

# Progress in Understanding the Reactive Element Effect Since the Whittle and Stringer Literature Review

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## Abstract

The 1980 literature review by D. P. Whittle and J. Stringer summarized a wide range of experimental results and proposed hypotheses regarding the reactive element effect. Reading this document in 2001 reveals exactly how far the study of the reactive element effect has come in the past 21 years. With the advent of advanced analytical techniques such as scanning transmission electron microscopy and secondary ion mass spectrometry (for detecting  $^{18}\text{O}$  tracers), many issues about RE effects on growth mechanisms and microstructure have been resolved. Emphasis now centers on the role of impurity elements (especially C and S) in conjunction with reactive element additions, the interfacial segregation and diffusion of RE ions, and the mechanical response of the substrate during oxidation. In several areas, there have been changes in the interpretation of results and there are several new sub-topics pertinent to the reactive element effect that were not covered in the 1980 review

## Introduction

In 1980, David Whittle and John Stringer published a review paper on the reactive element effect that has been widely read and cited for the past 21 years.[1] In retrospect, it led off a decade which saw a significant advancement in the mechanistic understanding of the role of reactive elements (e.g. Y, Hf, La, Zr, Ce, etc.) in improving high-temperature oxidation resistance.

The so-called rare-earth or reactive element (RE) effect was first patented in 1937 by Pfeil [2]. The original work concerned cerium additions to a Ni-Cr alloy but since then the same effect has been found for a wide variety of elements with a high affinity for oxygen and sulfur, and benefits are observed for most chromia- and alumina-forming alloys. The RE effect was largely unstudied for 20 years until several papers appeared in the late 50's and early 60's. Since then it has been the subject of hundreds of papers and much controversy. Mechanistic models to explain the role of RE additions have come and gone, but their use is almost essential to the design of high-performance, high-temperature materials and, thus, the RE effect is still an important issue.

The 1980 Whittle and Stringer review gave an important

snapshot of the state of understanding at that time. The paper examined the role of RE additions in conventional M-Cr and M-Cr-Al alloys and provided discussion of the effects of both alloy additions and RE alloy dispersions (usually oxides). Various models to explain the RE effect were "discussed in the light of currently available experimental evidence".[1] One of the most important features of the paper is that, rather than merely listing all hypotheses, it critically differentiates between those that are unlikely and those that are more plausible.

The paper provided a thorough review with 70 references and listed many opportunities for further work. It is still an excellent starting point for those new to the field as it discusses mechanisms in terms of fundamental oxidation principles. However, the research conducted since then has made such a significant impact on understanding of the RE effect that reading only the 1980 review would leave the reader with many incorrect impressions.

The following is an attempt to summarize some of the important work done in the past 21 years and to put it into the context of the 1980 review. One of the recurring themes here is the advanced characterization techniques that have been developed and employed in these studies over the past 20 years. They range from better analytical balances and microbalances for measuring reaction kinetics, to field emission gun, scanning electron microscopes (FEG-SEM) which produce higher quality images of scales at high magnification, to high resolution and scanning transmission electron microscopes (HREM and STEM) which have allowed the detection and observation of RE ions segregated at scale grain boundaries and the metal-scale interface. Advancements also have been made using secondary ion mass spectrometry (SIMS) for detecting  $^{18}\text{O}$  tracers, scanning auger microscopes for detecting impurity segregants, and atomic force microscopes for quantifying microstructural features. Perhaps the newest technique to make an impact on the field is focused ion beam milling for preparing transmission electron microscope (TEM) specimens with more thin area for characterization.

In general, these advances in instrumentation and analysis have led to better understanding of RE effects on reaction rates, and growth mechanisms and to much more information on scale microstructure and the location of REs within the scale and

substrate. However, although progress has been made in understanding the role of REs, there is still not general agreement on the exact mechanism by which REs impart their beneficial effect.

### Advancements in Understanding Since 1980

Whittle and Stringer cite the two most important RE effects as improved scale adhesion and reduced scale growth rate. The latter applying to chromia scales but not alumina scales. Most would still agree with that assessment; however, the present understanding of those two effects has changed radically in the last two decades. There is now a better understanding of what critical factors are involved and the role of the RE. The following is an overview of some of the major advancements in understanding.

**The Sulfur Effect.** One of the biggest breakthroughs in the past 20 years has been the increased understanding of alloy impurity effects on scale adhesion, in particular, sulfur. The important detrimental role of indigenous sulfur was first identified by Ikeda[3] and then later studied by many others including Smeggil and co-workers,[4-6] Smialek and co-workers,[7-11] and Sigler.[12] These studies found a link between alloy S content and scale spallation. Combined with the studies that have identified sulfur segregation to the metal-scale interface,[3,4,10,13-16] even a skeptic must concede there is some connection between S content and scale adhesion. By removing S by a variety of techniques, alumina scale adhesion has been improved.[7-11,17,18] The S effect appears to be less important in chromia-forming alloys.[15] However, all of the studies agree that with the proper addition of a RE, the detrimental role of S can be neutralized either by gettering S or some other mechanism. With a RE addition (either oxide dispersion or alloy addition), S is no longer found to segregate to the metal scale interface.[19-22] This suggests an important role of REs that was not previously appreciated.

**Other Impurities.** Sigler[12] and other workers[17,23-25] have suggested that other impurities such as C, N, O and Na also may play an important role in determining scale adhesion. Sigler argued that while Y may getter S because it forms a very stable sulfide, other elements that form stable carbides and nitrides may getter C and N respectively. Carbon has long been suspected to play a role in scale adhesion but it has been difficult to isolate its influence. Recent work on single crystal, alumina-forming, Ni-base superalloys has been very informative in determining some of these additional effects.[11,17,18,24,26] These alloys typically contain low (<10ppm) S levels and 500ppm Hf. They also may contain low levels of Y and variable C contents. It has been shown that de-sulfurizing the alloy by hydrogen-annealing[10,11,17] or melt practices[17,24] improved scale adhesion on superalloys at 1100°-1200°C. It also has been observed that hydrogen annealing will remove C from these alloys and that the Hf/C ratio or the “excess” Hf (not tied up by C, S, N or O) will play an important role in determining the effectiveness of RE additions in improving scale adhesion. A chemical study of more than 40 elements showed that only S and

C were affected by the hydrogen anneal and concluded that these two elements were the most likely tramp elements to affect this class of superalloys.[18]

The idea of a critical Hf/C ratio also has been used to explain the oxidation behavior of low-S (<4ppm), Hf-doped NiAl.[24] Figure 1 shows the effect of varying the Hf/C ratio by increasing the C content on the scale morphology. The convoluted morphology with Hf/C=0.94 (high C) resulted in increased scale spallation.

**Improved Interfacial Chemical Bonding.** Whittle and Stringer downplayed improved chemical bonding at the metal-scale interface as a possible mechanism for increased scale adhesion. Their opinion was based on work suggesting that an Al<sub>2</sub>O<sub>3</sub> dispersion had the same effect as other RE oxide dispersions in chromia-and alumina-formers. Based on the information available at that time, they concluded that oxide dispersions had similar effects independent of composition. Subsequent studies [27-30] have not been able to reproduce those findings for an Al<sub>2</sub>O<sub>3</sub> dispersion in Ni- or Fe-based alumina-formers and instead have found very strong effects from varying the cation of the oxide dispersion. For example, Figure 2 shows the mass gain after 100h at 1000°C for a variety of different oxide dispersions in Ni-25wt.%Cr.[30] Compared to no addition, the scale growth rate was reduced when larger cations were added.

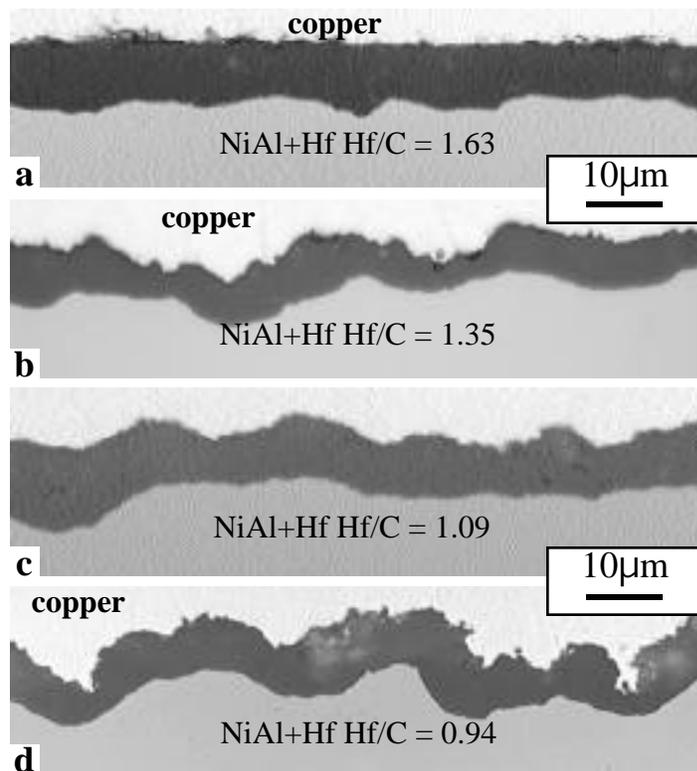


Figure 1. Optical microscopy of polished cross-sections of the alumina scale formed on various castings of NiAl+Hf after 10, 100h cycles at 1200°C. By varying the C content, different Hf/C contents were obtained. With decreasing Hf/C ratios, the scale became more convoluted and more spallation was observed during the test.[24,30]

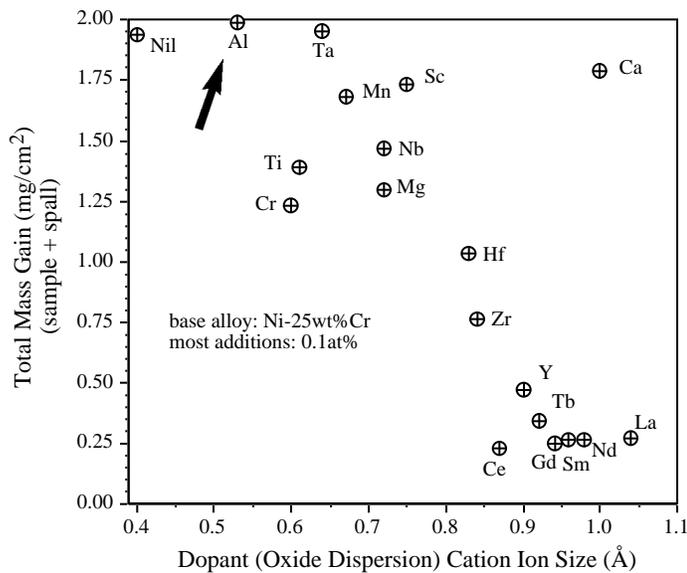


Figure 2. Total mass gain for Ni-25wt.%Cr alloys with various oxide dispersions added at a nominal level of 0.1cation% after 100h at 1000°C. The mass gain decreased for larger cation additions. The addition of an Al<sub>2</sub>O<sub>3</sub> dispersion had little effect on the scale growth rate.[30]

In that study, an Al<sub>2</sub>O<sub>3</sub> dispersion showed almost no effect on the scale growth rate and did not significantly improve scale adhesion. Furthermore, there is now evidence that in at least one of the studies on an Al<sub>2</sub>O<sub>3</sub>-dispersed Cr<sub>2</sub>O<sub>3</sub>-former the material was contaminated with a RE.[31]

Theoretical calculations[32] and experimental studies[16,20,33,34] suggest that interfacial segregants including REs or S may change the interfacial energies, thereby changing the oxide adhesion or making interfacial voids more stable. One hypothesis from the sulfur work was that clean metal-oxide interfaces are inherently strong and that de-sulfurizing produces the same benefit as adding a RE. However, recent work has shown that a de-sulfurized undoped alloy cannot match the scale adhesion on a RE doped version of the same alloy.[34] Therefore, the hypothesis that REs improve the chemical bonding at the metal-scale interface cannot be dismissed and should be further investigated.

**Mechanical Response of the Substrate.** Over the past ten years, there has been growing appreciation that the mechanical properties of the substrate play a role in scale adhesion.[35-39] The general idea is that a weak substrate is better able to dissipate strain energy by deforming. Therefore, thermal stresses (during heating or cooling) and/or growth stresses can be accommodated without scale spallation. A stronger substrate does not deform and thus more spallation is observed. An example of this effect is given in Figure 3 where stronger oxide-dispersion strengthened (ODS) FeCrAl alloys (MA956HT and PM2000) cannot match the life of FeCrAlY, although all contain Y. Thus, if the method of adding a RE, such as an oxide dispersion which strengthens the substrate, affects the mechanical properties of the substrate, the spallation behavior may be affected. Another example was

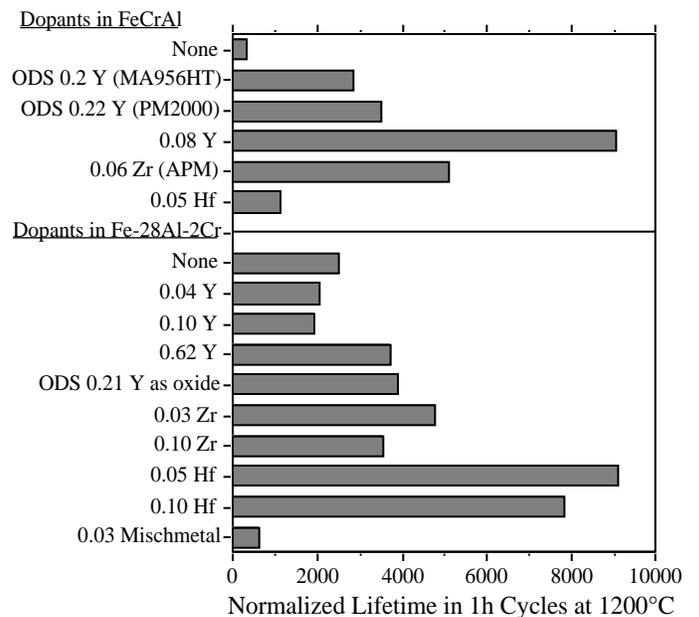


Figure 3. The effect of various reactive element additions to a base FeCrAl (20at%Cr-10at%Al) or iron aluminide, Fe-28Al-2Cr, on the time to breakaway oxidation (formation of FeO<sub>x</sub>) during 1h cycles at 1200°C, normalized to a 1.5mm specimen thickness.[30] For FeCrAl, the addition of 0.08Y had more impact than Y<sub>2</sub>O<sub>3</sub>, Zr or Hf additions. For Fe<sub>3</sub>Al, additions of Zr, Y and Y<sub>2</sub>O<sub>3</sub> only marginally improved lifetime. Hafnium additions were more effective in improving lifetime. Mischmetal is primarily Ce but also contains Nd, La and Hf.

found with Al<sub>2</sub>O<sub>3</sub>-dispersed Fe<sub>3</sub>Al, where the addition of a strengthening dispersion resulted in a flat alumina scale.[27] Cast, undoped Fe<sub>3</sub>Al, which has very little high temperature strength, formed a convoluted scale. Without a RE addition, both scales spalled but with different characteristics.

Recent work also has returned to thermal expansion as a means of explaining some effects. For example, RE additions are not able to produce the same benefit to scale adhesion in Fe<sub>3</sub>Al and NiCrAl as in FeCrAl or NiAl, no matter what type and amount of RE is added.[40-44] The apparent explanation is that the higher thermal expansion coefficients for Fe<sub>3</sub>Al and NiCrAl result in a greater mismatch between metal and oxide scale and thus higher thermal stresses compared to FeCrAl and NiAl. The basic finding was that no RE addition to Fe<sub>3</sub>Al can make the alumina scale as adherent as that on FeCrAlY.[42,43] The much larger thermal expansion mismatch between Fe<sub>3</sub>Al and alumina results in sufficiently high thermal stresses that the alumina scale begins to spall from a Fe<sub>3</sub>Al substrate at a much lower scale thickness than from a FeCrAl substrate. (However, due to its larger Al reservoir, Hf-doped Fe<sub>3</sub>Al can have similar lifetimes as FeCrAlY, Figure 3.)

**Interfacial Void Formation.** The Whittle and Stringer review mentioned several observations of REs eliminating or reducing interfacial void formation. This is one of the most widely recognized RE effects in alumina-forming alloys (especially intermetallics) and continues to be widely

observed[15,16,33,45-51] The formation of interfacial voids limits contact between the substrate and scale and is a primary cause of scale spallation. The literature on interfacial void formation has been reviewed recently.[33] However, the mechanism by which void formation is reduced by the addition of a RE still is not certain. If the voids are thought to form by a Kirkendall-type mechanism or vacancy coalescence, then the RE addition must alter the relative diffusion rates, the vacancy concentration, or some other aspect of the metal-oxide system. Very little experimental evidence is available on this subject. However, models cited in the Whittle and Stringer review which suggest vacancy annihilation at particles in the substrate have not been verified by experimental characterization.[20,22] Alternatively, indigenous sulfur may affect void formation by segregating to the interfacial region, thereby changing the interfacial energies and increasing the rate of void growth [16,22,33]. If a RE addition getters indigenous S or otherwise inhibits its interfacial segregation, the addition would prevent any detrimental role of S at the metal-oxide interface.

As more information has been learned about RE effects on scale adhesion, other factors are needed to explain the wide variety of results observed.

**Determination of Growth Mechanisms.** Until 1980, the use of Pt markers was the primary method for determining the scale growth mechanism. In the review,[1] one study using an  $^{18}\text{O}$  tracer to study the scale growth mechanism was cited. Over the past 20 years, it has become clear that Pt markers are not a reliable means for determining the scale growth mechanism. For alumina scales, thin Pt marker lines applied using a photolithographic technique[52] were found to always turn into a row of spheres at the alumina-gas interface[53] indicating that, due to the surface energy, Pt markers will float at the oxide surface and always indicate inward growth. Instead,  $^{18}\text{O}$  tracer experiments combined with SIMS or nuclear reaction analysis (NRA) are a much more reliable means of determining the scale growth mechanism.

The  $^{18}\text{O}$  tracer work done on chromia-formers[54,55] basically confirmed the results from Pt markers. The addition of a RE inhibits the diffusion of Cr and results in growth primarily by the inward diffusion of oxygen. On unalloyed Cr, a corresponding change in the scale microstructure also was observed using cross-sectional TEM.[54] With the addition of ion-implanted Y, the scale changed from columnar grains at the gas interface to a much thinner scale with smaller, equiaxed grains.

As noted above for alumina scales, Pt markers always show growth by inward diffusion of oxygen independent of RE additions. However, tracer experiments on various alumina-formers have shown a change in the growth mechanism of  $\text{Al}_2\text{O}_3$  from a combined Al and O contribution without a RE to predominantly O diffusion with a RE.[55-59]

A change in the scale growth mechanism is consistent with changes in the alumina scale growth rate and microstructure with the addition of a RE. With additions of Y or Zr, there is a 2-4X reduction in the parabolic rate constant for Ni-Al, Fe-Al and FeCrAl alloys [20,22,27-29,60] and a 10X reduction for Hf in

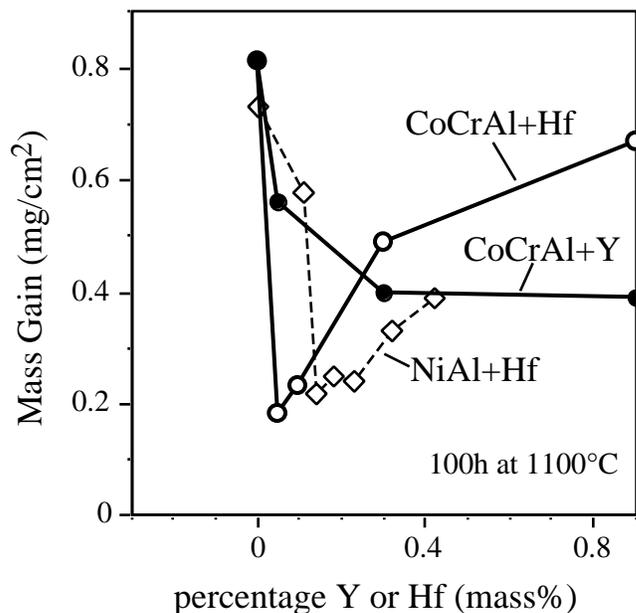


Figure 4. Mass gain for CoCrAl and NiAl after 100h at 1100°C with various reactive element additions. CoCrAl data are from Figure 3 in Ref. 1, NiAl data are from Ref. 30.

NiAl and Fe-Al.[41,43,61] Actually, these reductions are consistent with data in the Whittle and Stringer review. Figure 4 replots Figure 3 from the review[1] along with current data for Hf-doped NiAl.[62] The addition of low levels of Hf resulted in a substantial reduction in the specimen mass gain after 100h at 1100°C for both CoCrAl and NiAl. One of the key aspects of Figure 4 is that this reduction in mass gain is lost if higher amounts of dopant are used. The reason is that internal oxidation of the RE will increase the mass gain and incorporation of RE

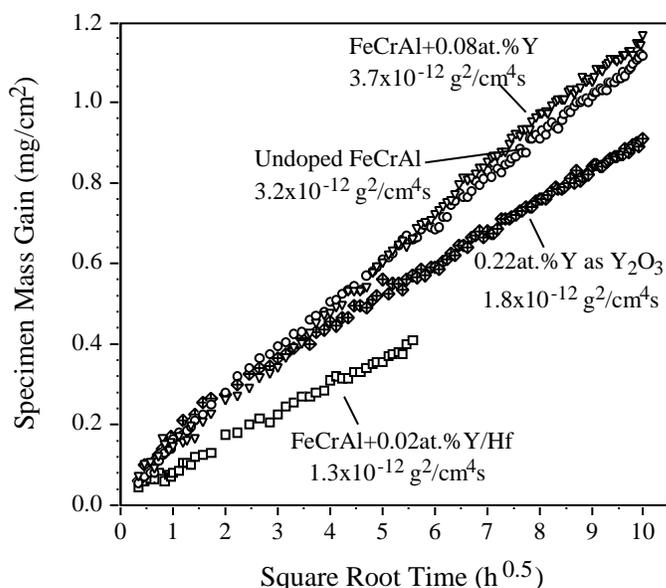


Figure 5. Isothermal mass gains and parabolic rate constants for various FeCrAl alloys at 1100°C. The mass gain due to internal oxidation can mask the mass reduction due to the change in scale growth mechanism.[30]

oxides in the scale appear to accelerate the scale growth rate. Therefore, many early studies where large quantities of RE were added found no reduction in the scale growth rate. Figure 5 illustrates this point for FeCrAl oxidized at 1100°C. Undoped FeCrAl and FeCrAlY have almost the same scale growth rate. However, when Y is added as an oxide in PM2000 and cannot internally oxidize, the scale growth rate is reduced. Furthermore, when lower dopant levels are used, the rate was even lower.

In all primary alumina-formers, the addition of a RE changes the scale microstructure formed at 1100°-1300°C from an equiaxed grain structure with whiskers at the gas interface to a columnar one without whiskers.[20,22,27-29,60,61,63,64] An example of this type of effect is shown in Figure 6 for alumina scales grown on oxide-dispersed FeCrAl. With an Al<sub>2</sub>O<sub>3</sub>-dispersion and no RE, the grains are large and equiaxed after 100h at 1300°C, Figure 6a. With a RE cation like Tb, the scale had a columnar grain structure and smaller grain diameters, Figure 6b. It has been shown by an x-ray pole figure characterization of the scale on PM2000 (ODS FeCrAl) that there is a preferred growth direction in the alumina resulting in the columnar structure.[65] The other reason for the smaller grain diameters with the addition of a RE is a solute drag effect on grain growth in the scale.[20,22,54] This mechanism is based on the numerous observations of RE ions segregating to alumina and chromia scale grain boundaries.

**Observations of Segregation.** While Whittle and Stringer had only the Auger work of Nanni [66] to cite regarding the segregation of RE ions, there has been an explosion of work in this area in both bulk ceramics and scales with the advent of STEM, where the electron beam size (and thus the sampled area) has dropped to 1nm. The first TEM-energy dispersive x-ray analysis (EDXA) observations of segregation to scale grain boundaries were by Ramanarayanan and co-workers,[67] followed by extensive work at MIT [20,22,54,68-71] and

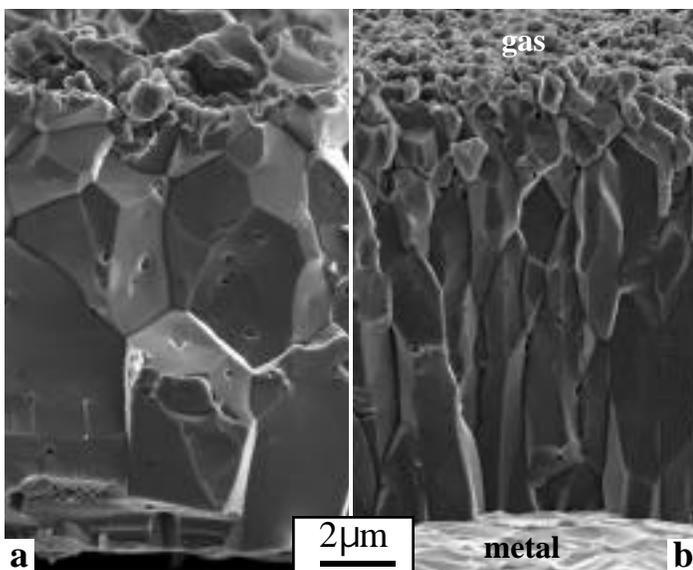


Figure 6. SEM secondary electron images of the scale formed after 100h at 1300°C on FeCrAl with an oxide dispersion of (a) Al<sub>2</sub>O<sub>3</sub> and (b) Tb<sub>4</sub>O<sub>7</sub>. Similar examples appear elsewhere.[28]

elsewhere[19,21,28,72-76] and included segregation observations at the metal-scale interface. Segregation observations in scales are now considered commonplace and have been observed for virtually all elements which demonstrate the RE effect.[28] While some of the initial studies concerned segregation in chromia scales, most of the recent work has focused on alumina scales. Also, HREM has shown that individual ions and not small particles are present on the scale grain boundaries.[77]

**Role of the Oxygen Potential Gradient.** Increased characterization of alumina scale microstructures also revealed an interesting phenomenon. Reactive element-rich oxide particles were observed to nucleate and grow at the scale-gas interface.[20,22,27,28,59,63,71] After short exposures or at lower temperatures, little or no RE-rich oxide particles were observed at the gas interface. After longer oxidation times, particles accumulated there. The time at which particles began to nucleate coincided with a drop in the concentration of RE ions segregated to the scale grain boundaries near the gas interface.[22,71] An example is given in Figure 7 for the scale formed on PM2000 (ODS FeCrAl) which contains Ti and Y<sub>2</sub>O<sub>3</sub>. After 100h at 1100°C, the volume of Y- and Ti-rich particles at the gas interface was much smaller than after 10,000h. The implication of this and other similar observations is that both Ti and Y diffused outward during oxidation and became enriched at the gas interface. The driving force for this diffusion is the same for the oxidation reaction - the oxygen potential gradient. As oxygen-active elements, REs diffuse outward during oxidation. However, because they have very low solubility in the scale, they diffuse along the scale grain boundaries. Thus, the segregated RE ions are not static on the grain boundaries but dynamic participants in the diffusion processes taking place there.[20] This is a key difference between dopant additions in bulk ceramics and scales.

These segregation observations have been made on alumina scales. Presumably a similar mechanism occurs in chromia

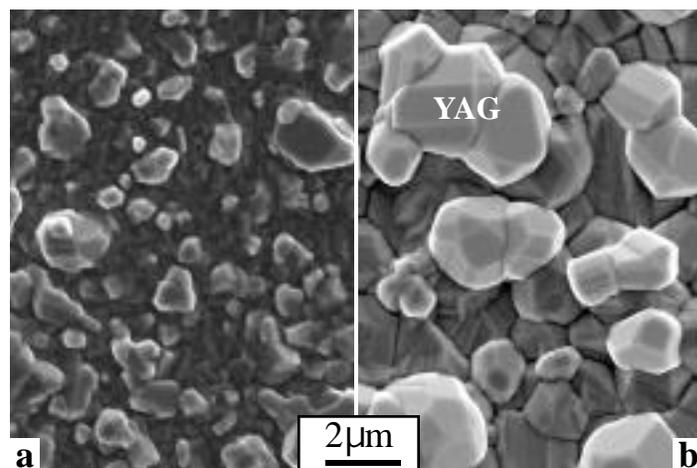


Figure 7. SEM secondary electron images of the gas interface of the scale formed on PM2000 (ODS FeCrAl) after exposure at 1100°C for (a) 100h and (b) 10,000h. Oxides rich in Y and Ti are observed to grow and coarsen with exposure time.[30]

scales. However, due to the evaporation of  $\text{Cr}_2\text{O}_3$  at higher temperatures, it has not been as clearly observed. Results for additions of Mn, Ti and Si to type 310 stainless steel found that Mn and Ti-rich oxide layers were observed to form above the  $\text{Cr}_2\text{O}_3$  layer, while  $\text{SiO}_2$  formed at the alloy- $\text{Cr}_2\text{O}_3$  interface.[78] Thus, the outward transport of RE ions does not fit the typical Wagner-type model of high temperature oxidation where the most stable oxide forms beneath layers of less stable oxides.[79] Silica forms an underlayer presumably because it forms slowly and has a low oxygen diffusion rate. Oxides of REs typically are fast oxygen conductors [80] and thus an underlayer of a RE oxide would not reduce the scale growth rate.

## Changes in Interpretation Since 1980

As more information has been collected about RE additions and their effects, it has been necessary to reevaluate some of the assumptions that had been made about their role and discard some of the models which were previously proposed. Some of these points may seem inconsequential but there are many subtleties necessary to understand the role of REs.

**Scale plasticity.** An increase in plasticity was assumed due to a smaller grain size in the scale.[1] In fact, the grain structure of the scale formed on a substrate with a RE is elongated but not significantly smaller in size, Figure 6, especially after long exposures. The addition of Y was not found to change the mechanical properties of bulk  $\text{Cr}_2\text{O}_3$ . [81] Furthermore, recent work on fine-grained, high purity alumina has shown that the addition of REs actually increases the creep strength of the material.[82] Thus, rather than being weaker, a scale with a RE is likely to be more resistant to deformation.

**Diffusion paths.** A broad assumption was made in the review that anions and cations travel on separate diffusion paths in the oxide. While this might be true in some ceramics, it is not likely the case in chromia and alumina scales. Bulk diffusion is too slow to account for the observed scale growth rates; therefore diffusion must occur along short-circuit paths. Various TEM observations have shown that only grain boundaries can accommodate the diffusion. There are no other diffusion paths in scales, such as dislocations, of sufficient density to account for the flux of ions.[83] Therefore, both cations and anions diffuse along grain boundaries. This is clearly true in the case of RE doped scales where oxygen ions diffuse inward and RE ions diffuse outward to form oxides at the gas interface, e.g. Figure 7.

**Vacancy sinks.** Another model outlined in the review suggested that oxide dispersions act as vacancy sinks thus preventing the formation of interfacial voids. However, this has not been confirmed experimentally. The large number of vacancies attracted to an oxide particle in the metal might be expected to nucleate a void adjacent to the particle, but TEM observations have not shown such voids.[20,22]

**Blocking mechanisms.** A substantial discussion about possible mechanisms where RE oxide particles or layers build up to block transport was included in the review. The “graded seal” model of a layer of, for example,  $\text{YCrO}_3$  at a Cr- $\text{Cr}_2\text{O}_3$  interface was considered but thought to be unlikely [1] and not confirmed

experimentally. Subsequent work has shown that RE ions on scale grain boundaries and not particles are responsible for blocking transport through the scale.

**Oxide doping.** Some discussion in the review suggested that REs dope the scale, changing the defect structure of the oxide. However, two things are now clear: first, the incorporation of base metal cations in the scale (e.g. for a NiCr alloy, 1%Ni is present in the  $\text{Cr}_2\text{O}_3$  scale) dominate the defect structure of the scale [84] and second, the solubility level of most REs in the scale is so low that they would not affect the bulk defect structure. REs are mainly found in the scale as second phase particles and as grain boundary segregants, not in solution.

**Selective oxidation.** While improved selective oxidation is discussed throughout the review as an important RE effect, a number of studies now suggest that alloy grain size effects need to be separated from RE doping effects.[84,85] With RE alloy additions, one result is a finer substrate grain size due to the formation of RE-rich precipitates (particularly with Ni and Fe). These precipitates also inhibit alloy grain growth during annealing or extended high temperature oxidation exposures. A fine alloy grain size promotes protective scale formation by increasing the diffusivity of Al or Cr in the substrate.[84-87] A similar benefit could be attributed to the subgrain structure created by the addition of an oxide dispersion.[20,22] The one benefit of adding an  $\text{Al}_2\text{O}_3$  dispersion to Fe-Al alloys was improved selective oxidation, which was attributed to the fine ODS alloy grain size.[85] However, no additional benefit was observed when a  $\text{Y}_2\text{O}_3$  dispersion was added. In Co-Cr, ion implantation did not result in improved selective oxidation [88] which is a further indication that grain size and not RE doping is the most important factor. Thus, while it is not possible to achieve benefits in scale adhesion or growth rates with any addition, it does appear that anything that reduces the substrate grain size will improve selective oxidation.

**Nucleation effects.** Along with changes in selective oxidation, studies of the transient stages of oxidation suggested that a finer scale grain size could be the result of oxide particles acting as nucleation sites for the first-formed oxides.[1] Thus, any dispersion could produce this result. However, more recent studies of  $\text{Al}_2\text{O}_3$  dispersions in alumina-formers (FeCrAl,  $\text{Fe}_3\text{Al}$ , NiCrAl and NiAl) have found that the alumina scale grain size was nearly identical to alloys without dispersions.[27-29,60] As mentioned previously, an  $\text{Al}_2\text{O}_3$  dispersion did produce a flatter scale on Fe-base alloys, likely because the dispersion strengthened the substrate. The finer scale grain size when RE oxides were added was attributed to a solute-drag effect due to RE ions segregated to the scale grain boundaries.[20,22,54]

**Type and method of addition.** As mentioned above, it has now been established that there are different effects on oxidation behavior depending on which element is added and the method by which it is added. Both are extremely important variables. Several recent results suggest that there are two essential attributes of a RE: (1) a high affinity for oxygen and also for sulfur [7] and (2) a large ion size relative to Al or Cr.[28] The second point is illustrated in Figure 2 where there is a clear effect of ion size on the rate of scale growth.

The review also suggested that oxide dispersions may be more effective in improving performance than alloy additions. This has been observed in some cases,[60,89] but is not generally true. The results for Fe-base alloys in Figure 3 suggest that alloy additions result in longer oxidation lives than oxide dispersions. The strengthening associated with the addition of oxide dispersions may provide an extremely important practical benefit for many high-temperature applications, but it likely results in increased scale spallation compared to a weaker alloyed version of the same substrate. Thus, the method of addition is an important consideration.

Surface additions, either by coatings or ion implantation, have been widely studied both as model systems and as a cheaper method of improving alloy performance. The review noted that the “improvement affected by coating was not always as great as when the additive was included in the alloy”.[1] Subsequent work has confirmed this view and shown that coatings are more effective in improving the performance of chromia-formers than alumina-formers.[90-92] Ion implantation also has been found to be more effective for chromia-formers[54,93] but, because of the small amount of dopant implanted, the duration of the benefit is limited.[94] However, several studies have determined that ion implantation is severely flawed as a method for studying the RE effect in alumina-formers and does not produce effects comparable to RE alloy additions or oxide dispersions [94-97]. The limited performance of coatings and implantations can be explained by the proposed need for a constant flux of outward diffusing RE ions to dope the metal-scale interface and the scale grain boundaries.[22,94] Without a continuous supply of RE in the substrate, the beneficial effects are soon lost.

**Mechanical keying.** The obvious formation of oxide pegs or stringers when the RE is added as an alloy addition and internally oxidized beneath the scale has long attracted attention as a “decisive factor” in improving scale adhesion.[1] The distribution of oxide pegs can be controlled because it is a function of the solubility and amount of RE in the substrate. For example, the higher solubility of Hf results in finer pegs than Y, which has a lower solubility.[1] However, the observation that ODS alloys do not form pegs and still exhibit good scale adhesion indicates that pegs are sufficient but not necessary for improving scale adhesion. The longer life observed for specimens with RE alloy additions (Figure 3) suggests that pegs may provide some additional benefit. However, minimizing the RE alloy addition and thus minimizing the volume of pegs formed also increased lifetime for this set of alloys.[30] Thus, the role of oxide pegs still has not been completely clarified.

## Topics of Increased Importance Since 1980

If the Whittle and Stringer review were written today, it would need to cover a number of additional topics in order to adequately review the current literature on RE effects.

**Defining and Quantifying Effects.** One of the most difficult issues in interpreting some results on the RE effect is the qualitative nature of many of the observations. This has led to a great deal of confusion about what is a RE. At present, there is

now quantification of growth rates, spallation rates and oxidation lifetimes (i.e. time to breakaway oxidation) in standardized tests which more clearly define the benefits expected for RE additions. Commercial alloys with standard RE additions can be used to produce baseline data and allow for comparisons with experimental alloys. Examples are given in Figures 2 and 3. This type of quantification allows a more rigorous discussion of the beneficial effects.

**Limitations of reactive element additions.** Another benefit of quantification is that it allows a clearer definition of the limitations of RE additions. The main limitation is that, in most cases, RE additions do not make marginal alumina- or chromia-formers into oxidation resistant alloys. For example, additions to TiAl may result in slight benefits[98,99] but do not provide improvements like the 30X increase in life observed for the addition of Y to FeCrAl, Figure 3. Likewise, Y or Y<sub>2</sub>O<sub>3</sub> additions to Ni<sub>3</sub>Al do not prevent the transient formation of Ni-rich oxide, the spallation of this transient oxide and oxidation problems associated with Al depletion.[100,101] Also, while REs produce improvements for Fe<sub>3</sub>Al, the alloy still exhibits more scale spallation than doped NiAl or FeCrAl [42,43,60]. This point has been appreciated for some time as similar limitations for chromia-formers with relatively low Cr contents were included in the review.[1]

**Performance optimization.** In their concluding remarks, Whittle and Stringer state “at present there is no absolute indication of which type of additive is more effective or at what concentration level”.[1] Particularly over the past 10 years, there has been increased work to define optimal additions for high temperature alloys.[28,43,73,102] While Y is one of the most often discussed REs, its applicability is limited because of its low solubility which tends to lead to the formation of Y-rich precipitates that can lead to non-ideal behavior.[100] In aluminides, Hf and Zr are preferable.[29,43,61,102] In NiCrAl and FeCrAl, a combination of Y and Hf or Zr may produce the best benefit but, as a single addition, Y is superior to Hf or Zr (e.g. Figure 3). Combinations of dopants are already found in commercial alloys such as Haynes alloy 214 (NiCrAl) and in second generation single crystal superalloys (e.g. General Electric’s René N5). They appear to work by replacing some of the Y addition by a second dopant, thus providing a sufficient dopant level while keeping the Y content closer to its solubility limit. For chromia-formers, La is suggested as optimal because of its large ion size (Figure 2) and its higher solubility, especially in ferritic alloys.[103]

It has long been recognized that minimizing the amount of dopant minimizes the amount of internal oxidation and reduces the scale growth rate, e.g. Figure 4. However, the *optimum* amount is more difficult to define. As mentioned above, the optimal amount of dopant to add to alumina-formers appears to be a function of the other impurities in the alloy, particularly S and C. If, in earlier studies, impurity levels were higher, larger additions may have been necessary, but impurity levels were generally not reported. Based on recent work for alumina-formers, Hf and Zr additions are best at 0.05at%, La additions at lower levels and Y additions at somewhat higher levels

(0.1at%).[29,30,43,60,62,73,102] When Y is added with another element like Hf or Zr, it is only added at 20-100ppma.[18,24,62] Little work has been conducted on optimized levels for chromia-formers. For ODS alloys, the amount of oxide may be a compromise between mechanical properties and oxidation performance. The amount of  $Y_2O_3$  which produced the minimal scale growth rate was lower than that observed in commercial alloys.[73] However, the amount is generally near 1 vol% and many early studies contained significantly higher concentrations.

**Intermetallics.** Conspicuously missing from the review is a discussion of RE effects in intermetallics, particularly aluminides. Most of the examples given were M-Cr and MCrAl alloys.[1] A significant amount of materials research has been devoted to intermetallics over the past 20 years and oxidation studies have been conducted both to improve their high-temperature performance and also as model systems to study fundamental oxidation issues. Many of the examples given in this paper are from intermetallics.

**Coatings.** Another area that was not discussed in the Whittle and Stringer review was the addition of REs to oxidation-resistant coatings. This is a critical issue for turbine engines and especially thermal barrier coatings, where spallation of the alumina scale beneath the ceramic top coat is a primary cause of coating failure. Many of the same issues apply to coatings, where optimizing performance is critical.

**Alumina phase transformation.** Alumina scales were not discussed in as much detail as chromia scales in the review.[1] One area of importance that was not mentioned was the phase transformation that can occur in alumina scales. The formation of metastable cubic phases ( , , ) at lower temperatures and/or short times instead of the stable phase was noted by Hagel in 1965.[104] The possibility of forming cubic alumina scales appeared to be forgotten for about 20 years, which led to critical misinterpretations when some kinetic and growth mechanism studies incorrectly assumed the scales being examined were  $\gamma$ - $Al_2O_3$ . Unlike  $\alpha$ , cubic alumina scales grow faster and by the outward diffusion of Al.[105,106] Another source of confusion is that large ions, like REs, generally stabilize the transient alumina phases.[102,107] This effect is well known in the catalysis field for stabilizing  $\gamma$ - $Al_2O_3$ . [108] This also leads to problems in interpreting the effect of RE additions on the oxidation mechanism.[57,106].

**Long-term data/lifetime models.** Another area that has gained prominence in the last 10 years is lifetime prediction, particularly for alumina-forming alloys and coatings.[42,109-113] In order to verify such models, it also has been necessary to collect long-term data. Rather than the <100h experiments common in earlier studies and discussion of the transient stages, now >1000h tests are common, e.g. Figure 3. This move to longer tests and modeling is an indication that the study of the RE effect is a maturing field that requires predictive capabilities in order to confidently implement commercial alloys with RE additions.

**Future Work.** While many questions have been answered since 1980, there are certainly many left unresolved. As mentioned above, the issue of the role of impurities has still not

been resolved either mechanistically or in strategies to improve performance in commercial alloys. Also, impurity effects have not been as carefully studied in chromia-formers. There appear to be important effects of the mechanical response of the substrate, but it is not clear which are the key mechanical or physical properties. Little is still known about the nucleation and growth of interfacial voids and why REs additions reduce their presence. More quantification is needed in this area. Regarding optimization, little is known about the reason why Hf can reduce the alumina parabolic rate constant by a factor of 10. A combination of experimental and theoretical work is needed to more precisely examine its presence on scale grain boundaries compared to other dopants. Ultimately, the long-term goal will be to transfer some of the insights found in model alloys to commercial products. Finally, while much of the current research focuses on alumina-formers, there may be applications where the performance of chromia-formers may be optimized to improve performance.

## Summary and Conclusions

The Whittle and Stringer review can be considered in two ways. First of all, it was a very thorough review of the relevant literature in 1980. It has stood the test of time in that it did not miss any of the significant research results made before 1980 and likely spurred much of the excellent work done since then. Furthermore, it did not just list the various experimental results (a shortcoming of many reviews) but also tried to interpret and evaluate their significance. Many people new to the field could learn a great deal from the review, including many of the basic concepts of high temperature oxidation, and thereby not reinvent the wheel (or the peg, as the case might be).

On the other hand, so much progress has been made in the last 20 years in understanding the role of RE additions that the review no longer gives an accurate view of the current level of understanding. Many of the new analytical instruments were not available (or had not been applied to this topic) at that time and their subsequent use has shown that many of the proposed models listed in the review are not correct. But acknowledging that the paper is outdated should not detract from its importance in the development of the current level of understanding. It would be a sad reflection on the field of high-temperature oxidation if the Whittle and Stringer review still gave an accurate picture of the RE effect. In fact, reading the paper now clearly shows how much progress has been made by a large number of talented and dedicated researchers in this field. Reviewing the literature today reveals that there are still a number of areas that are poorly understood and are ripe for further research. (Also, some of the assessments made here are still subject to debate.) One can only hope that in 20 years the current review papers will be considered outdated.

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