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Effect of Surface Applied Reactive Element Oxides on the Oxidation of Cr-Containing Binary Alloys

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ABSTRACT

The influence of surface applied Ca, Ce, Hf, La, Y and Zr nitrate-converted oxides on the oxidation behavior of Co-15wt%Cr, Co-25wt%Cr and Ni-25wt%Cr alloys at 1000°C in 1 atm. O\(_2\) has been studied. The surface oxides appeared to be most beneficial on the established Cr\(_2\)O\(_3\) forming alloy, showed no effects on the non-Cr\(_2\)O\(_3\) forming alloy and acted as a semi-barrier on the borderline Cr\(_2\)O\(_3\) former. Results are compared and discussed with the effects found when the reactive element oxides are present as dispersions within the alloys.

Introduction

The addition of reactive elements (e.g. Y, Ce, Hf) or their oxides to heat resisting alloys forming Cr\(_2\)O\(_3\) or Al\(_2\)O\(_3\) protective scales is known to have a number of beneficial effects. The various theories proposed to explain these effects and the supporting experimental evidence have been recently reviewed by Whittle and Stringer (1). For Cr\(_2\)O\(_3\) forming alloys, the beneficial effects are essentially the following: 1) enhanced selective oxidation of Cr into the scale, particularly during the initial stage, making it possible to develop a continuous external Cr\(_2\)O\(_3\) layer at alloy Cr levels below those required in the absence of the reactive element, 2) reduction in the rate of Cr\(_2\)O\(_3\) growth at elevated temperatures, 3) change in the growth mechanism of the

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oxide from predominantly metal transport to predominantly oxygen transport, and 4) improvement in scale-alloy adherence.

The present understanding of these 'reactive-element effects' has been accumulated by a vast amount of studies carried out with alloying additions of the reactive elements or their oxides. Several mechanisms have been proposed to account for these effects, particularly the aspect regarding the improvement in scale-alloy adherence, but none is universally accepted. Interestingly, however, one of the original patents (2) concerning the reactive element addition indicated that these elements were not only effective as alloying additions but were effective to similar degrees when applied as a surface coat with a thickness of approximately 2-3 μm. The coatings can be the elements, their oxides, hydroxides, or other salts which would decompose to oxides at high temperature. Furthermore, Antill et al (3) demonstrated that ion-implantation of the reactive elements into a subsurface depth of less than 1000 Å can also be beneficial. From the point of view of elucidating the mechanism of the 'reactive-element effect', these superficial techniques are particularly interesting, since several aspects of the most successful current model imply that the reactive element is present within the alloy.

Very recently, several investigators have studied the effects of these superficial treatments to heat resisting alloys. Application techniques include ion-implantation (4-6) as well as surface oxide coats (7-9). However, these studies concentrated on alloy systems that are already strong Cr₂O₃ formers; therefore, neglecting one of the important effects, that dispersions of the reactive element oxides in the alloy could promote Cr₂O₃ scale formation on ordinarily non-Cr₂O₃ forming alloys (10-12).

The present paper is concerned with the effect of oxide deposits produced by the thermal decomposition of aqueous nitrate solutions on alloy systems ranging from non-Cr₂O₃ to good-Cr₂O₃ forming. Three binary alloys are used: Co-15wt%Cr, a non-
Cr₂O₃ former which can be induced to form the protective Cr₂O₃ scale by an internal dispersion of a reactive metal oxide (12); Co-25wt%Cr, a border-line Cr₂O₃ former which undergoes a transition from fast growing duplex CoO scale to slow growing Cr₂O₃ scale when the ambient P₀₂ is lowered (13); and finally, Ni-25wt%Cr, a good Cr₂O₃ former. The nitrates of Ca, Ce, Hf, La, Y and Zr are selected since all of them except Ca have been shown to be beneficial as alloying additions. Ca was chosen because it forms one of the most stable oxides and it was applied as a surface coat in the original patent (2) and proved to be particularly beneficial. This study concentrates on whether these surface deposited reactive element oxides can promote Cr₂O₃ scale formation on non-established Cr₂O₃ formers, and on the characterization of the effects they have on established Cr₂O₃ formers. Results are compared with those found when these oxides are present in the alloys in order to gain further understanding of the 'reactive element effect'.

Experimental Procedure

The three alloys used in this study were prepared from high purity elements by induction melting and casting under an argon atmosphere. The alloy ingots were cleaned by machining off the outer surface layers, and then homogenized by annealing in evacuated, sealed quartz tubes for 24 hours at 1100°C. Specimens approximately 10 x 15 x 1 mm were cut from the center of the homogenized blocks. All surfaces were polished to a 600-grit SiC finish and cleaned with alcohol before testing.

Deposition of the nitrate salts were carried out via a "hot spraying" method. The specimens were first oxidized at 400°C in air for half an hour to increase the surface wettability. 10 wt% nitrate solutions adjusted with HNO₃ to pH = 2 were then sprayed onto the two main faces of the specimen using a commercial air brush while keeping the specimen at approximately 200°C. Immediately following the deposition,
the applied nitrate salts were decomposed to oxides in air at 400°C for another hour. The resulting oxides stayed dry on the specimen surface except CaO which absorbed water from the atmosphere. As a consequence, the CaO coated specimens usually had a high concentration of CaO near the bottom of the specimen, leaving a thin film of the wet oxide on the rest of the surface. This absorbed water was quickly removed during heating of the specimen in the subsequent oxidation experiment.

Oxidation tests were carried out in pure, dry oxygen at 1 atm. total pressure. A Cahn 2000 microbalance was used for kinetics measurements at 1000°C. Specimens were loaded into the apparatus and equilibrated with oxygen before the furnace was turned on. The heating rate of the radiation furnace was high enough to achieve a stable specimen temperature of 1000°C in 10 minutes. Duplicate oxidation runs were made in a horizontal tube furnace. In this system, the temperature was first allowed to stabilize at 1000°C while the reaction tube was equilibrated with oxygen. Specimens either hung from a holder or were contained in alumina crucibles which could then be pushed into the hot zone to start the oxidation reaction.

Analyses of the oxidized specimens involved initial observations of the oxide top surfaces under a scanning electron microscope equipped with an energy dispersive X-ray (EDX) analyzer. Subsequently, these specimens were mounted and polished for cross section examinations using both an optical microscope and the EDX equipped SEM. Occasionally, some of the coated specimens were imaged under the SEM using backscattered electrons in order to visualize the location and distribution of the applied oxides in the oxide scale. Fracture cross sections of scales formed on Co-15Cr alloys were made by mechanically breaking the scales from the metal. This was possible since the scales formed on this alloy was quite thick and fractured at the alloy-scale interface.
Results

Characterization of Deposited Oxides

Chemical and physical characteristics of the coatings have been examined to some degree. The oxides were identified by X-ray diffraction to be CaO, CeO₂, Y₂O₃, La₂O₃, HfO₂ and ZrO₂. Macroscopic uniformity was usually achieved with the spraying technique. Microscopically, the distribution varied considerably from area to area, but even in the thinnest area, the deposited reactive element was still present. Usual thickness of the deposited oxide coats was between 1-3 μm. Surface topographies of the various nitrate converted oxides are shown in figure 1. The La, Y and Ca oxides are seen to have a crystalline structure which is somewhat continuous across the entire specimen surface. The Ce, Hf, and Zr oxides on the other hand, show a dense but cracked structure. The cracking presumably developed from drying, and flakes of oxides were easily detached from the substrate. The deposited nitrates of all the elements before decomposition showed the same morphology as their corresponding oxides.

Kinetics

The weight gain vs. time curves of bare Co-15Cr and the same alloy coated with three different amounts of Y₂O₃ oxidized at 1000°C are indicated in figure 2. The Y₂O₃ addition on the alloy surface is seen to render no change in the oxidation kinetics when the amount applied is relatively small, and shows a very slight reduction with heavier applications. Results of oxidation tests with all the different surface oxide coats carried out in the horizontal tube furnace are summerized in the enclosed table. The weight gain data lay within a scattered band of 5%, and it is seen that none of the applied oxides showed an influence on the oxidation rate.

Effects of all the surface deposited oxides on the oxidation rate of the Co-25Cr alloy is shown in figure 3. Coated HfO₂ is seen to increase the oxidation rate, but this
effect diminished after longer periods of oxidation as observed with a 50-hour oxidation run. The rest of the surface coated oxides, as seen in figure 3, reduce oxidation rate to different degrees with Ca being the most effective, and Y and La better than Ce and Zr. Those surface coated with Y, La and Ca oxides were also more resistant to spallation as shown in table 2, and it is noted that the more beneficial surface coats are those oxides that deposit to the dense, non-flaky morphologies. (fig. 1)

Kinetics curves for Ni-25Cr alloys coated with all the oxides under study is shown in figure 4, and in table 3 spallation of the oxidized scales upon cooling is recorded. An obvious difference between the effects of these salts on this alloy and on the Co-25Cr alloy is the change in relative effectiveness between Ce and Ca coats. While the applied CeO$_2$ still has its mud-cracked shape, it is now as effective as Y and La oxides. On the other hand, CaO with its usual dense morphology shows little beneficial effects.

The surface deposited HfO$_2$ is again seen to increase the rate as well as the degree of spallation. The large weight increase occurred after the first 6-7 hours of oxidation, after which, the weight gain behavior becomes similar to that of the untreated specimen.

Cyclic oxidation of a cerium coated and an untreated specimen were carried out at 1000°C in 1 atm O$_2$ in the horizontal furnace. Results of weight gain and weight lost due to spallation are shown in figure 5. The presence of CeO$_2$ on the surface did improve scale adherence under these oxidizing conditions.

Scale Morphologies and Compositions

The uncoated Co-15Cr alloy oxidized to its typical two layer oxide morphology with an outer columnar CoO layer and an inner layer consisted of CoO, Cr$_2$O$_3$ and CoCr$_2$O$_4$ (13,14). The same morphology was observed for the surface coated specimens. Figure 6 compares the fractured cross section of the scales formed on an
uncoated and a Hf-coated specimens. The backscattered electron image clearly indicates that Hf concentrates at the inner/outer scale interface.

Oxidized Co-25Cr alloy also developed the duplex structure as shown in figure 7a. The scale/alloy interface is quite irregular and the occasional presence of large nodules were often observed. Similar cross section micrographs of a Hf-coated and oxidized specimen is shown in figure 7b. There is no longer any nodular formation, instead, the thickness of the overall scale approximates the nodules found on the untreated specimen. The presence of cerium or zirconium oxide coats also eliminated nodular formation. Unlike the Hf case, the overall oxide is thinner (Fig. 7c) although still duplexed with the applied surface oxide concentrated at the inner/outer scale interface as observed using EDX.

The oxide scales developed on La and Y coated specimens can be best illustrated by their surface morphologies. Figure 8 shows SEM photographs of the oxide outer surface of a Y-coated specimen. The surface is seen to have a random mixture of three types of grains as labeled A, B and C on figure 8a. Type A is the same as that found on untreated specimens. Type C seems to be locally promoted Cr$_2$O$_3$ scale. However, since the presence of these Cr$_2$O$_3$ regions were too small, they were not observed in cross section preparations. The type B grains are believed to be also duplexed with an Cr enrichment in both the outer and inner scales as observed in cross-section preparation. Large nodules were also absent from these specimens.

Surface deposited CaO was found to be the most effective in promoting Cr$_2$O$_3$ scale formation. These Cr$_2$O$_3$ scales were usually more abundant and covered larger areas than that found on the La or Y treated specimens, but the occurrence of these scales was still quite localized. In cross section preparations, Cr$_2$O$_3$ scale could only be observed near the bottom of the specimen, where coverage had been the thickest due to the wetting effect of the CaO. The scale is purely Cr$_2$O$_3$. Ca concentrates on the
scale/gas interface and the amount of Ca present is relatively high. At the same interface, some 30 at% Co is also detected.

The untreated Ni-25Cr alloy oxidized to a single layer Cr$_2$O$_3$ scale with some NiO present on the outer surface. Occasional internal oxides of Cr$_2$O$_3$ were also observed penetrating into the alloy. The Ca and Zr coated specimens oxidized to similar morphologies except with thinner scales. In most parts, NiO formation was prevented. The deposited oxides either remained on the outer surface or became embedded into the oxides.

Figure 9 shows the scale formed on a Hf-treated, oxidized specimen. Unlike the untreated Ni-25Cr, this specimen oxidized to a two layer scale. The top layer consisted of NiO, Cr$_2$O$_3$ and some NiCr$_2$O$_4$ phases as indicated by X-ray diffraction, while the inner scale is purely Cr$_2$O$_3$. Although X-ray maps only reveal the large Hf flake on the surface, backscattered electron image (fig. 9e) showed that Hf is actually distributed throughout the entire outer scale.

Kinetics results have shown that the most effective surface deposited oxides for this alloy were that of La, Y and Ce. Morphology of the scales formed on these specimens are very similar. Figure 10 shows the backscattered electron image of such scale formed on a Ce-coated specimen. In fig. 10a, individual oxide grains of Cr$_2$O$_3$ are clearly seen delineated within the alloy matrix, and small CeO$_2$ particles which appear brighter under this imaging mode are observed to be concentrated at the outer surface. Most of the oxide lay beneath the Ce particles, but occasionally, there are also grains growing above the original CeO$_2$ deposit. No internal oxides were found anywhere across the entire cross-sectioned specimen, and NiO was also not found on top of the Cr$_2$O$_3$ scale. The small amount of Ce found in the scales shown in fig. 10a are only those that have been embedded in the growing scale. Most of the applied CeO$_2$ remains as a loosely attached layer on the surface of the specimen, and this CeO$_2$ layer
detaches during polishing as shown in figure 10b. X-ray analysis of this detached CeO₂ shows only the presence of Ce, indicating that there had not been any interaction between the bulk of the coating and the underlying Cr₂O₃ scale. Similar detachment of Y and La coats were not found since these coats were more adherent to the underlying alloys.

Discussion

Co-15Cr

None of the surface applied reactive element oxides showed any significant effect on the oxidation behavior of this alloy. The scale formed had its usual duplex morphology with the applied oxides concentrated at the inner/outer scale interface which is believed to be the initial specimen surface by previous investigators (13,14).

A continuous Cr₂O₃ scale was far from being promoted by these surface coatings unlike that observed with alloying addition of the reactive element oxides. Stringer and Wright (11) observed a continuous Cr₂O₃ layer formation on Co-21wt% Cr with 3 vol% Y₂O₃ addition. Whittle et al (12) found the same protective Cr₂O₃ formation on Co-Cr alloys containing as low as 10 wt% Cr with 1 wt% Hf, Ti or Zr internally oxidized prior to the oxidation test. In both cases, the dispersoid particles, whether mechanically added or interally formed in the alloy, were responsible for the selective oxidation of Cr to form a continuous Cr₂O₃ layer. This ability to promote Cr₂O₃ scale formation at lower chromium level was probably best explained by Stringer et al (15) using the 'nucleation model'.

If the dispersoid particles acting as nucleation sites for the initially-formed oxides is the reason for the promoted Cr₂O₃ scale, then externally applied particles on the surface of the alloy are expected to do the same. However, this is only possible if the externally applied particles are fine enough, distributed close enough and remain
heterogeneous rather than forming a somewhat continuous layer. Present studies indicate that the coatings formed by the nitrate deposition method do not generally have the required type of morphology. Instead, the applied oxides appear in the form of thin layers on the surface. When the amount of application was small, there would be localized areas with apparently discrete reactive element oxide particles of approximately 1000-2000 Å in diameter and spaced on an average of ~1000 Å apart as revealed by SEM micrographs. However, the spacing between these particles so deposited may be too large for them to be effective for alloys with such low Cr₂O₃ forming tendency.

Co-25Cr

The surface coated Co-25Cr alloys usually exhibit a variety of oxidation behavior within each specimen. Therefore, it is important to view the recorded oxidation rate as a sum of all the local action taking place throughout the entire specimen surface. The morphology of the scale developed with the different oxide treated specimens can be characterized into two groups: those that developed with the flaky, mud-cracked oxide coatings (i.e. Hf, Ce and Zr), and those with denser coatings like La, Y and Ca. The oxide scale developed on the flaky coatings show the typical duplex morphology of the uncoated alloy, and these scales spall upon cooling. Surface HfO₂ increased the overall oxidation rate by increasing the tendency of nodular growth. As a result, the final scale thickness approximates that of the nodules on the untreated alloy. Ce and Zr oxide flakes on the other hand, prevented the nodular formation and therefore, slightly reduced the overall oxidation rate.

With the denser coatings, the overall oxidation rates are even further reduced. The scales formed usually have several morphologies varying from area to area: they can be either duplex with a similar composition to that formed on the untreated alloy, or duplex with Cr enrichment in the inner scale along with Cr present in the outer
scale, or singly layered \( \text{Cr}_2\text{O}_3 \). These scales usually spall much less upon cooling. All the duplex layer structures have the deposited oxides concentrated at the inner/outer scale interface while these oxides are located at the scale outer surface on the single layer \( \text{Cr}_2\text{O}_3 \) scales. These experimental results seem to point out that the influence due to the surface oxide coats is strongly dependent on the morphology of the applied oxide layer.

The oxidation behavior of this alloy has been well characterized by Kofstad and Hed (16) and by Wood et al (14). From their studies it appears that this alloy may oxidize relatively rapidly, forming an outer scale of \( \text{CoO} \) and an inner scale of \( \text{CoO}, \text{CoCr}_2\text{O}_4 \) and \( \text{Cr}_2\text{O}_3 \). It may also develop a protective layer of \( \text{Cr}_2\text{O}_3 \) with an associated reduction in reaction rate. The transition between these two types of oxidation depends sensitively on the pressure. At 1000°C, for example, Kofstad and Hed (13) report rapid oxidation at 760 Torr oxygen pressure, but an order of magnitude reduction in the rate at 100 Torr pressure. Such behavior was demonstrated on the Co-25Cr alloy used in this study. When the partial pressure of oxygen was kept between 10-30 torr with a total pressure of 1 atm., a continuous \( \text{Cr}_2\text{O}_3 \) scale was promoted at 1000°C. However, this scale was very non-adherent. Convoluted morphology was observed and more than half of the scales spalled upon cooling.

It is reasonable then, in light of the experimental results and the general oxidation behavior of this alloy, to conclude that the primary effect of the surface deposited oxides was to act as a barrier layer. When the deposited layer is dense enough, as on parts of the surfaces of the Ca, La and Y coated specimens, a \( \text{Cr}_2\text{O}_3 \) layer was formed beneath the applied oxide. This would suggest that the applied coating decreased oxidant ingress, consequently reducing the oxygen potential beneath the coating to a sufficiently low value to promote \( \text{Cr}_2\text{O}_3 \) formation. These so-formed \( \text{Cr}_2\text{O}_3 \) scales were much more adherent, with no apparent convolutions indicating that the presence of
the applied oxides also greatly improved the adhesion of these \( \text{Cr}_2\text{O}_3 \) scales.

**Ni-25Cr**

The most effective surface oxides deposited on this alloy prior to oxidation were the oxides of Ce, Y and La. Their effects on the oxidation behavior may be summarized as follows:

1. The oxide growth rate in terms of a gravimetric parabolic rate constant is reduced by nearly a factor of ten.
2. Scale adhesion is enhanced.
3. Formation of a thin NiO layer above the \( \text{Cr}_2\text{O}_3 \) scale is totally eliminated by selective oxidation of the chromium.
4. Except for some occasional small nodules, the growth direction of the scale seems to be altered as indicated by the morphology of the grown oxide grains and the position of the initially deposited surface oxides.

The effectiveness of La, Y and Ce surface oxides relative to the rest of the deposited oxides confirms the result reported by Landkof et al (9). The general effects of these oxides also agree with previous studies on \( \text{Cr}_2\text{O}_3 \) forming alloys such as Ni-25Cr (8,9). It is most interesting that these observed effects correlate excellently with those found with bulk alloying additions.

The exact mechanism involved in producing these effects by the surface oxides is not yet clear. However, these surface oxides, particularly La, Y and Ce, are no longer believed to act as a semi-blocking layer as with the non-\( \text{Cr}_2\text{O}_3 \) forming Co-25wt%Cr alloy, since the majority of these applied oxide coatings simply stay loosely on the oxide surface and they can easily fall off upon tapping the specimens. When a scale cross-section of a Ce-coated specimen is prepared metallographically, the CeO\(_2\) coat even detached from the oxide indicating negligible interaction between the coat and
the underlying oxide. While the bulk of the coating is only loosely attached to the oxide surface, small particles of the applied CeO₂ is present within the top surface of the oxide. These particles could be what is responsible for the observed beneficial effects, since they are present throughout the entire coated surface areas of the flaky CeO₂ coatings even within cracks.

It seems possible then, that these small particles present on the surface acted as nucleation sites, as proposed by Stringer et al (15), which reduced the spacing between first formed Cr₂O₃ and promoted a continuous Cr₂O₃ scale at an earlier stage. As a result of the higher density of nuclei, a very fine grained oxide was formed on the scale surface. This fine grained layer may have been responsible for the change in oxide growth direction which is related to the slowed growth rate.

The effects due to surface HfO₂ proved to be detrimental, even though bulk addition of HfO₂ particles were reported to be as effective as other reactive element dispersoids by Goncel, Whittle and Stringer (17). A possible mechanism by which these surface HfO₂ flakes enhanced oxidation can be explained in light of the kinetics behavior and the final oxide morphology. From figure 4, the kinetics curve of the Hf-treated specimen clearly shows three stages of oxidation. During the first 3-4 hours, normal growth takes place and the behavior approximates to that observed with ZrO₂ or CaO deposits on the surface. However, due to the non-adherent nature of these HfO₂ flakes, a number of them would be lifted and become embedded into the growing scale. The presence of these thin flakes in the scale could enhance local cracking which exposes the underlying Cr-depleted alloy to the oxidant. This leads to the fast oxidation of the Cr-depleted zone to form a Ni rich layer until a healing Cr₂O₃ layer is developed. After which, the growth rate becomes the same as the untreated alloy and further weight gain results from the growth of this Cr₂O₃ layer.
The effect of some of the surface applied oxides on improving the scale adhesion for those alloys forming Cr$_2$O$_3$ scales is surprising. Earlier explanations in the case of alloys containing the reactive elements or dispersions of their oxide have included (1):

(a) The internal oxide particles act as vacancy sinks, preventing vacancies from condensing at the oxide-metal interface to generate voids.

(b) The internal oxide particles initiate the growth of oxide intrusions - "pegs" - into the metal.

(c) The reactive element collects at the oxide/metal interface, and modifies the binding energy, or forms a compound oxide intermediate layer.

(d) The reactive element prevents the diffusion of impurity elements from the interior of the alloy to the metal surface; these impurities are believed to reduce the scale-metal adhesion (18).

Since the reactive element oxide is generally located at the outer surface of the scale, when applied in this way, it is very difficult to see how any of the above mechanisms can be effective. It is possible that the reactive element oxides may getter surface impurities present either as a result of specimen preparation, or diffusing to the surface during the heating of the specimen prior to the formation of a thick oxide, but clearly they would be ineffective in preventing further migration of impurities in the later stages of the reaction.

Conclusions

The surface applied nitrate converted reactive element oxides show no effect on the oxidation behavior of non-Cr$_2$O$_3$ forming alloys. The deposited oxides become degraded and embedded in the growing scale as oxidation progresses. When the alloy's Cr concentration is increased to a borderline Cr$_2$O$_3$ former, its oxidation behavior becomes sensitive to the ambient oxygen pressure. As a consequence, some of
the applied coatings can act as a semi-blocking layer and reduce the oxidation rate or even locally promote Cr$_2$O$_3$ formation. The extent of the beneficial effect greatly depends on the integrity of the applied oxide coatings. The most dense and continuous coatings seem to be the most effective.

The effects on the Cr$_2$O$_3$ forming alloy vary from reactive element to element. This variation is not dependent on the apparent morphology of the applied oxide coatings, but is believed to be associated with the tendency to form small particles on the alloy surface in contact. When these particles are formed most efficiently, as in the case of La, Y and Ce oxides, the effects are the most dramatic and appear to be similar to those observed when reactive element oxide dispersions are present within the alloy.

The improved oxide adhesion promoted by this superficial treatment is remarkable, and appears to cast doubt on some of the earlier models proposed to account for this effect. Further study of this aspect is required.

**Acknowledgement**

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References
18. J. G. Smeggil, A. W. Funkenbusch and N. S. Bornstein, Presented at the 114th TMS-AlME annual meeting, N. Y., N. Y., February 1985
Figure Captions

Figure 1 - Surface topography of La, Y, Ca, Ce, Hf and Zr nitrate converted oxide coats.

Figure 2 - Kinetics curves showing the effect of coated $Y_2O_3$ on the oxidation behavior of the Co-15Cr alloy at 1000°C in 1 atm $O_2$. Numbers in parentheses are the amount of $Y_2O_3$ applied in mg/cm$^2$ prior to oxidation. The unclosed table shows the effect due to the different surface applied oxides.

Figure 3 - The effect of different surface applied oxides on the oxidation kinetics of the Co-25Cr alloy oxidized at 1000°C in 1 atm. $O_2$.

Figure 4 - Kinetics curves for Ni-25Cr alloys coated with various reactive element oxides oxidized at 1000°C in 1 atm. $O_2$.

Figure 5 - Influence of deposited CeO$_2$ upon a) the kinetics of oxidation and b) the oxide spallation from thermal cycling (20-hour cycles) of the Ni-25Cr alloy at 1000°C in 1 atm. $O_2$.

Figure 6 - Fractured cross section of scales formed on a) an uncoated Co-15Cr alloy and b) a Hf-coated Co-15Cr alloy (backscattered electron image), oxidized at 1000°C in 1 atm $O_2$. Since the tilt angles have been different for the two specimens, direct comparison of scale thickness from these micrographs cannot be made.

Figure 7 - Optical micrographs of cross sectioned scales developed on a) untreated Co-25Cr b) Hf-treated Co-25Cr and c) Zr treated Co-25Cr alloy oxidized at 1000°C in $O_2$ for 24 hours.

Figure 8 - a) SEM image of the surface oxide formed on a Y-coated Co-25Cr alloy oxidized at 1000°C for 24 hours. b)-d) are magnified views of areas A-C respectively with their corresponding EDX analyses given in the table.

Figure 9 - a) SEM image of the scale formed on a Hf-coated Ni-25Cr alloy oxidized at 1000°C for 100 hours. b)-d) are Cr, Ni and Hf X-ray maps respectively. e) Backscattered electron image of the scale formed on the same specimen.

Figure 10 - a) Backscattered electron image of a Ce-coated scale formed on the Ni-25Cr alloy oxidized at 1000°C for 100 hours. b) Backscattered electron image showing the detached CeO$_2$ coat on the polished scale.
Table 1: Oxidation Data for Co-25Cr and Co-25Cr(coated oxide) after 24 hours at 1000°C.

<table>
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<th>Deposited oxide</th>
<th>Weight gained from oxidation</th>
<th>Weight spalled from cooling</th>
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<tbody>
<tr>
<td>Untreated</td>
<td>5.11</td>
<td>7.72</td>
</tr>
<tr>
<td>Hf(0.3)</td>
<td>6.64</td>
<td>10.34</td>
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<tr>
<td>Ce(0.4)</td>
<td>3.65</td>
<td>2.89</td>
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<tr>
<td>Zr(0.3)</td>
<td>3.14</td>
<td>3.27</td>
</tr>
<tr>
<td>Y(0.4)</td>
<td>2.42</td>
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<td>La(0.2)</td>
<td>2.12</td>
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<tr>
<td>Ca(0.5)</td>
<td>1.46</td>
<td>0.18</td>
</tr>
</tbody>
</table>

All figures are in units of mg/cm². Numbers in parentheses are the weight of deposited oxide.

Table 2: Oxidation Data for Ni-25Cr and Ni-25Cr(coated oxide) after 45 hours at 1000°C.

<table>
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<th>Deposited oxide</th>
<th>Weight gained from oxidation</th>
<th>Weight spalled from cooling</th>
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</thead>
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<td>Untreated</td>
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<td>Y(0.4)</td>
<td>0.36</td>
<td>0</td>
</tr>
<tr>
<td>La(0.2)</td>
<td>0.35</td>
<td>0</td>
</tr>
<tr>
<td>Ce(0.6)</td>
<td>0.26</td>
<td>0</td>
</tr>
</tbody>
</table>

All figures are in units of mg/cm². Numbers in parentheses are the weight of deposited oxide.
Figure 2.

<table>
<thead>
<tr>
<th>Deposited oxide</th>
<th>Wt. gain from oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>40.4</td>
</tr>
<tr>
<td>Ca (0.5)</td>
<td>42.0</td>
</tr>
<tr>
<td>Ce (0.8)</td>
<td>42.0</td>
</tr>
<tr>
<td>Hf (0.4)</td>
<td>41.7</td>
</tr>
<tr>
<td>La (0.3)</td>
<td>42.2</td>
</tr>
<tr>
<td>Y (0.7)</td>
<td>39.9</td>
</tr>
<tr>
<td>Zr (0.7)</td>
<td>43.4</td>
</tr>
</tbody>
</table>

All figures are in mg/cm².
Figure 3.

Co-25 wt% Cr

Weight gain (mg/cm²)

Time (hr)

Hf

(−)

Ce

Zr

Y

La

Ca

XBL 854-6039
Figure 4.
Figure 5.
Figure 6.
Figure 7.
EDX Analyses

<table>
<thead>
<tr>
<th>Wt.%</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>97.70</td>
<td>4.72</td>
<td>53.36</td>
</tr>
<tr>
<td>Cr</td>
<td>2.30</td>
<td>28.40</td>
<td>46.64</td>
</tr>
<tr>
<td>Y</td>
<td>-</td>
<td>66.88</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 8.
Figure 9.
Figure 10

(a) Ni-25Cr

(b) Ni-25Cr

XBB 858-6443
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