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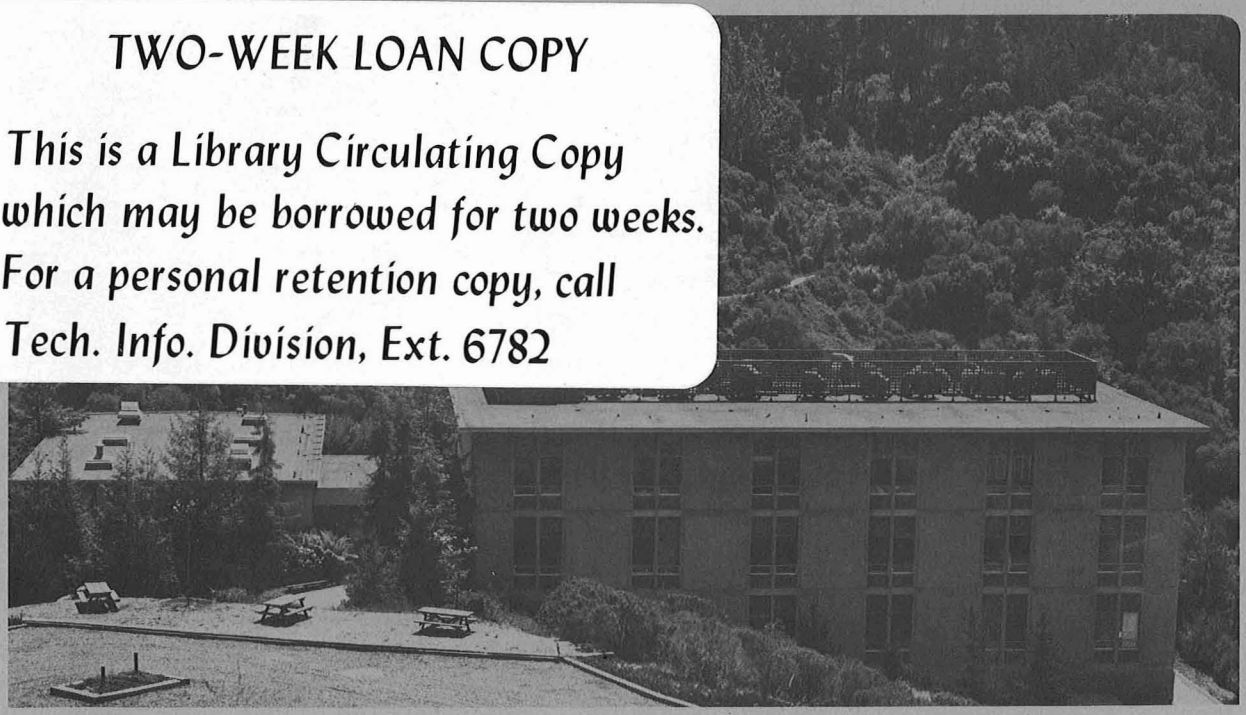

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THE ROLE OF ACTIVE ELEMENTS AND OXIDE DISPERSIONS IN THE DEVELOPMENT OF OXIDATION-RESISTANT ALLOYS AND COATINGS

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In developing oxidation-resistant materials for service at elevated temperatures, two requirements must be satisfied: diffusion through the oxide scales must occur at the slowest possible rate, and the oxide scale must resist spallation. Al_2O_3 adequately fulfills the former requirement, but its adhesion to the substrate is poor. Attempts to improve the adhesion have largely centered on the so-called "rare-earth effect," Y being the particular element used to improve the adherence of Al_2O_3 scales on MCrAlY-type alloys and coatings. The present work was initiated to study the effect in more detail and establish the critical parameters to aid the design of alloys having improved oxidation resistance.

Alloys in the CoCrAl system which form Al_2O_3 scales were studied, Co-10Cr-11Al being the basis composition. The alloys also contained between 0 and 1 wt. % Y or Hf. Oxidation kinetics in dry air were measured over the temperature range 1000-1200°C for times up to 1000 h; thermal cycling tests were also carried out. The morphological development of the scales was studied in detail.

Preferential oxidation of Hf and to a lesser extent Y, results in the formation of numerous oxide protrusions penetrating into the substrate alloy and these are largely responsible for the improvement in scale adherence. The pegs consist predominantly of Al_2O_3 which has grown inwards encapsulating the Hf- or Y-rich internal oxide particles. The size and distribution of the oxide protrusions play a decisive role in maintaining scale adherence over long exposure periods. Hf additions are better in this respect than Y additions, because other than at very low Y contents, most of the Y is present as the intermetallic yttride, which gives rise to relatively large, more widely spaced pegs. Hf is completely soluble in the alloy up to at least 1.5 wt. %, and thus the consequent, more uniform distribution of Hf in the alloy matrix results in a better size and distribution of the oxide pegs at the alloy-scale interface. The distribution can be improved even further by a pre-internal oxidation treatment which converts the Hf to a fine dispersion of oxide particles in the alloy. Again, these act as sites for peg development and a finer, more uniform distribution is achieved.

Introduction

There are two essential requirements for alloys which are designed to withstand degradation by oxidation during high temperature exposure. Firstly, they must form a surface oxide which thickens only at a slow rate, and secondly this oxide layer must remain adherent to the alloy surface under all conditions. Cr_2O_3 and Al_2O_3 are generally regarded as the best protective oxides: diffusion through them is relatively slow in comparison to most other oxides, and since they are also stable, relatively little difficulty exists in selecting an alloy which contains sufficient chromium or aluminum to provide, by selective oxidation, a protective Cr_2O_3 or Al_2O_3 scale under various service environments.

The second requirement is that of adhesion, since during exposure, environmental changes or stresses accompanying scale growth, can cause loss of adhesion and spallation of the oxide. Numerous factors may affect oxide adhesion, but, if consideration of mechanical disturbance is neglected, probably that of most importance is thermal cycling. During heating or cooling, stresses are developed due to differences in thermal expansion or contraction of the oxide and alloy and these lead to spallation of the protective oxide and excessive rates of metal loss.

Empirically, it was discovered over 40 years ago that additions of rare earth metals as a melt deoxidant to Nichrome (Ni-20% Cr) heating elements produced substantial increases in their lifetimes to failure in cyclic heating and cooling tests (1): the protective oxide was more adherent. Yttrium and scandium additions were included in the original patent, and it was also shown that by the combined addition of rare earths, alkaline earths and carbon, the life of heat resisting alloys could be further improved. The amounts of the additions were such that 0.01-0.5% rare earth, about 0.001-0.05% Ca and up to about 0.25% C remained in the finished alloy. This "rare earth effect" as it became known, was not confined to rare earth element additions. In fact, elements from Groups II, III, IV and V of the Periodic table could be used although their effectiveness decreased on passing from Group II to Group V, but increased with increasing atomic weight within a particular group.

Subsequent work has confirmed that a wide range of additions can have a similar effect. Indeed fine distributions of stable oxides in the alloy are perhaps even more effective in improving an alloy's performance under thermal cycling conditions. In many cases the two effects are indistinguishable, and may indeed be identical.

Detailed studies (2-5) of alloys forming Cr_2O_3 indicate that the presence of the active element or stable oxide dispersion in the alloy has the following effects:

(i) the amount of chromium required to form a continuous, external Cr_2O_3 scale is reduced;

(ii) the growth rate of the scale is reduced, the effect being more marked at higher temperatures;

(iii) the transport mechanism in the oxide is changed from predominantly metal transport to predominantly oxygen transport; and

(iv) the adhesion of the scale is greatly improved, this being particularly noticeable during thermal cycling.

It has not been clearly established whether the effect of adding a reactive element to an alloy is identical to that of adding a stable oxide

dispersion. It has been suggested (4) that the oxide dispersion in the alloy nucleates the external scale, thus curtailing the transient stage of oxidation and thereby reducing the tendency of the stable Cr_2O_3 from being disrupted by less stable, but faster growing oxides. As a consequence, the grain size of the scale is reduced; and it appears that the predominant transport mechanism becomes grain boundary diffusion of oxygen. In alloys containing reactive element additions only, it is probable that the reactive element oxidizes internally ahead of the scale/alloy interface, but this is unlikely to have any effect in the early stages of oxidation.

A number of mechanistic models have been proposed to explain the improved scale adhesion and the most significant are:

(a) Mechanical keying or "pegging" of the scale to the alloy (6-9). In the case of an active element addition the peg is supposed to be produced by the selective oxidation of the addition at the scale/alloy interface: in the case of the stable oxide dispersion, the fine oxide particles are regarded as the pegs.

(b) Provision of sites for vacancy condensation (10) by the internal oxide particles of the active element, or the stable oxide dispersion, thus eliminating interfacial porosity.

(c) Formation of a compound oxide layer (11) between scale and substrate which has a coefficient of thermal expansion that gradually changes from a value similar to that of the alloy to a value close to that of the scale--a graded seal.

(d) Modification of the oxide scale plasticity (12) allowing accomodation of the thermally induced stresses.

Al_2O_3-forming alloys have been studied in less detail. Scale adhesion is also greatly improved, but there appears to be little effect on the isothermal growth rate of the scale (11). Al_2O_3 scales always grow by grain-boundary transport of oxygen, so there seems to be no change in transport mechanism. Furthermore, the grain size of the oxide is usually so small that nucleation effects are less likely, and no significant change in the aluminum content required to form a continuous external Al_2O_3 scale has been reported.

The majority of alloys containing dispersed oxide phases have been produced as a result of efforts to improve their high temperature creep strength, and the particle sizes, volume fractions and interparticle spacing has been determined on these grounds. There is no good evidence as to the effect of these variables on the oxidation behavior. It is difficult and expensive to produce alloys containing dispersions. The common methods include vapor phase deposition of metal on oxide particles, followed by conventional powder metallurgical fabrication, or mechanical alloying. An alternative method for producing oxide dispersions may be using a technique of controlled internal oxidation which has had some success with Cr_2O_3-forming alloys (13). With alloys forming external Al_2O_3 layers, the conditions are more restrictive, since the alloy element to be internally oxidized must have a higher oxygen affinity than aluminum, and the oxidation must be conducted at oxygen pressures below the dissociation pressure of Al_2O_3.

Thus, the essential aims of this research are:

(1) to examine the feasibility of producing dispersed oxide phases in Al_2O_3-forming alloys using a controlled internal oxidation technique;

(2) to study the effects of these dispersions on the development, growth and adherence of the Al_2O_3 scales;

(3) to elucidate the mechanisms of any beneficial effects which are produced, and relate this to the distribution, size and morphology of the oxide dispersion;

(4) to optimize the particular reactive metal addition, its content and the internal oxidation pre-treatment to produce the maximum oxidation resistance.

Experimental

The alloys were prepared by vacuum melting at 10^{-5} Torr in a high frequency induction furnace and casting in vacuo into 250 g ingots of approximate dimensions 3.5 × 3 × 2 cm. The ingots were then machined to remove about 2 mm from the outer surface. The purity of the starting materials is given in Table I.

Table I. Analysis of Starting Materials

Element	Analysis (p.p.m.)
Cr	400 O_2, 15-20N_2, 5 Fe, 5 Al, 40 H_2, 10 S
Al	50 Si, 30 Cu, 40 Fe, 20 Mn, acid insolubles 50, nitrogen compounds 10
Co	24 Cu, 12 S, 1 Al, 10 Fe, 7 Sb, 110 O_2, 3500 Ni, 12 Pb, 20 C, 1 H_2

Co-10Cr-11Al was the main alloy composition used as representative of Al_2O_3 formers; Hf, Y or Ce were the reactive elements.

The nominal compositions of the alloys are shown in Table II.

Table II

Base metal	Cr	Al	Y	Hf	Others
Co	10	11	--	--	
	10	11	0.1	--	
	10	11	0.3	--	
	10	11	1.0	--	
	10	11	--	0.05	
	10	11	--	0.10	
	10	11	--	0.3	
	10	11	--	1.0	
	10	11	--	1.5	
	10	11	--	--	1.0 Ce
	15	8	--	--	
	15	8	1		

The Hf-containing alloys (up to 1.5 w/o Hf) contained no Hf-rich phase, nor any apparent Hf-enrichment in either the β'- or the α-phases, indicating that Hf is completely soluble in the CoCrAl alloys.

Isothermal oxidation experiments were performed at 1000, 1100 and 1200°C in static air, slowly flowing oxygen or slowly flowing air.

Oxidation kinetics were obtained by continuous weight gain measurements using a Sartorius automatic recording microbalance mounted above a vertical high temperature resistance furnace. Long term isothermal oxidation experiments were carried out at 1000, 1100, and 1200°C in horizontal muffle furnace. Samples were placed in Al_2O_3 crucibles and left for 1000 hours.

Cyclic oxidation experiments were carried out in a horizontal muffle furnace in static air at 1100 and 1200°C. Specimens were placed in recrystallized Al_2O_3 crucibles placed in the furnace for 20 hours, then removed and allowed to cool to room temperature in a dissicator before weighing. Test specimens were oxidized in duplicate up to a total time of 340 hours.

Identification of oxidation products in the early part of the present work was accomplished by in situ x-ray diffraction using a "Mcleans x-ray diffractometer utilizing AEI-RAYMAX 60 x-ray generator." "Chromium" target was used with filter, and the resulting x-ray patterns were identified using ASTM data "cards."

Qualitative analysis in order to identify the elements present and their distribution in the alloy substrate as well as in the oxide scale were performed using a "JEOL JXA 50A" electron probe microanalyzer. An energy dispersive x-ray analyzer, incorporating an "EDAX" Detector and "Link" system processor where all x-ray energies are recorded simultaneously, was used in some of the examinations, for example, for internal oxide particles. A "Kevex" Si-Li detector for EDA with a "Link" system processor attached to a "JEOL JSEM 200B" transmission electron microscope (TEM) with a scanning transmission attachment (STEM and SEI modes) was used for the examination of small features at both interfaces of stripped oxides.

Results and Discussion

The results of the experiments performed on CoCrAl alloys involving yttrium and hafnium additions and a comparison with related studies in the literature reveals that there is no single factor involved in the improvement of Al_2O_3-scale adherence. The major cause of scale spallation, however, appears to be thermally induced stresses which act in a plane parallel to the oxide surface; specifically along the scale/alloy interface.

During the oxidation of CoCrAl alloys, voids develop along the oxide /alloy interface during the very early stages of oxidation: Figure 1. These voids continually grow during oxidation and may cover up to approximately 50% of the interface area after extended exposures, as shown in Figure 2. All the evidence in the present work is consistent with a model in which the Al_2O_3 grows inwardly, by the enhanced movement of oxygen ions down oxide grain boundaries towards the oxide/alloy interface. There is no evidence of outward diffusion of aluminum ions. Thus, large columnar oxide grains develop near the oxide/alloy interface and they increase in diameter upon longer exposures: Figure 3. The outermost portion of the scale near the gas/oxide interface is formed of small equiaxed grains which do not exhibit any change in size during exposure, Figure 4. It seems likely therefore that with the present alloys, voids result from the selective removal of Al from the alloy and an unequal flux inwards of Co and Cr. Thus, there is a nett vacancy flux towards the oxide/alloy interface where they coalesce

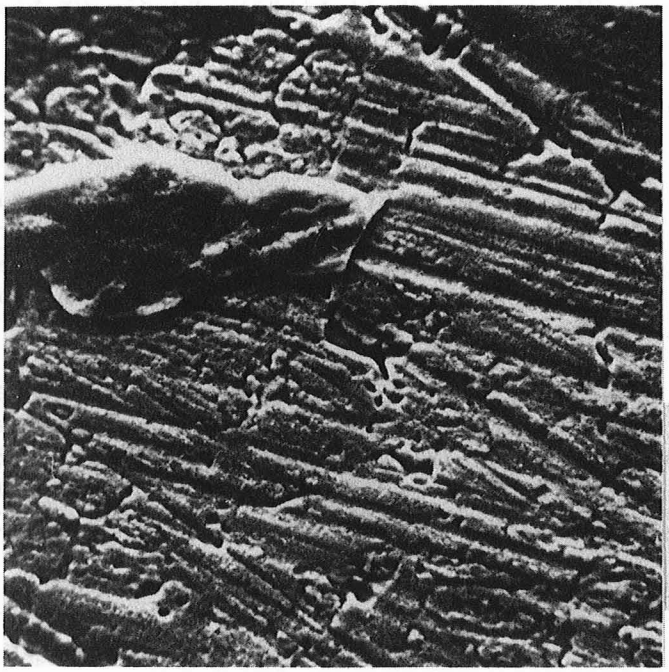

Fig. 1. Surface of Co-15Cr-8Al following scale spallation: samples exposed for 5 minutes at 1100°C, (×1075).

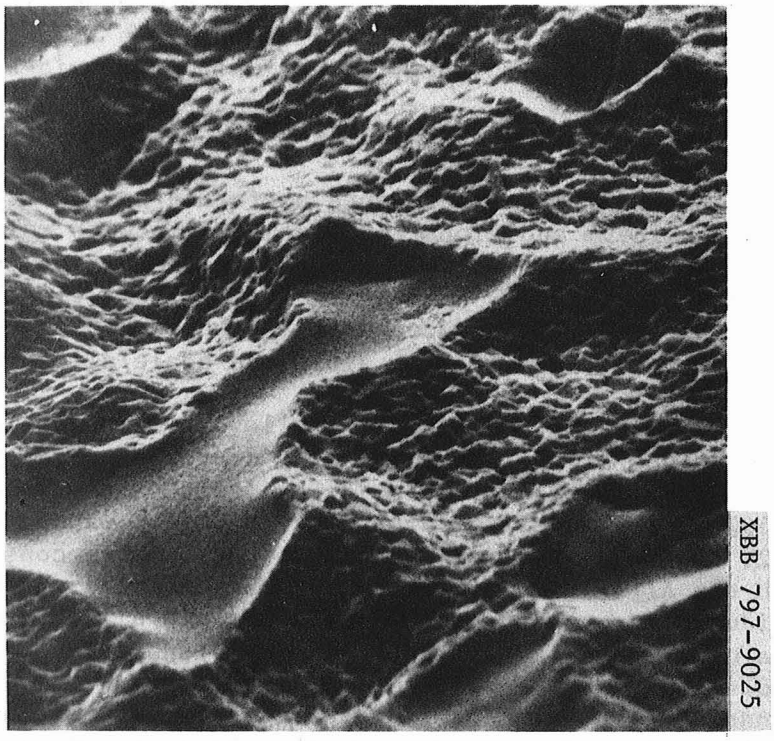

Fig. 2. Surface of Co-15Cr-8Al following scale spallation: sample exposed for 190 hrs at 1200°C, (×1000).

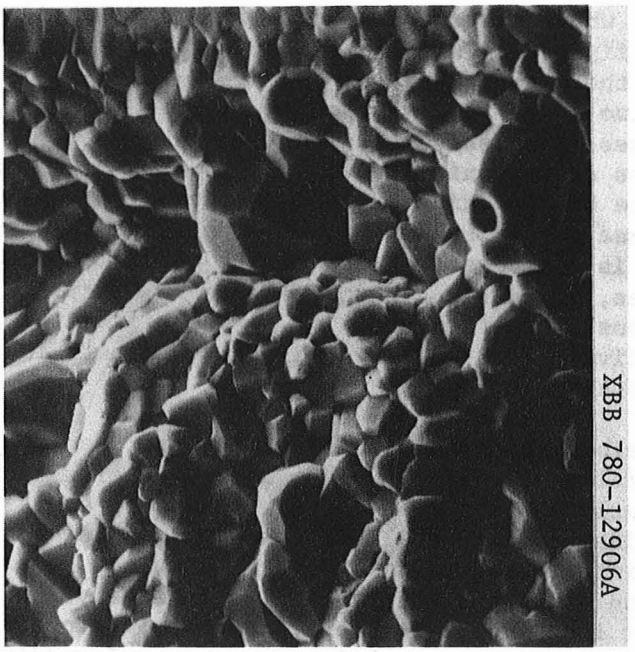

Fig. 3. Large Al_2O_3 grains formed within depressions at the scale underside after oxidation of Co-15Cr-8Al for 1000 hrs at 1200°C, (×1000).

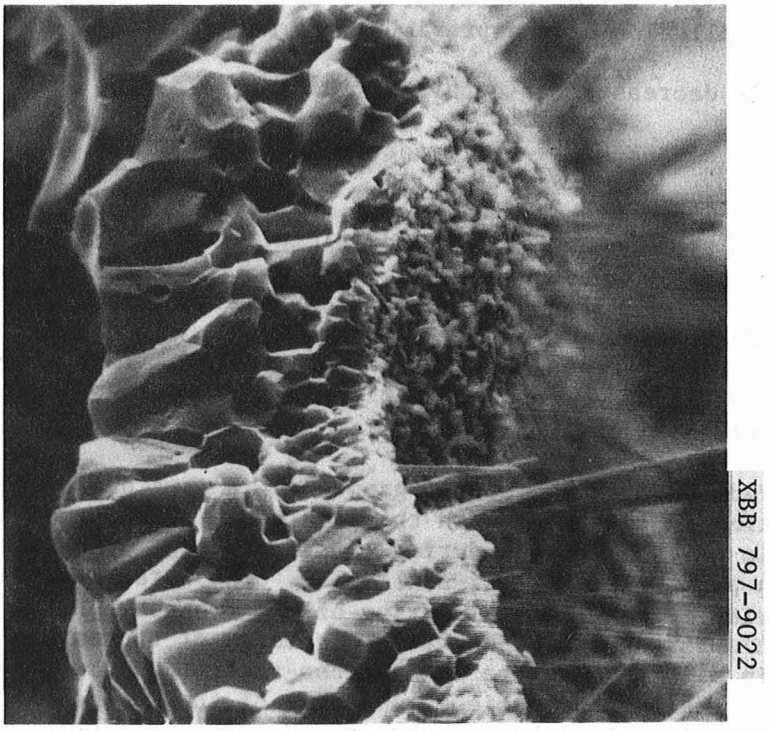

Fig. 4. Transverse section of Al_2O_3 formed on Co-15Cr-8Al after 1000 hrs oxidation at 1200°C, (×2000).

and grow by vacancy precipitation. Although interfacial voids represent areas of lost contact between the scale and the alloy, the uniform scale thickness suggests that they exert no influence on the Al_2O_3 growth rate.

At areas where interfacial voids were developed, oxide wrinkles usually form in a configuration similar to that of the corresponding voids. The magnitude of the shape change of the Al_2O_3-scale due to the formation of wrinkles is too large to be caused by plastic deformation in response to growth stresses. Instead, it seems more likely that the generation of oxide wrinkles during oxidation is due to the growth of large oxide crystals on the surface of the oxide exposed to the voids, which impinge upon each other and cause scale buckling. It is believed that the presence of interfacial voids is a necessary prerequisite condition for the formation of oxide wrinkles, since the growth of large Al_2O_3 crystals takes place only at those locations where the supply of Al vapor from the substrate side of the void is relatively fast and the oxide grain growth is not restricted by the retarding substrate.

The development of interfacial voids represents areas of lost contact at the oxide/alloy interface which, under the effect of thermally induced stresses greatly enhance scale spallation. For short oxidation periods, where the oxide scale is still thin and only a few voids have formed at the oxide/alloy interface, scale failure takes place by fracture of the oxide and separation along the interface simultaneously. When thick scales are formed, after long exposures, separation becomes predominant as interfacial voids have grown to cover much larger areas. In addition, scale breakaway is enhanced along the weak boundaries "in the oxide" between the interfacial voids and the remaining areas, which result into crack initiation and increased spallation during temperature changes.

The addition of yttrium and hafnium to CoCrAl alloys produces three main effects:

(1) it speeds up the formation of a continuous layer of Al_2O_3 during the initial exposure period, or when fresh alloy is exposed after spallation of the previously formed scale;

(2) it decreases the apparant growth rate of the Al_2O_3 scale; and

(3) it enhances the scale adherence.

Figures 5 and 6 show examples of the first two of these effects for Co-10Cr-11Al containing Hf and Y additions. The curtailment of the transient period is probably due to the formation of the Y or Hf oxide particles near the surface of the alloy. These particles may act as nucleation sites for all the oxide phases and hence, promote the Al_2O_3-scale to grow laterally as the interspacing between Al_2O_3 nuclei is reduced. This results in a fine grained Al_2O_3 layer which when completed, may undercut the growth of the faster growing oxides.

The reduced overall rate of growth is in part due to the prevention of scale lifting and cracking with the resultant formation of multi-layered Al_2O_3-scale which is common during even isothermal oxidation of the undoped alloys, in particular Co-10Cr-11Al alloy. The rate, however, may be reduced further, with a significant lowering of the transport rates through the scale. This latter can be explained in terms of the marked changes in the Al_2O_3 grain size through the scale cross-section on the doped alloys: similar changes are less dramatic in the case of the undoped alloys. Thus, some of the short circuit paths for the inward oxygen diffusion are eliminated. In these terms, the sharp decline in oxidation rate during the transition

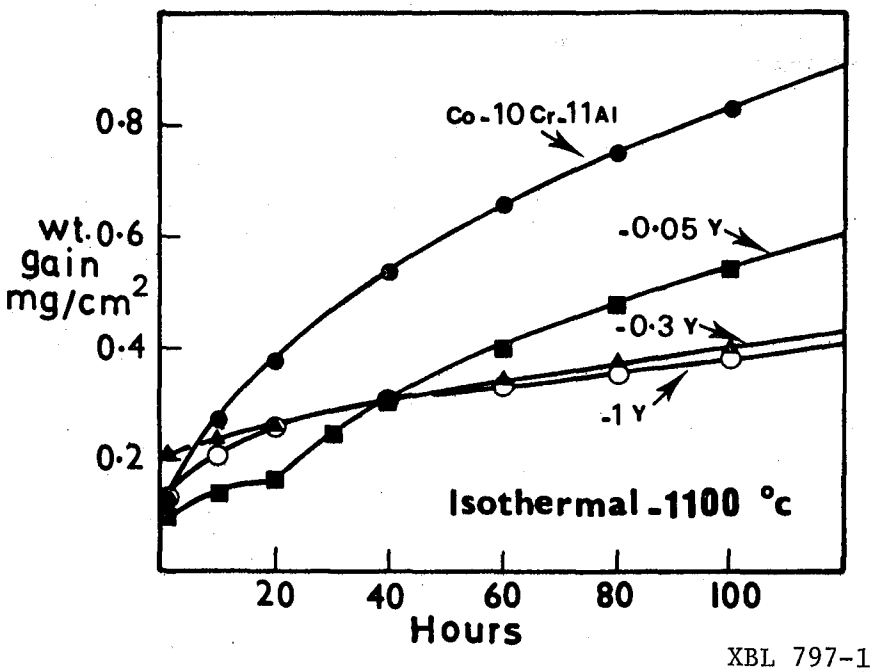

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Fig. 5. Isothermal oxidation kinetics at 1100°C of Co-10Cr-11Al containing 0, 0.05, 0.3 and 1.0 wt.% yttrium.

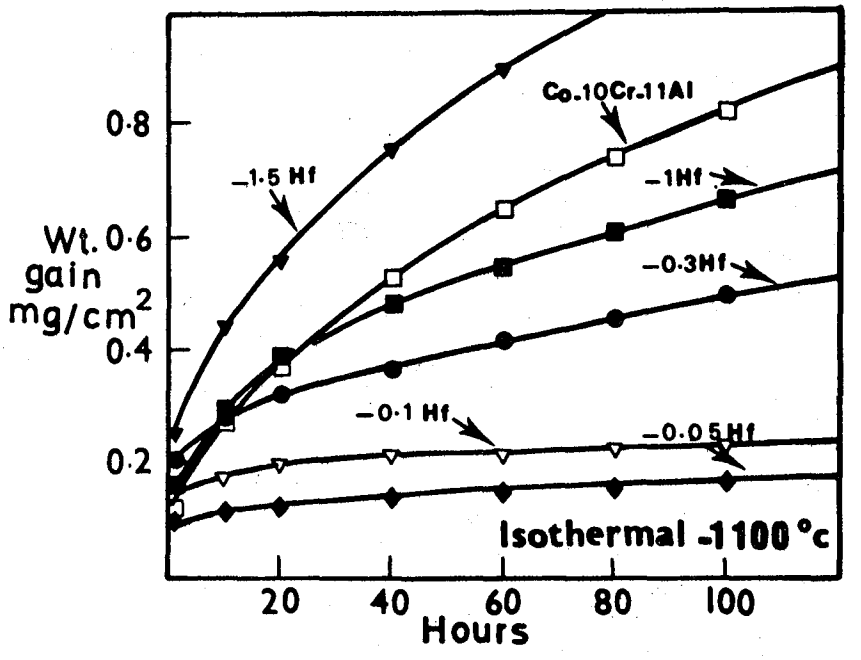

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Fig. 6. Isothermal oxidation kinetics at 1100°C of Co-10Cr-11Al containing 0, 0.05, 0.10, 0.30, 1.0 and 1.5 wt.% hafnium.

from the transient stage to the steady state stage is consistent with the fewer grain boundaries in the latter stage.

The mechanism by which both Y and Hf influence the Al_2O_3-scale adherence is independent of the type of the addition, although, the degree of improvement produced varies according to the type and the amount of the addition. The graded seal mechanism seems to be unlikely since there is no evidence of the formation of Y- or Hf-rich compound oxide layers at the oxide/alloy interface of any of the alloys. It is believed that any mechanism involving the accommodation of compressive stresses in the scale through a graded seal or increased plasticity is unlikely since it has been indicated that oxide stresses have not been relieved during cooling.

The removal of interfacial voids by either Y or Hf, even at very low concentrations (0.05%) of the latter, can account for some improvement in the Al_2O_3-scale adherence. Alloys containing 0.05% Y, a concentration which is too small to prevent void formation, showed considerable tendency for oxide spallation during cooling. For the same Hf concentration, which appears capable of eliminating interfacial voids, the scale showed a relatively marked resistance to spallation. The effect of void formation in these two particular alloys is distinguishable from any contribution of a mechanical keying effect, since at these low concentrations, there have been no signs of any significant peg formation. There was no evidence of the formation of fine dispersion of internal oxide particles immediately below the oxide/alloy interface in the 0.05% Hf alloy in spite of the elimination of the interfacial voids. It appears that the active element atoms themselves could act as vacancy sinks, or that fine internal oxide particles below the limit of resolution of the analytical equipment used have probably formed and acted as sinks.

Further support to the vacancy sink mechanism is the reappearance of interfacial voids in alloys containing low Y or Hf concentrations after long exposures: Figure 7. For those alloys, the effect of the internal oxide particles formed ahead of the interface as vacancy sinks eventually stops

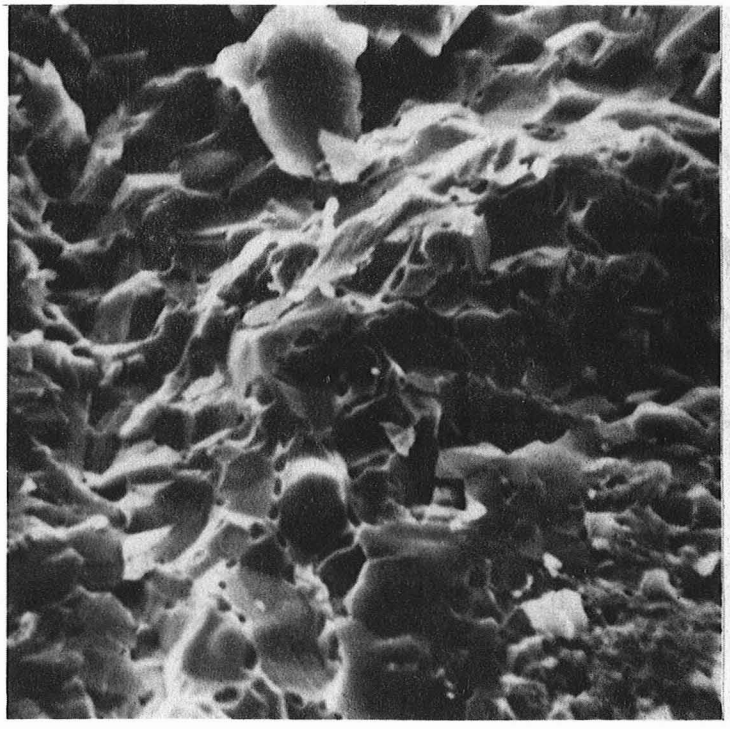

Fig. 7. Alloy surface following scale spallation. Co-10Cr-11Al-0.3Y oxidized for 1000 hrs at 1200°C, (×4500).

when these particles are incorporated into the ingressing scale after long exposures. Hence, as for undoped alloys, the Kirkendall vacancies produced during these late stages start to precipitate as voids at the oxide/alloy interface, and this is usually accompanied by localized loss of scale adherence.

The presence of either Y or Hf exerts no apparent influence on the mode of Al_2O_3 growth. Al_2O_3 is believed to grow inwardly by the diffusion of oxygen along the oxide grain boundaries whether the alloy contains active elements or not. For the undoped alloys, there has been no evidence of the formation of oxide within the existing oxide layer. Consequently, there is no evidence that trace elements may prevent this process. Y and Hf additions are believed to prevent ridge formation by preventing the coalescence of interfacial voids, the presence of which is necessary for ridge formation and consequent loss of adherence.

The improved Al_2O_3 scale adherence is mainly attributed to the mechanical keying of the scale to the substrate caused by the development of oxide intrusions which penetrate into the alloy. These intrusions are formed of Al_2O_3 which grow inwardly, encapsulating the reactive element oxide particles and are thus connected to the external scale. For given oxidation conditions, the size of these intrusions depends on the concentration of the reactive element. Comparing alloys containing equal amounts of Y or Hf, larger oxide intrusions often develop in the Y alloys and these are usually localized at the intersections of the alloy grain boundaries with the oxide scale. For Hf-containing alloys, the average size of oxide intrusion is less than that in Y-containing alloys, and their distribution is far more homogeneous, as shown in Figure 8. These conditions result from the complete solubility of Hf in the base alloy and the absence of Hf segregation in the form of intermetallic compound. The presence of Hf in solid solution leads to a uniform distribution of fine internal oxide particles beneath the interface. This allows the Al_2O_3 to form into a branched pattern around the HfO_2 particles which, although contributing markedly to the overall weight gain, ensures greater anchoring of the scale to the alloy substrate.

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Fig. 8. Cross section of the scale formed on alloy Co-10Cr-11Al-11Hf oxidized for 200 hrs at 1200°C, (×850).

Figure 9 shows that the formation of large oxide pegs, more commonly noticed in Y-containing alloys, is accompanied by localized scale failure. Thus there is clearly an optimum size and distribution of oxide pegs with which the highest scale adherence could be obtained. Hf additions of 0.3-1.0 w/o seem more efficient in producing the right size and distribution of oxide pegs than Y-containing alloys.

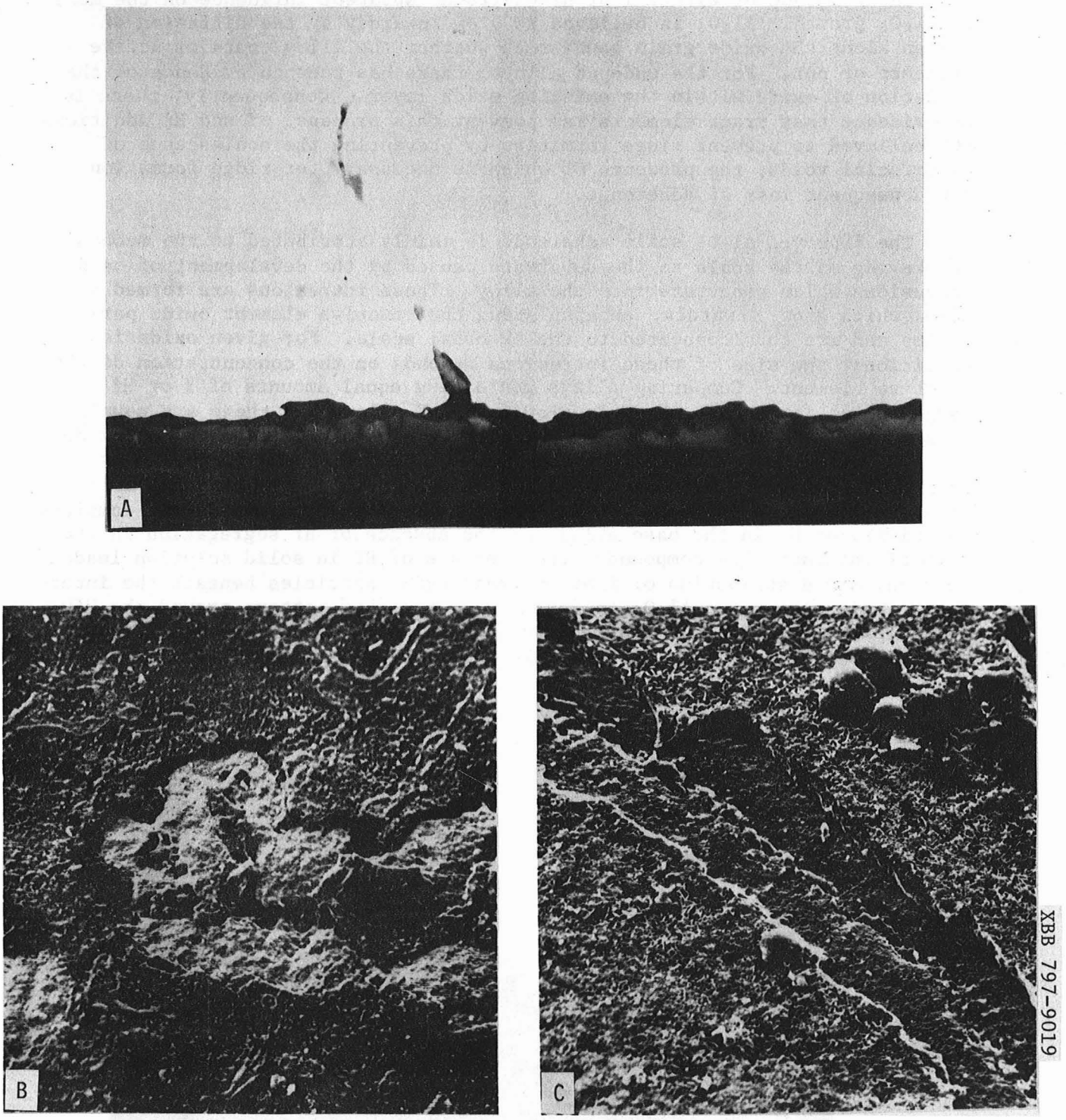

Fig. 9. Scales formed on Co-15Cr-8Al-1Y. (A) Cross section of sample oxidized 1000 hrs at 1200°C, (×750); (B) Surface of a sample oxidized 1000 hrs at 1100°C, (×200); (C) Surface of a sample oxidized 120 hrs at 1200°C, (×200).

The beneficial effects can be further extended by the presence of an oxide dispersion. Maximum benefits can be obtained when the dispersoid configuration is controlled to produce a fine distribution of HfO_2 particles which upon oxidation of the alloy results in a more uniform distribution of oxide intrusions penetrating into the alloy and more efficient keying of the scale to the substrate: Figure 10. The presence of the dispersoid speeds up the establishment of the steady state scale in comparison to alloys containing no dispersoid since it increases the number of particles which may act as nuclei for all oxides at the free alloy surface at the beginning of oxidation.

HfO_2 dispersoid produces further reduction in the overall isothermal oxidation rate than alloys containing Hf: Figure 11. This is attributed primarily to the reduction of the amount of Hf remaining in the alloy which on oxidation can contribute significantly to the overall weight gain and secondly, to the marked improvement in scale adherence and the prevention of multi-layered scale formation.

The marked improvement in Al_2O_3 scale adherence due to the dispersoid is also attributed to the production of a homogeneous distribution of fine oxide intrusions during oxidation. The presence of HfO_2 dispersoid particles in a fine distribution promote the development of small size, narrowly spaced oxide intrusions as Al_2O_3 grows inwardly along the incoherent boundaries of the particles. The internal oxidation treatment results in a reduction in the Hf content in the alloy which means a lesser amount of Hf diffusing towards the interface during oxidation. This prevents the gross oxygen diffusion around the particles and consequently reduces the tendency to form large oxide intrusions.

The other important factor contributing to scale adherence is the prevention of void formation of the oxide/alloy interface. Unlike the Hf containing alloys, the dispersoid containing alloys, even at low Hf levels (0.1%), did not show any reappearance of interfacial voids even after extended exposures at high temperatures. Thus it is concluded that dispersoid particles remain as effective vacancy sinks after long exposures since their presence extends very deeply through the sample section, which makes them unlikely to be saturated.

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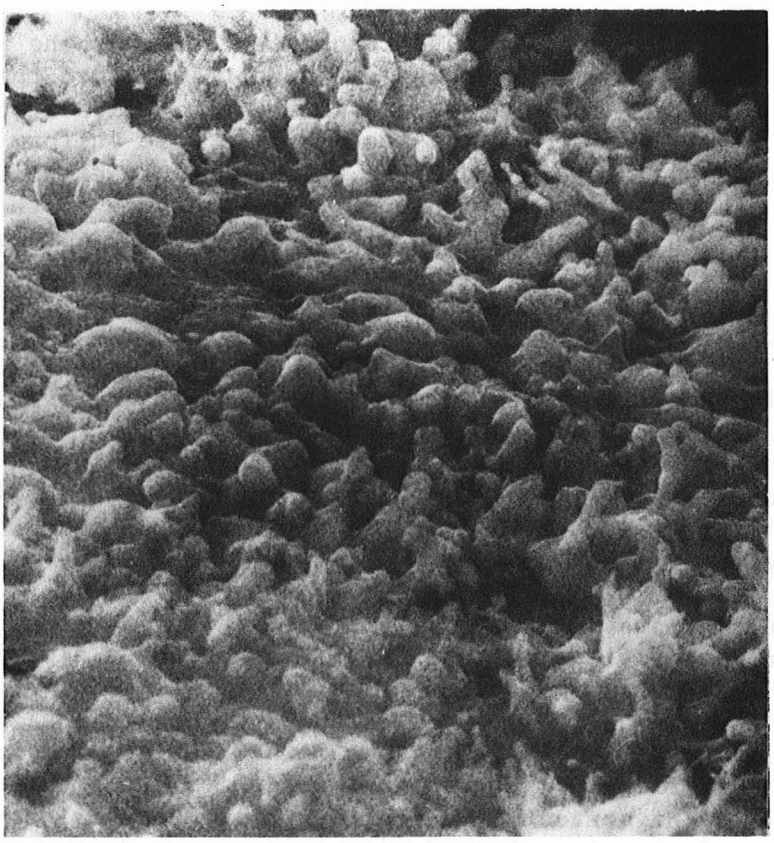

A

B

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Fig. 10. Underside of Al_2O_3 scale stripped from Co-10Cr-11Al-1Hf oxidized for 75 hrs at 1200°C. (A) Sample internally oxidized at 1100°C for 150 hrs in $CoAl/Al_2O_3$ mixture, (×1000); (B) No internal oxidation treatment, (×1000).

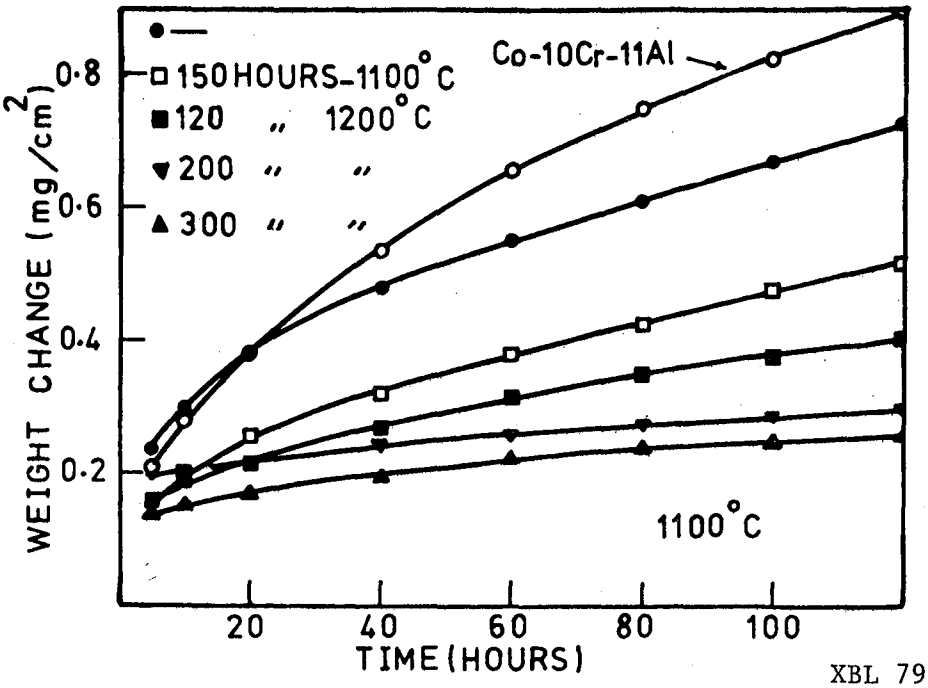

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Fig. 11. Isothermal oxidation of Co-10Cr-11Al-1Hf at 1100°C after receiving different internal oxidation treatments.

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