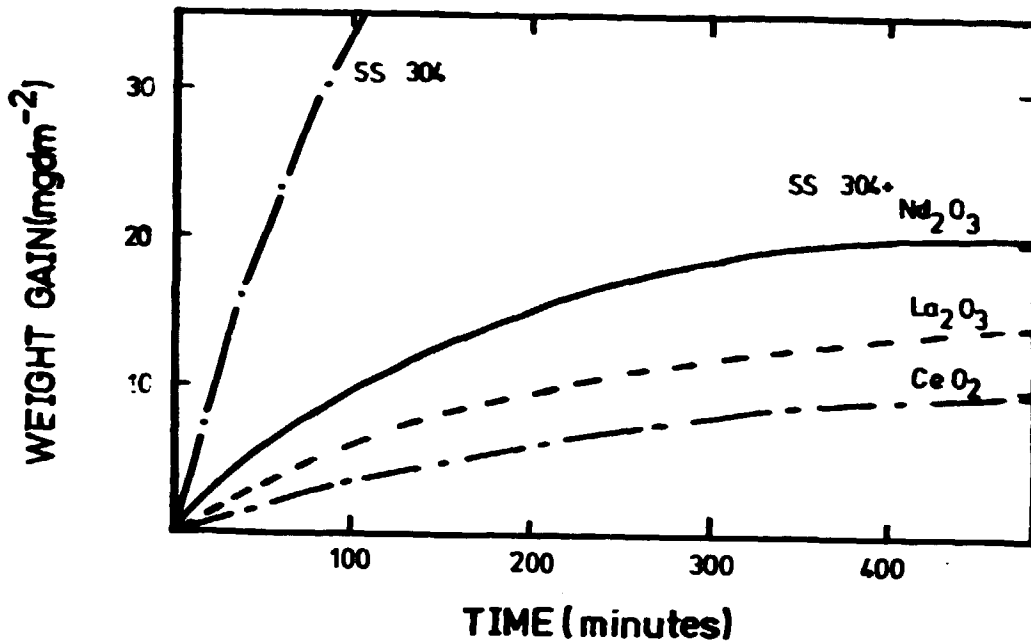


Figure 2. Isothermal oxidation curves of REO covered AISI 304 at 900 C.

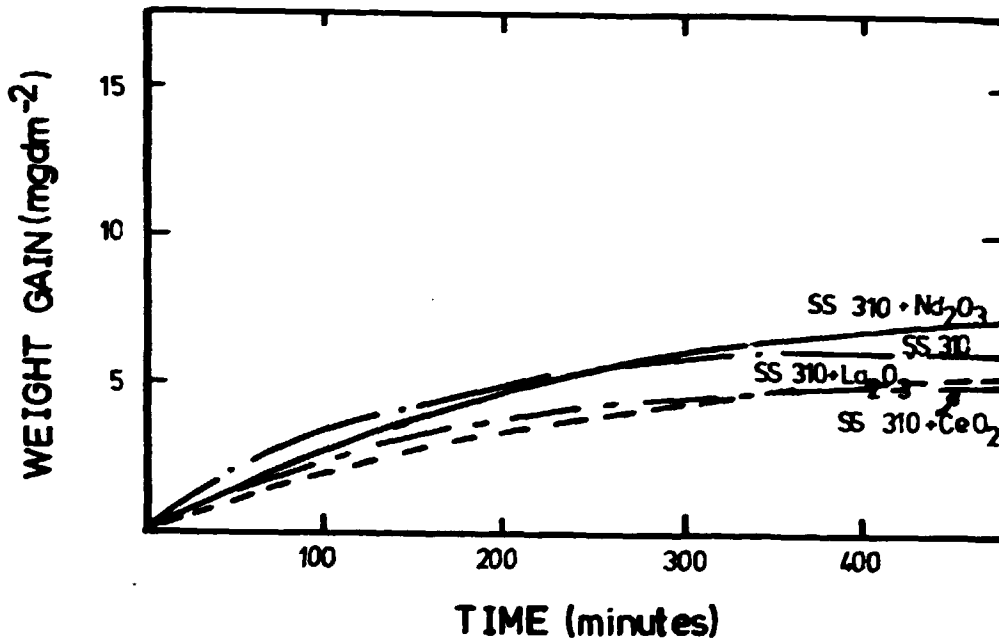


Figure 3. Isothermal oxidation curves of REO covered AISI 310 at 900 C.

oxidation. Ce exercises a greater level of influence than the other two RE elements, and La influences more than Nd. From figure 3 it can be observed that SS 310 oxidises to a lesser extent than SS 304, due to its higher Cr content. Superficial application of REO to SS 310 does not considerably alter its oxidation behavior. Similar observations were made by Landkop et al (9). The results of cyclic oxidation of SS 304 are summarized in Table III. In the presence of Ce, spalling was observed only after the

fourth cycle, where as with La and Nd, after the second and first cycles respectively. No significant spalling was observed on SS 310 .

Table III. Summary of scale spalling behavior on SS 304 cycled between RT and 1000°C. Each cycle was for 20h at 1000°C

S- Spalling; NS- No Spalling.

Rare earth oxide of	specimen surface after cycle					
	1	2	3	4	5	6
Ce	NS	NS	NS	S	S	S
La	NS	S	S	S	S	S
Nd	S	S	S	S	S	S

Morphological examination.

The morphology of the outer oxide surface on RE free SS 304 (shown in figure 4a) revealed the typical spikes of Fe rich oxide. The inner surface of the spalled oxide from SS 304 oxidised at 1000°C (figure 4b) revealed small grained oxide. Surface addition of REO markedly alters the morphology of the outer surface of the oxide as shown in figure 5. The presence of Gd and Sm oxides does not considerably vary the morphology, and the oxide is very similar to that formed on RE free SS 304. The presence of Nd results in an oxide that is fine grained but feathery, Lanthanum and to a greater extent cerium result in the formation of convoluted oxide. The morphology of the oxide in the mid layers on specimens containing Ce,La Nd oxides are fine grained with faceted crystals as shown in figure 6.

Optical macrographic investigation of the outer surface of oxidised REO containing SS 304 specimens revealed that: (a) the extent of spalling increased with oxide thickness which in turn increased with time of oxidation;

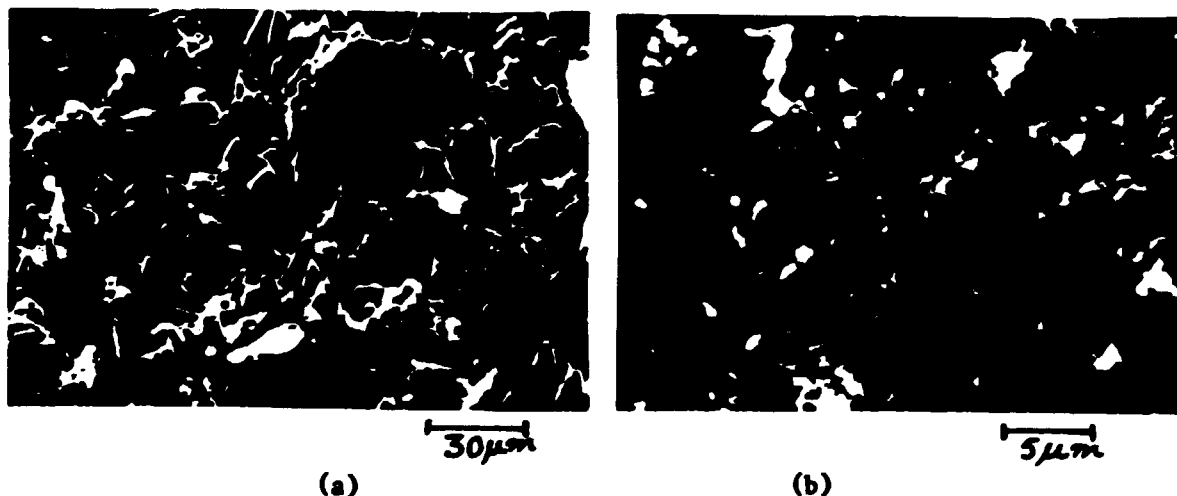
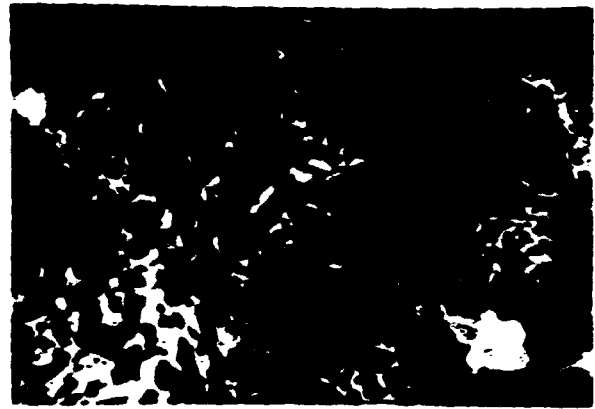


Figure 4. Scanning electron micrographs of oxide on AISI 304 oxidised for 20 hours at 1000 C. (a) oxide/air interface (b) substrate/oxide interface.



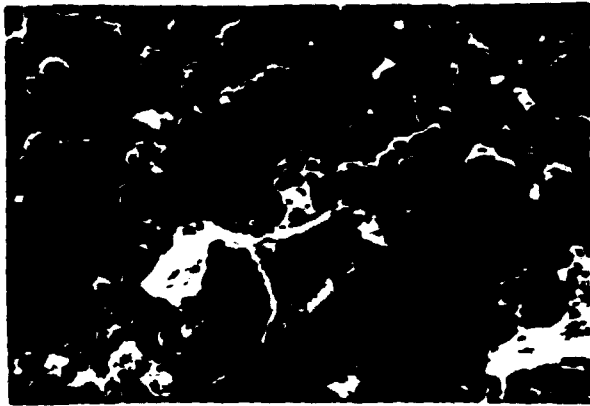
(a)

5 μm



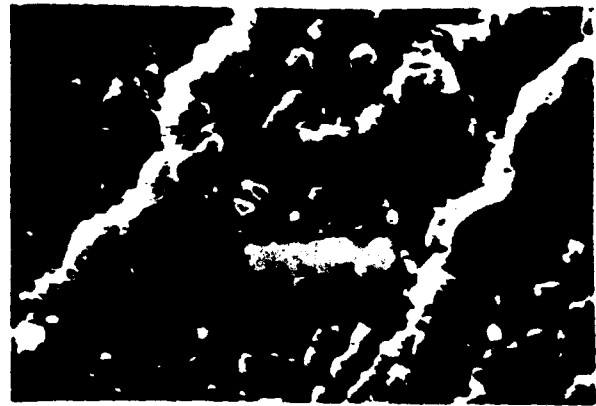
(b)

3 μm



(c)

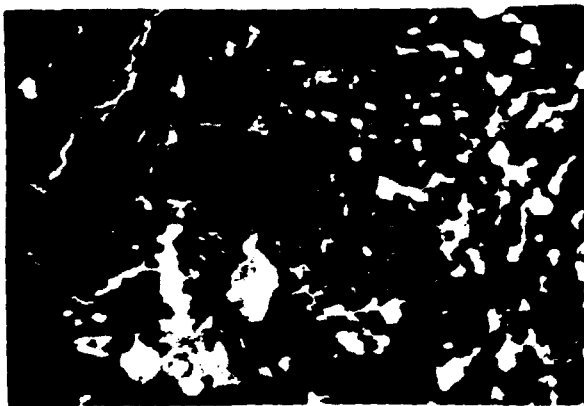
10 μm



(d)

5 μm

Figure 5. Scanning electron micrographs of outer surface of oxide scale on AISI 304 superficially covered with (a) Gd_2O_3 , (b) Nd_2O_3 , (c) Al_2O_3 and (d) CeO_2 and oxidised for 20 hours at 1000 C.



3 μm

Figure 6. Scanning electron micrograph of inner layer of oxide scale on AISI 304 covered with Nd_2O_3 and oxidised at 1000 C for 50 hours.

(b) the first oxide to form is bluish grey or metallic grey, typical of iron oxide. This was observed on the CeO_2 covered specimens even after 100 hours and no spalling occurred; (c) spalling of outer grey oxide exposed a reddish brown oxide, indicating the presence of higher quantities of Fe; (d) spalling of the reddish brown oxide exposed, a dark grey oxide. On the La oxide covered specimens, spalling and rupturing were observed only after 50 hours of oxidation. The oxides on specimens covered with Nd, Sm and Gd oxides revealed spalling after shorter times.

Overall, it can be stated that surface application of REO on SS 304 surface markedly increases the high temperature isothermal and cyclic oxidation resistance. Among the RE elements investigated, they can be arranged in order of increasing influence as Gd, Sm, Nd, La and Ce. The reduced influence of Gd on the oxidation resistance of SS 304 may be attributed to the low solubility of Gd_2O_3 in aqueous nitrate solution and consequent non-uniform distribution on the SS 304 surface. Nd and La influence isothermal oxidation resistance to the same extent. They influence the formation of fine grained compact oxide of Cr_2O_3 at the Metal/metal oxide interface. The reduced influence of Nd on the cyclic oxidation behavior of SS 304 is probably due to the position of Nd_2O_3 in the scale, which inhibited the formation of compact oxide grains and therefore resulted in spalling. The presence of CeO_2 promotes the formation of compact and dense convoluted oxide on the SS 304 surface. Also, the overall oxide thickness on the specimen containing CeO_2 is low. The most probable mechanism through which CeO_2 and to lesser extents La_2O_3 and Nd_2O_3 improve oxidation resistance is by increasing the number of scale nucleation sites which results in the formation of a thin layer of fine grained Cr_2O_3 . The amount of iron that diffuses through to the scale increases from Ce to La to Nd. The improved adhesion of the scale in the presence of Ce is due to higher plasticity of the oxide, brought on by the fine grained structure.

Surface application of REO to SS 310 did not alter its overall oxidation behavior. Only slight variations in the oxide grain size were observed.

CONCLUSIONS

1. Immersion of degreased SS 304 sheet specimens in an aqueous solution of RE elements, followed by oxidation at the test temperature has been found to be an effective method for superficial application of rare earth oxides.
2. Superficial application of REO to SS 304 significantly increases the high temperature isothermal and cyclic oxidation resistance.
3. In decreasing order of influence on the oxidation resistance of SS 304, the REO investigated can be mentioned as those of Ce, La, Nd, Sm, Gd.
4. Superficial application of REO is thought to increase resistance to oxidation by increasing the number of scale nucleation sites and forming fine grained Cr_2O_3 .
5. The higher adhesion of scale formed on CeO_2 covered SS 304 is probably due to increased plasticity of the fine grained scale.

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