

The effect of reactive element additions on the selective oxidation, growth and adhesion of chromia scales

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Abstract

The addition of minor amounts of reactive elements to Cr_2O_3 or Al_2O_3 forming alloys has been known to produce a number of beneficial effects in improving their oxidation resistance. The mechanism by which these elements influence oxidation is, however unclear. In this paper, the effect of reactive element addition, whether as surface or alloying additives, on the development, growth and adhesion of Cr_2O_3 scales is discussed. It is pointed out that the development of a continuous external Cr_2O_3 layer and the elimination of base metal oxidation are not coupled processes; reactive element additions can eliminate the latter, but not always affect the former. The incorporation of a reactive element in oxide scales is essential for modifying scale growth. However, a slower oxidation rate or a change in the overall oxide growth direction are not critical factors in improving scale adhesion. In light of these and other experimental results, current theories concerning the reactive element effect are critically evaluated.

Keywords: Reactive element effect; Chromia scales

1. Introduction

All metallic components operating at elevated temperatures need the protection of a slow growing and adherent oxide scale, or a coating which can easily develop such a scale, to resist oxidation. The most common protective oxides in practice are alumina, Al_2O_3 , and chromia, Cr_2O_3 . It was empirically discovered over 50 years ago [1] that minor additions of rare earth elements in these Al_2O_3 - or Cr_2O_3 -forming alloys greatly improved their oxidation resistance. Whittle and Stringer [2] reviewed the early literature on this effect, and noted that almost any elements which have a higher affinity for oxygen than the scale-forming element or fine dispersions of their oxides may be effective and termed it the “reactive element effect” (REE).

For Cr_2O_3 -forming alloys, the presence of a reactive element (RE) in the alloy can [2]: (i) enhance the selective oxidation of chromium, by either lowering the amount of Cr required to form a continuous protective Cr_2O_3 layer, or by reducing the formation of base metal containing oxides in the external scale; (ii)

reduce the growth rate of the chromia scale, particularly at temperatures above 900 °C; (iii) change the transport mechanism through the scale from principally metal transport outward for alloys without the reactive element addition to principally oxygen transport inward; and (iv) increase the resistance of the scale to spallation, both on thermal cycling and mechanical straining.

The amount of reactive element needed in the alloy to produce the REE is typically between 0.1 and 0.2 at.%. Amounts over 1 at.% generally lead to a deterioration in the scale adhesion. It is important that the reactive element is finely and uniformly distributed. All the REE can also be manifested by dispersions of reactive element oxides in the alloy. The amount of oxide dispersion needed is typically 1–2 vol.%, and they too need to be finely and uniformly distributed. Other than alloying of the REs or their oxides, reactive elements that are superficially applied on alloy surfaces can also show similar beneficial effects.

In spite of the commercial application and importance of the REE, and the long time that it has been

recognized and investigated, there is still a lack of understanding of the basic mechanisms involved. Many theories have been proposed to explain the various aspects of the reactive element effect. Earlier models were reviewed by Whittle and Stringer [2], and more recent ones have been examined by others [3–8]. Over the last several years, we have studied aspects of the mechanism of the REE, primarily using ion implantation, not as a potential protection procedure, but as an experimental tool. A major reason for studying Cr_2O_3 scales was due to the greater range of RE effects manifested on chromia-formers. All experimental results and discussions in this paper will be confined to chromia scales unless stated otherwise. The purpose of this paper is not to present a comprehensive review of the subject, but to discuss critically some of the more widely accepted theories concerning the REE in light, mostly, of our own work.

2. Selective oxidation of chromium

According to Whittle and Stringer [2], the effect of reactive elements or dispersions of their oxides in enhancing the selective oxidation of chromium in M–Cr alloys, where M is Fe, Co or Ni, is manifested in two ways: (i) a continuous layer of Cr_2O_3 is formed at a lower chromium content than would be required in the absence of the reactive element, and (ii) the transient oxidation stage is curtailed and less base metal oxidation occurs.

In the past, the two processes have often been considered to be coupled, i.e. one leading to the other. This is especially true if one accepts the “nucleation theory” that was proposed to explain the selective oxidation effect of the reactive elements [9]. In the theory, reactive element oxide particles emergent on the alloy surface are proposed to act as nucleation sites for the first-formed oxide, thus greatly increasing the number of nuclei and decreasing the internuclei spacing. By decreasing the distance between adjacent Cr_2O_3 nuclei, the time required for the lateral growth process to form a complete Cr_2O_3 layer and terminate the formation of base metal oxides is consequently reduced. Results from more recent studies, however, suggest that the two aspects of the so-referred “selective oxidation” are actually different processes. Although one may lead to the other in some instances, they are also distinct in other situations.

2.1. Base metal oxide formation on chromia-forming alloys

The presence of base metal oxide in the outer region of a scale is often considered to be a residue of the initial non-steady state period [10]. This is true for

many alloys, Ni–20wt.%Cr being one example, but not for all. In the case of Ni–25wt.%Cr, for instance, the first formed oxide was always a continuous layer of Cr_2O_3 , but NiO nodules grew on top of the Cr_2O_3 layer, increasing in number and size with further isothermal oxidation [11]. The way these nodules developed did not resemble local breakaway oxidation, in which the protective scale fractures to expose the underlying alloy to the oxidant. Rather, the presence of base metal oxide seems to arise as a steady-state phenomenon involving the transport of the base metal through the initially-formed chromia layer. With the presence of reactive elements, whether as surface or alloying additions, base metal formation of this kind can be entirely eliminated. Although base metal transport through stable oxide layer has been known for a long time on selected systems, the mechanism by which it occurs is not entirely clear. From the Ni–25Cr alloy studied here, it appears that the process is not related to the development of the initially-formed Cr_2O_3 layer.

A possible explanation for the preclusion of NiO on RE-modified Ni–25Cr is that the presence of reactive elements somehow prevented the transport of nickel out through the chromia layer. This may be achieved by the development of a chromia scale that is less permeable to material transport. According to TEM observations [12–14], the first-formed Cr_2O_3 scale on RE-containing alloys was denser and finer-grained than that developed on RE-free alloys. A modified microstructure of this kind has been suggested to have an effect on material transport through the scale [12]. However, the exact mechanism by which this occurs is unclear. Our results have also shown that the elimination of NiO formation is not influenced by the reduction in Cr_2O_3 growth rate, nor by the change in its growth direction [11,15]. The path for nickel transport through the oxide would then be different from those involved in the transport of chromium and oxygen.

2.2. Formation of a continuous external Cr_2O_3 layer

In recent years, many investigators have studied the REE using surface-applied reactive metals via ion-implantation, or reactive element oxides via some kind of surface coating. Studies involving these techniques have been reviewed respectively by King and Grabowski [16] and Bennett [17], and by Moon and Bennett [18]. In all cases, if the alloy was a good chromia-former, the applied reactive element was able to prevent base metal oxide formation. However, if the alloy was not a good chromia-former, a continuous, stable Cr_2O_3 layer could not be formed as one would have found with alloying addition of the same reactive element.

We have carried out a series of tests to investigate the ability of ion-implanted and surface-coated reactive elements in promoting external Cr_2O_3 scale formation

on normally non-chromia forming alloys such as Co–15wt.%Cr and Co–25wt.%Cr [19–21]. Results showed that none of the surface-applied reactive metals or oxides had any effect on the subsequent oxidation of the Co–15Cr alloy. A thick duplex Co-rich oxide layer formed while the applied RE concentrated at the boundary between the outer and inner oxide layers. The behavior is dramatically different from results reported by Stringer and Wright [22], where an addition of 3 vol.% of Y_2O_3 in Co–21wt.%Cr completely changed the oxidation behavior of the alloy from developing a Co-rich scale to forming a continuous stable external Cr_2O_3 layer.

For the Co–25Cr alloy, only on surfaces where RE oxides were densely deposited was a temporary and localized Cr_2O_3 scale formed. Implantation of a very high dosage, 4×10^{17} ions cm^{-2} , which was equivalent to a maximum Y concentration of 23.5 at.%, also resulted in the formation of an external Cr_2O_3 scale, but its integrity was again disrupted with further oxidation, resulting in outward growth of CoO. The development of these chromia scales is envisaged to be the result of a temporary blocking effect. In the case of surface oxide coatings, a thick and dense surface layer acted to physically block the ingress of oxygen to the alloy surface [19,20]. In the case of implantation, large amounts of RE incorporated into the surface region of the alloy significantly changed its composition, resulting in a modified oxidation until the implantation affected depth was exceeded [21].

With less densely deposited surface coating, or lower implantation dosage, the incorporated RE exerted a minor effect on the overall oxidation rate of the Co–25Cr alloy. Although the scale that formed was still rich in Co with a duplex structure, formation of a Cr_2O_3 healing layer at the scale-alloy interface was easier. However, establishment of this healing layer only happened after prolonged oxidation and was never complete. Furthermore, local breakdown of the layer from CoO overgrowth continued to occur. In contrast, when 0.2 wt.% Y was added as an alloying addition to the Co–25Cr [21], a continuous Cr_2O_3 layer developed after only a few hours of oxidation, and it was stable and did not show any CoO overgrowth with further oxidation.

2.3. Two different aspects of selective oxidation

In summary, surface-deposited reactive elements or their oxides are insufficient in promoting the formation of a continuous Cr_2O_3 scale on alloys that are non-chromia formers, but are effective in reducing base metal oxide formation on good chromia formers. It follows then that the two aspects of the selective oxidation phenomena brought about by the presence of reactive elements: the ability to develop a surface chromia layer with less chromium in the alloy, and the

suppression of base metal oxidation during initial transient stage or in the presence of a stable chromia scale, are two different processes. While the nucleation theory alone can explain the latter, more explanation and understanding is needed for the former. Perhaps an enhanced chromium diffusion in the alloy, as originally proposed by Davis et al. [23], is important in changing the behavior of the alloy from a non-chromia former to a chromia former.

An enhanced chromium diffusion in the alloy could either come from a reduced alloy grain size, which is often a result of RE addition, or come from enhanced short circuit diffusion which may accompany mechanically alloyed specimens. Although the diffusion studies performed by Selzer and co-workers [24,25] are often quoted to dispute the importance of an enhanced chromium diffusion, one should note that those studies only compared chromium diffusion in already strong Cr_2O_3 -forming alloys. Only one non-chromia forming alloy, Co–21wt.%Cr with a dispersion of 3 vol.% Y_2O_3 , was examined. The chromium diffusivity in this alloy was found to be 3-times higher than the value found for a coarse-grained Ni–20wt.%Cr. Unfortunately, a direct comparison of Cr diffusion in Co–21wt.%Cr without the dispersion was not made.

3. Modification of chromia scale growth

Above 900 °C, chromia scales grow predominantly by cation outward transport through oxide grain boundaries [26–28]. The addition of reactive elements reduces the growth rate by nearly an order of magnitude, and changes the dominant transport process through the scale from cation outward to anion inward transport [2]. Since the oxygen and chromium diffusion rates in chromia vary over an order of magnitude [29], the reduced growth rate is often attributed to the change in transport process through the scale. For these effects to be manifested, the reactive element can be added as minor alloying addition, as oxide dispersions, or as superficially applied surface additives via ion-implantation or some kind of surface coating [3,5].

Two different mechanisms have been proposed in recent years to explain the effect of reactive elements on oxide growth. One suggests that the segregation of RE to oxide grain boundaries greatly retards cation outward transport through the scale, and consequently, scale growth becomes dominated by anion inward transport [14,30–32]. The other model, the “interface poisoning model”, stresses the importance of interfacial reactions and argues that segregation of reactive elements to the oxide–metal interface stops cation vacancy annihilation; therefore cation transport through the scale is impeded and anion transport becomes dominant [33,34].

3.1. Grain boundary segregation model

Segregation of reactive elements, whether surface-applied or alloyed, to oxide grain boundaries has been well documented by electron microscopy studies [14,31,32,35–38]. Excess RE in the scale are often found to precipitate as perovskite or oxide particles [14,35–36]. These particles are considered as a source of RE supply for its continuous segregation to neighboring grain boundaries [6,18,34]. In the case of surface-applied RE, where initial concentration is high at or near the surface, a concentrated band is usually found within the oxide scale [6,14,15]. This band has been considered as a similar reservoir for RE segregation to oxide grain boundaries throughout the scale [39]. The often observed dose effect with ion-implantation [15,16,39,40] has accordingly been explained as a critical concentration for effective grain boundary coverage [39], even though such concentration seems overly high.

Stringer and Hou [3] have questioned the relevance of RE grain boundary segregation on scale growth based on a study carried out by Wright et al. [41], where fine dispersions of Al_2O_3 altered chromia scale growth to the same extent as Y_2O_3 additions. From thermodynamic considerations, aluminum should not segregate to chromia grain boundaries, because Al_2O_3 and Cr_2O_3 form complete solid solutions with one another [42]. Due to the importance of this result in understanding how reactive elements may affect chromia scale growth, we have reexamined the oxidation behavior of the same batch of alloy used by Wright et al. [41]. The same results were found, namely that the Al_2O_3 -containing Ni–20Cr exhibited all the reactive element effects upon oxidation. However, detailed chemical analysis of the starting material by GDMS (glow discharge mass spectrometry) showed that the alloy was contaminated with 700 ppm of yttrium [43]. This contamination may have resulted from the ball milling process in producing the alloy, since the same balls were used to make a Ni–20Cr–2vol.% Y_2O_3 alloy prior to making the Al_2O_3 -containing one [44]. Other studies concerning the effect of Al or Al_2O_3 on chromia-forming alloys have shown that these additives did not significantly modify the growth of chromia scales [11,45], except in the case [46] where a continuous Al_2O_3 layer can be developed at the scale–alloy interface.

Some preliminary results from Saito et al. [47,48] pointed out that reactive elements which have a higher solubility in Cr_2O_3 are usually less effective in modifying its growth behavior. The higher solubility is thought to lead to less segregation, thus producing less effect. Earlier work by Ecer et al. [49] also reported that while surface-applied CeO_2 were effective in reducing the Cr_2O_3 scale growth, MgO particles were not. The difference was proposed to result from the similar radius

of Mg^{2+} and Cr^{3+} , so Mg^{2+} would not segregate to Cr_2O_3 grain boundaries, but the larger Ce^{4+} would. Unfortunately, no trim experimental data exist which would directly relate the degree of segregation to the effectiveness of the RE on modifying scale growth.

Although many experimental results may be explained in light of the grain boundary segregation model, the model is unsatisfactory in relating the segregation phenomenon to material transport through the scale. The rationale given is that cation transport through oxide grain boundaries is impeded, or significantly retarded, by the presence of reactive elements there, thus allowing anion transport to dominate in the scale growth process. However, the preferential path for anion transport through Cr_2O_3 at these oxidation temperatures is also grain boundaries [50]. It is difficult, then, to envisage how the presence of RE could so effectively prohibit the transport of one but at the same time allow the transport of the other.

Furthermore, diffusion studies using radioactive tracers often contradict the belief that REs in the oxide retard cation transport [51]. For example, Park et al. [52] have studied chromium diffusion in sintered Cr_2O_3 with or without Y_2O_3 addition. The presence of yttria did not affect the bulk diffusion rate of chromium, but caused a 3-fold increase in the Cr grain boundary diffusion rate. It is true that thermally grown oxides have an oxygen potential across the scale and possess a different microstructure than sintered ones. Even so, one would not expect these differences to be so significant as to invert the effect of the added Y_2O_3 on transport properties. The discrepancy has been suggested by Atkinson [51] to be due to a lack of control over dopant concentrations at oxide grain boundaries. It seems probable that grain boundary diffusivity may be so strongly influenced by the dopant concentration that it may either increase or decrease depending on the amount present. Before the effect of grain boundary segregation can truly be understood, more diffusion studies performed on thermally grown oxide scales will have to be conducted. Some recent results [53,54], contrary to past belief, even suggest that chromia scale growth at 900 °C or greater is achieved by both oxygen and chromium diffusion, and their contribution is equally important.

3.2. Interface poisoning model

Recently, Rapp and Pieraggi [33] proposed a new mechanism to explain the reactive element effect on chromia scale growth. They argue that oxide growth should be treated by considering not only diffusion through the scale, but also reaction kinetics at interfaces. When a scale is grown predominantly by cation transport, vacancies move toward the scale–alloy interface and become annihilated by climb of interfacial

misfit dislocations. Reactive elements, due to their large sizes, segregate to the scale–alloy interface and block edge dislocations from climbing, thus stopping the vacancy annihilation process. As a result, cation transport through the scale is greatly impeded to allow anion transport to dominate. Anion transport is not believed to be affected by reactive element blocking at the scale–alloy interface, because vacancies in this case are annihilated at the scale–gas interface. New oxides can still form at the scale–alloy interface by the translation of interfacial ledges with reactions taking place particularly at kink sites. These reactions correspond to lateral climbs of misorientation dislocations.

The proposal, in essence, suggests that segregated RE poisons the interface by eliminating available sites for cation vacancy annihilation. Recent TEM studies on alumina scales grown on NiAl or FeCrAl alloys have demonstrated some RE segregation to the oxide–metal interface [55,56]. However, segregation phenomena alone are not enough to verify the proposal. Stawbridge and Rapp [57] have attempted to provide proof for the poisoned interface model by studying the effect of surface-coated Ca, Sr or Ba on the oxidation behavior of Ni, Co, Fe or Cu. Their results may be consistent with the model in that REs with an appropriate size relative to that of the substrate can segregate to the interface to exert an effect. However, the same results can also be treated as yet another example of the manifestation of the REE, and be subjected to other interpretations. It should be noted that Sr, Ba as well as Ca were all included in the original patent by Pfeil [1], along with Ce, Y and other reactive elements.

If interface poisoning is indeed important to the overall scale growth, one should expect an interfacial segregation of sulfur or phosphorus to slow down oxidation as well, since both of these elements are well known to be strong surface poisons and have been shown to greatly retard surface reactions [58,59]. Uniform sulfur [60,61] and phosphorus [62] coverage has been found to exist at scale–alloy interfaces, but in neither case was the growth of the scale reduced. On the contrary, when these impurities were removed from the alloy, the growth rate of the scale was found to decrease [63,64], implying that the effect of any segregation of S and/or P is to enhance, rather than retard, cation transport.

The presence of reactive elements within the oxide scale has been proved to be important in affecting the scale growth process. Using Ni–25wt.%Cr alloy as the substrate, we have carried out an experiment whereby Y, Hf or Zr was implanted into a pre-formed Cr_2O_3 layer, followed by oxidation under normal conditions [65]. The pre-formed layer was between 1 and 2 μm thick without any spallation. RBS analysis showed that the implanted reactive elements were only present within the outer 20% of the scale. Subsequent oxidation of

these specimens showed an equally reduced rate as if the RE were implanted directly into the alloy substrate. Furthermore, the scale which developed also showed a change in growth direction, indicating that modified scale growth is a direct result of having the RE incorporated in the oxide scale. It is not known whether any RE diffused through the pre-formed oxide to the oxide–metal interface to exert an effect on interfacial reactions. However, the reduction in growth rate was observed at the beginning of the second oxidation stage, i.e. after implantation into the pre-formed oxide. It is inconceivable that diffusion across 1–2 μm of oxide to the interface would take place within only minutes. Therefore, this experiment shows the importance of RE present in the oxide scale in reducing the scale growth rate and modifying the growth mechanism.

4. Improved scale adhesion

Numerous mechanisms have been proposed to explain the role of reactive elements in improving chromia or alumina scale adhesion. In the past, when a model was proposed, a distinction was usually not made whether the mechanism was applied specifically to alumina or chromia scales. Proposed mechanisms are usually presented with the consensus that it works for both, even though the experimental evidence was sometimes obtained using solely alumina-formers or vice versa. Because so much work has been concentrated on alumina spallation, a main objective in studying Cr_2O_3 scales are to determine how general the proposed models were. Furthermore, since it has been suggested [61,66] that the dominating mechanism of the REE on scale adhesion may be different for Al_2O_3 and Cr_2O_3 scales, it seems more appropriate to discuss the two systems separately. For the present discussion, the experimental evidence cited and the importance of different mechanisms being discussed will be limited to chromia scales.

Three groups of mechanisms have been proposed. One deals with changing the driving force for spallation, namely reducing the growth stress by perhaps a slower oxidation rate or a modified scale growth mechanism. The second group suggests enhanced plasticity of the resulting oxide scale, making it less susceptible to fracture and spall. The last group emphasizes the importance of the scale–alloy interfacial strength. These include several mechanisms, and the role of the reactive elements is proposed to: (i) provide vacancy sinks at the RE oxide–alloy interface to prevent vacancies from condensing at the scale–alloy interface to form voids [67]; (ii) enhance oxygen inward transport down RE oxide–alloy boundaries to form internal oxides (or pegs), resulting in an irregular interface that is more resistant to crack propagation [68]; (iii) segregate to the

scale–alloy interface to enhance the interfacial bond strength [69]; and (iv) scavenge impurities in the alloy that would otherwise segregate to the interface to weaken it [70–72].

4.1. Reduction in growth rate

The reduction in oxidation rate itself can not be the explanation for a good scale adhesion. For example, when aluminum was added in a Ni–25Cr alloy [11], the growth rate of Cr_2O_3 was unchanged from that of the binary alloy, but scale adhesion was significantly improved. In other words, strong adhesion was achieved without a slowed oxide growth rate. We have also implanted Y, Hf, Zr or Cr into a pre-formed Cr_2O_3 layer, about 1–2 μm thick, on Ni–25Cr [65]. Subsequent oxidation showed that the scale growth rate was reduced with Y, Hf or Zr implants to the same degree as if the implants were made directly into the alloy. However, the scale adhesion was not improved. The degree of spallation was the same as the untreated alloy when similar scale thickness was compared. In this case, slower growth rate did not produce a more adherent scale. It was found that the implanted RE concentrated ahead of the preformed oxide layer. New oxides were formed mainly at the preformed oxide surface. The scale–alloy interface remained unaffected by the modified growth process and had a similar morphology to that found on the untreated alloy.

4.2. Enhanced scale plasticity

Whether RE changes scale plasticity has not been experimentally demonstrated. King et al. [73] have tested the plasticity of sintered Cr_2O_3 , with or without Y_2O_3 addition, at 1200 °C, and found that the Y_2O_3 addition had no effect. Tortorelli and co-workers [74,75] have recently attempted to measure the mechanical properties of thermally grown oxide scales at room temperature using a nano-indentor. Their preliminary results showed that Ce additions, whether bulk alloyed or ion-implanted, did not affect the mechanical properties of Cr_2O_3 scales, even though scale adhesion was significantly improved. Indeed, by evaluating the necessary condition for scale failure, Nicholls and Hancock [8] have concluded that the addition of reactive elements does not alter the plasticity of the oxide scales, but more importantly causes a reduction in the number and size of flaws within the scale which may act as crack initiators. Along the same argument, Bennett and Tuson [76] suggested that the effect of RE was to produce a more crack-resistant scale, which explained why the critical scale thickness to initiate spalling would increase 4-times with RE addition. Through-scale cracking was considered to be the major mode of failure, so that flaws within the entire scale would be

equally important. However, Hou and Cannon [77] have recently shown that the most critical flaws which cause scale failure under residual compressive stress are interfacial pores. Therefore, the fracture resistance of the scale–alloy interface seems to be more important than that of the scale itself.

4.3. Reduced growth stress

Oxide growth stress is a quantity that needs better experimental determinations. Very limited in-situ stress measurements have been carried out. Only two studies so far [78,79] directly compare the stress level in Cr_2O_3 scales at the oxidation temperature with or without RE addition. The earlier of the two [78] used a deflection technique and found some reduction of growth stress by the addition of implanted yttrium. However, the implanted Y also reduced the amount of base metal oxide and spinel formation. The difference in the type of oxide formed on the specimen surface may very well have an effect on the total growth stress observed during oxidation. The second study [79] used in-situ X-ray diffraction to compare oxide strain, and found less stress in Cr_2O_3 when Y was present in the alloy. However, the difference was small, and the magnitude of growth stress was insignificant compared to the thermal stresses caused by differences in thermal contraction between the substrate and the oxide during cooling.

Much more work exists where residual stress was measured after the samples have been cooled to room temperature [80]. Often the following assumptions were made in an attempt to obtain the level of growth stress from these room temperature measurements: (i) there are no stress relief processes of any kind during cooling; (ii) with or without RE addition, the degree of thermal stress developed upon cooling would be the same. Based on these assumptions, the relative level of growth stress in different systems was then deduced from the measured residual stress at room temperatures. However, this approach is not always correct.

By comparing the degree of residual strain in equal thickness of chromia scales formed on Ni–25Cr, and Ni–25Cr containing Y or Al, we have found that scales formed on the Y and Al-containing alloys possess a higher degree of residual strain than those formed on the undoped Ni–25Cr [81]. This, however, is not due to any apparent difference in growth stress, but because small areas of scale had separated from the underlying Ni–25Cr alloy to release part of the combined growth and thermal stresses. Separations of this kind, i.e. small blisters or buckles, have been shown to be mechanisms of stress relief [82]. They may have happened during oxidation due to growth stress, or may have happened during cooling. In any case, the important comparison was that the scale formed on the Y or Al-containing

alloys never showed any scale–alloy separation, even under strong externally applied forces such as those from indentation or scratching. Any occasional scale spallation, especially with thicker oxides, only occurred within the scale, rather than at the scale–alloy interface. This study demonstrated that the good adhesion provided by the addition of reactive elements is mainly due to the formation of a stronger scale–alloy interface, which can withstand much higher stresses. Oxide growth stress or oxide plasticity may or may not be altered by the presence of RE; they must be minor factors in affecting scale adhesion.

4.4. Strengthened scale–alloy interface

The cause of the establishment of a stronger scale–alloy interface has been the focus of several mechanistic proposals. An irregular or tortuous interface, pegging as an example, has been shown by theoretical calculations [83,84] and some qualitative experimental evidence [85,86] to significantly increase interfacial strength by resisting crack propagation. However, chromia scales often do not form pegs; many RE-containing alloys even develop very flat interfaces [9], and surface-applied RE is simply not present in the alloy to assist in peg formation. Although it has been suggested that implanted RE can back diffuse into the alloy during oxidation [87,88], such back diffusion is very limited when the oxidation temperature is as high as 1000 °C. Hou et al. [89] have found that as little as 0.1 at.% of implanted Y was left in the underlying alloy after only 15 min of oxidation at 1000 °C, and this small amount quickly became incorporated within the scale as the scale continued to grow inwardly. The fact that surface-applied RE is no longer present within the alloy after initial oxidation, but the scale adhesion continues to be greatly improved, indicates that pegging, vacancy sink or impurity gettering mechanisms, as the way they are proposed, cannot be important for improving chromia scale adherence.

It is true that nearly impurity-free alloys oxidize to form adherent scales even without any addition of reactive elements. This has been proven extensively for Al_2O_3 -formers [90]. For Cr_2O_3 -formers, high concentrations of impurities in or on the specimen, such as sulfur [91], chlorine [92] or carbon [89,93], have been found to greatly deteriorate scale adhesion, indicating a strong detrimental effect caused by these excess impurities. Impurity-free alloys have also been shown to produce adherent scales; however, growth of these scale is noticeably affected as well. Substantial oxygen inward transport through the scale was observed [94]. Growth rate was reduced by about a factor of three [63]. The resulting scale was not only noticeably thinner, but was also free from internal oxidation [64]. These results seem to suggest that the presence of indigenous sulfur

not only affects scale adhesion, but also alters the transport processes through chromia. The important question is whether the change in oxide growth affects adhesion in any way, and if the effect due to the modified growth can be separated out from that due to a cleaner scale–metal interface.

An important question concerning the impurity effect is whether segregation to the scale–alloy interface truly occurs, and furthermore, whether such segregation can indeed affect scale adhesion. Grabke and co-workers [62,91] believe that sulfur segregation only occurs at free surfaces. Therefore, the role of sulfur is to enhance interfacial pore formation; scale adhesion is made poor by the development of interfacial voids. However, large areas of sulfur coverage at the interface, where the scale appeared to be in contact with the substrate, have been reported both with scanning Auger and SIMS techniques [60,61,95].

In order to relate segregation to scale adhesion, we have studied the fracture and spalling behavior of Cr_2O_3 formed on Ni–25Cr at 900, 1000 and 1100 °C in relation to the degree of interfacial sulfur segregation [61]. Using in-situ scratching in a high vacuum scanning Auger chamber, all of the metal surfaces studied were found to be covered by about 1/3 of a monolayer of sulfur. This is true regardless of the oxidation temperature or the interfacial morphology, i.e. whether it was a void or an oxide imprinted area. In spite of the rather uniform sulfur coverage at the interface, spallation behavior of these scales changed dramatically with the temperatures at which they were formed. Scale fracture was more directly related to the number of interfacial voids, which increased with increasing oxidation temperature, suggesting that such void formation was related to the oxide growth process. Hussey et al. [95] reported similar findings that scale adhesion is not directly related to the amount of segregation. In their study using SIMS depth profiling, sulfur and carbon were detected near the scale–alloy interface, whether the alloy had a surface-coated RE or not. However, the RE-coated alloy showed remarkably better scale adhesion than the uncoated one.

To summarize the impurity effect, it seems well established that impurities are detrimental to scale adhesion. However, the role of impurities in producing such effects and the role of the reactive elements in preventing them are still not clear. If the reactive elements are to scavenge impurities in the alloy, then it is very difficult to explain the excellent adherence found with surface-applied REs. The fact that surface-applied RE showed very little effect on alumina scale adhesion [66,96], but great and long lasting effects for chromia scales, suggests that the modified growth associated with RE addition for chromia may play an important role on scale adhesion; even impurity-free alloys develop chromia scales with a slightly modified growth

process. Impurity segregation can indeed occur at oxide–metal interfaces. However, scale adhesion seems unrelated to the amount segregated. Spallation behavior, on the other hand, relates more to interfacial morphology, particularly void density. The cause of void formation is another ambiguous subject. It may be affected by the oxide growth mechanism, the growth stress, the microstructure of the interface, the impurity level near the interface, or all of the above.

Segregation of RE to the scale–alloy interface can exert a strengthening effect based on theoretical calculations using molecular orbital theories [97]. Surface-applied RE may not be present in the alloy after a few hours of oxidation, but a finite amount seems to exist at the scale–alloy interface [89]. However, if “clean” chromia-forming alloys can by themselves establish very adherent scales, strengthening the interfacial bonds by RE segregation at the interface must not be important.

Several investigators have also commented that the improved adhesion may simply be a result of the change in diffusional growth mechanism of the oxide scale. Kofstad [98] has suggested that while pores and voids may form at or near the scale–alloy interface when cation outward transport predominates, such defects would be absent in a scale grown predominantly by anion inward transport. Although the growth process of chromia scales may very well be an important factor in determining scale adhesion, strong adhesion does not always require a change in the overall transport through the scale. We have found with a Ni–25Cr–1Al alloy that although the scale grew predominantly by cation outward transport, as indicated by Pt markers, the scale–alloy interface was very strong owing to some oxide inward growth close to the scale–alloy interface [11]. Perhaps the important step is not how the bulk of the scale is formed, but rather, the scale growth at the interface.

5. Conclusions

1. Surface applied reactive elements or their oxides cannot induce selective oxidation of chromium to form a continuous, external Cr_2O_3 scale, but are as effective as alloying additions in eliminating base-metal oxide formation on good chromia formers.

2. The presence of base metal oxides can arise in two ways: as a residue of the initial non-steady-state period, or as a steady-state phenomenon involving the transport of the base metal through the chromia layer.

3. The selective oxidation of chromium should be considered as involving two processes. First, the ability to develop a surface chromia layer with less chromium in the alloy; and second, suppressing base metal oxide formation during the initial transient stage. The two processes are not always coupled. While reactive ele-

ment oxides emerging on alloy surfaces or within the alloys may act as nucleation sites for the second process, it alone is not sufficient to produce the first effect. An enhanced chromium diffusivity in the alloy may be more important than previously believed.

4. The reactive elements exert their effect on chromia scale growth by being incorporated in the scale. This is demonstrated when implantation of reactive elements into a pre-formed oxide layer reduces the scale growth rate to the same extent as if the implants were made directly into the alloy.

5. Reactive elements have been found to segregate to oxide grain boundaries and to scale–alloy interfaces. The importance of such segregation on the mechanism of scale growth is still unclear, due mainly to a lack of understanding of material transport through the scale and through the interface.

6. A slower oxide growth rate or a change in the overall transport process through the scale are not important factors for improved adhesion. Aluminum addition in Ni–25Cr could not produce either of the above effects on chromia scale growth, but greatly enhanced scale adhesion. Incidentally, implantations made into oxide scales could reduce further growth rate of the scale, but not improve the adhesion. Although the overall transport mechanism through the scale is not important, it is not known how minor changes in scale growth, particularly at the scale–metal interface, can affect adhesion.

7. The most important effect of reactive elements in improving scale adhesion is to cause the formation of a stronger scale–alloy interface. This is why higher compressive residual stress was found at room temperatures on RE-doped chromia scale compared to the undoped. In the undoped case, localized scale decohesion with subsequent buckling relieved some of the stress. With RE addition, scale failure never took place at the scale–alloy interface, but was within the scale whenever it occurred.

8. The effectiveness of surface-applied reactive elements in improving chromia scale adhesion can rule out mechanisms such as pegging, vacancy sink and impurity gettering, as least based on the way they are proposed. Impurities, such as sulfur, chlorine and carbon, are detrimental; reducing the impurity contents in the alloy can indeed improve adhesion. However, eliminating impurities also slightly affected the growth mechanism of the Cr_2O_3 scale. It is not known how much of this affected growth would influence adhesion. It is also not clear the mechanism by which impurities affect scale adhesion, or the role reactive elements have in preventing their detrimental effects.

9. Indigenous impurities in the alloy can segregate to scale–alloy interfaces during oxide growth, but chromia scale adhesion is not directly related to the amount of such segregation. Spallation or fracture resistance of

the oxide film is more strongly influenced by the density of interfacial voids whose development appears to be related to the oxide growth process.

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