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Authors
Whittle, D.P.
Hindam, H.

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D.P. Whittle and H. Hindam

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MICROSTRUCTURE AND GROWTH OF PROTECTIVE Cr₂O₃ AND Al₂O₃ SCALES
AT HIGH TEMPERATURE

D. P. Whittle+ and H. Hindam

Molecular and Materials Research Division
Lawrence Berkeley Laboratory*

and

Department of Materials Science and Mineral Engineering
University of California
Berkeley, CA. 94720

ABSTRACT
Current understanding of the complex interrelationships between growth kinetics, scale microstructure and scale adhesion for Cr₂O₃ and Al₂O₃ protective scales has been critically reviewed. Similarities and differences in these two oxides have been highlighted. The morphology of the alloy/scale interface appears to be a critical factor, and recent ideas concerning the development of an irregular interface due to localized variations in scale growth rate are included.

INTRODUCTION
All alloys and coatings designed to withstand degradation at high temperatures rely on the formation of a continuous layer of Cr₂O₃ or Al₂O₃ for continued protection. With the possible exception of SiO₂, these are the only two oxides which have the potential to grow slowly enough to permit useful lifetimes of components. This, then, sets certain composition limits on the Al and/or Cr content which an alloy must contain to ensure the formation of a continuous Al₂O₃ or Cr₂O₃ scale. Nevertheless, such an alloy will not necessarily develop a continuous Cr₂O₃ or Al₂O₃ scale immediately;

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nor indeed will it last indefinitely: the constitution (morphology and composition) of the oxide scale is also time-dependent. Generally, three stages in the oxidation of an alloy are recognized. Upon initial exposure, the oxides of essentially every reactive component are formed in a proportion given by the composition of the bulk alloy (1). Oxide nuclei with high intrinsic growth rates overgrow the nuclei of the slower growing oxides, \( \text{Cr}_2\text{O}_3 \), \( \text{Al}_2\text{O}_3 \), etc. The rapid kinetics of the overgrowth formation contribute to a relatively high initial rate of oxidation. Whilst the overgrowth is forming, the underlying nuclei of the slower growing, and usually more stable, oxides grow laterally. Eventually, they impinge on one another and form a continuous layer, and thus, the transient oxidation period gives way to a steady state.

Any oxidation-resistant alloy depends on this steady state period for continued protection, and as indicated earlier, on the formation of \( \text{Al}_2\text{O}_3 \) or \( \text{Cr}_2\text{O}_3 \) during this period. The steady state period cannot last indefinitely, since selective removal of one of the alloy components is taking place, and as a consequence, it must end at least when all that component has been removed from the alloy. The ultimate (equilibrium!) state of an alloy in oxidizing conditions is an oxide containing the alloy components in the same ratio as the original alloy. Usually the end of the steady state period occurs before all the selectively oxidized element has been consumed, by some type of mechanical disruption of the oxide scale. Then, because the alloy is a different composition than originally, it does not necessarily regain its steady state (protective) oxide.

Figure 1 shows typical, schematic kinetic curves for the oxidation of a protective oxide-forming alloy. In terms of practical oxidation behavior, three critical factors can be identified, their relative importance depending on the particular application the alloy is required to function: (a) the duration of the steady state period, or time to "breakaway"; (b) "pre-breakaway" oxidation rate, which is essentially the growth rate of the protective oxide; and (c) the "post-breakaway" oxidation rate. For most applications, (a) is most critical; however, it is often very dependent on the growth rate, morphology, composition, etc. of the protective oxide, i.e., factor (b).
This paper, then, concentrates on the critical factors which affect the growth of the protective oxides, Al$_2$O$_3$ and Cr$_2$O$_3$, and which ultimately lead to their breakdown. This involves a complex interplay between the growth kinetics of the scale, and its microstructure and adhesion to the substrate, as depicted schematically in Figure 2. In addition, the influence of active element additions on the latter factors cannot be ignored although it is not the intention of this paper to review the "active element" effect per se, since a comprehensive review of this phenomenon already exists (2). The growth of Al$_2$O$_3$ (3) and Cr$_2$O$_3$ (4) have also been reviewed recently, and emphasis in this paper is placed on a comparison between the two oxides. The initial establishment of the protective oxide is not considered.

GROWTH KINETICS OF THE PROTECTIVE SCALES

Cr$_2$O$_3$ - In order to remove compositional complications (with limited success! - See Figure 3), many workers have studied the growth kinetics of Cr$_2$O$_3$ on pure Cr (4-12). With some reservations, the kinetics are generally diffusion controlled (parabolic) at least at some stage of the reaction. Reported values of the parabolic rate constants are summarized in Figure 3. The most striking conclusion is that the growth of Cr$_2$O$_3$, even on pure Cr, is far from simple. Rate constants at 1000°C for example, can differ by a factor of $10^4$, which means that the observed thickness of Cr$_2$O$_3$ formed after a given exposure can vary by a factor as much as 100.

Considerable effort has been expended in attempts to explain these large differences, but little consensus has been achieved. There seems little point in repeating all the arguments here, although it is appropriate to mention briefly some of the factors which have been suggested. Firstly, oxidation of Cr$_2$O$_3$ to the volatile CrO$_3$ is important (7) at temperatures greater than about 1000°C. Thus, weight change data will include a weight loss contribution which will depend on gas flow conditions, oxygen pressure, the design of the reaction chamber, etc. The data reported in Figure 3 have been either corrected for this weight loss (4, 11), or the evaporation has been suppressed (7, 12), or the authors have ignored the weight loss entirely (5, 8-10).
Secondly, differences in purity of the starting Cr metal and hence impurity doping of the \( \text{Cr}_2\text{O}_3 \) has been suggested, although there have not been any successful correlations. Indeed, the growth of \( \text{Cr}_2\text{O}_3 \) on alloys is marginally less reproducible (see later). Thirdly, differences in surface preparation (electropolishing, etching, mechanical abrasion, etc.) and, related to this, the experimental procedure used in initiating the oxidation reaction (hot, bare insertion of the sample, heating up in vacuo prior to admitting the oxidizing gas, etc.) have received much attention, although again, direct correlation is not possible. Most of the differences are thought to be in the morphology of the scale with this sometimes being essentially monocrystalline (slow growth rate) and in other instances (sometimes on the same sample) consisting of fine-equiaxed grains. However, correlation between a particular scale morphology and a specific surface preparation is not possible. Specimen pre-treatment, such as hot rolling, annealing or mechanically working the surface are presumably also important.

Finally, as a further consequence of the last factor, and an additional complicating one, is the often observed non-uniform growth in the formation of oxide nodules, blisters, convoluted and multi-layered scales. These are discussed in a little more detail in a later section. Suffice to say here that they obviously can contribute very significantly to weight change measurements. Detachment of the \( \text{Cr}_2\text{O}_3 \) scale from the alloy as a result of poor adhesion, or stress development during growth supposedly does not stop its growth since the vapor pressure and transport rate of Cr from the metal to the underside of the oxide is high enough to sustain continued growth. Indeed, it has been suggested (10) that Cr vapor transport could occur through the entire scale via continuous micropores thereby short circuiting solid state diffusion processes. Cracking of this detached oxide and formation of a second or more layer of \( \text{Cr}_2\text{O}_3 \) is a common occurrence. Again, there is little correlation with experimental variables, although the grain size and distribution in the oxide is clearly involved.

Turning now to \( \text{Cr}_2\text{O}_3 \) growth on alloys, principally binary alloys of Cr with Fe, Ni and Co, and alloys which contain sufficient Cr to form \( \text{Cr}_2\text{O}_3 \) as the principal scale constituent, two additional factors in determining the growth kinetics are potentially involved. The first is doping of the
oxide: both Ni and Co have small, but significant solubilities in \( \text{Cr}_2\text{O}_3 \), and \( \text{Fe}_2\text{O}_3 \) and \( \text{Cr}_2\text{O}_3 \) are completely isomorphous. Thus, the oxide formed is not necessarily pure \( \text{Cr}_2\text{O}_3 \), but contains Fe, Ni or Co (depending on the system), at different concentrations (depending on alloy composition), and this may modify the point defect concentration. Secondly, as indicated in the Introduction, \( \text{Cr}_2\text{O}_3 \) is not necessarily established immediately on exposure, even with alloys of relatively high Cr content, and consequently, there is always the possibility that rate constants measured gravimetrically contain a contribution from base metal oxidation. Nevertheless, the measured parabolic rate constants for \( \text{Cr}_2\text{O}_3 \) growth on binary alloys, shown in Figure 4, actually show somewhat less scatter than do those for Cr. (see Figure 6 also for a comparison). The rate constant variation is only by a factor of \( 10^2 \), making the scale thickness variation after corresponding exposure times only 10 times. Although not apparent in Figure 4, the rate constant tends to increase with Cr content in a given system (24); in addition, Ni-Cr alloys show somewhat less scatter than Fe- or Co-Cr alloys. Although separation of the \( \text{Cr}_2\text{O}_3 \) scale from the alloy is possible, it appear to be a less frequent occurrence than with pure Cr: for reasons discussed in part later, the scale is more adherent. In addition, multilayers of \( \text{Cr}_2\text{O}_3 \) are rarely observed, except perhaps with high Cr content alloys, since if detachment and scale fracture takes place, the surface Cr content of the alloy is considerably lower than the bulk alloy due to the alloy diffusion limited depletion, and is insufficient to re-form \( \text{Cr}_2\text{O}_3 \) as a continuous layer. Stratified scale of the base metal oxides develops and grows at a far more rapid rate. These data are obviously excluded from the rate constant data in Figure 4, which may account for some of the decrease in scatter when compared to the pure Cr data.

Comparison of Figure 3 and 4 indicates that \( \text{Cr}_2\text{O}_3 \) on the alloys, can grow neither as fast, or as slow as that on pure Cr. However, if \( \text{Cr}_2\text{O}_3 \) - forming alloys containing reactive elements or their stable oxide dispersions are included, then Figure 5 shows that \( \text{Cr}_2\text{O}_3 \) growth on these alloys is generally somewhat slower than on binary alloys, and can grow as slowly as the slowest growing \( \text{Cr}_2\text{O}_3 \) on pure Cr. (These latter values were in fact from scale thickness measurements by Caplan, when the scale was apparently
monocrystalline). One of the consequences of adding active elements or oxide dispersions to these alloys is that Cr$_2$O$_3$ is established more rapidly upon initial exposure (33). This is probably not what has affected the kinetic data in Figure 5 relative to those in Figure 4, since by and large, the rate constants included are representative of the later stages of oxide growth. Scale/alloy adhesion is also markedly improved (2), and consequently, there is less ballooning of the oxide, and multiple layer formation, which might contribute to some of the reduction in kinetics. However, of more significance perhaps is the considerable evidence that there is a change in growth mechanism. Marker experiments (18, 31, 33) indicate that the scale grows outward by cation transport on binary alloys and by inward oxygen transport on alloys containing dispersed oxides. The significance of this is discussed in more detail later.

In rationalizing the parabolic growth rate of an oxide, it is usual to compare the magnitude of the rate constant with that calculated from independent diffusion experiments of the transport rate of the predominantly mobile species in the oxide. This has been carried out in Figure 6, where for clarity, the individual experimental points have been omitted. In addition, the ranges of values for the growth constants on alloys both with and without additions (Figs. 4 and 5) have been combined. The wide scatter range surely dictates that any calculated value would fall in the range! However, what is perhaps most significant, is the fact that the calculated values lie at the upper limit of the experimental band, but before discussing this, some discussion of the calculated values must be included.

Firstly, there are not many diffusion data for Cr$_2$O$_3$ (36-40): what data there are, are reasonably conclusive that Cr diffusion is at least 3 orders of magnitude faster than oxygen diffusion. The measurements were made on polycrystalline materials (albeit of fairly large grain size) and should contain a contribution by grain boundaries, as well as lattice diffusion. The Cr diffusion coefficient was higher (by approximately 10) in hot pressed (36) as opposed to sintered compacts, and the original authors believed that that measured in the hot-pressed compacts was more representative. Kofstad (4) has suggested, however, that the differences are due to differences in oxygen partial pressure, which alters the degree of non-stoichiometry
(concentration of point defects). Hagel and Seybolt (36) report that the hot pressed samples contain free Cr, suggesting to Kofstad (4) that the effective oxygen pressure within the samples was close to the Cr/Cr$_2$O$_3$ dissociation pressure and lower than that existing within sintered samples which were annealed in oxygen at $10^{-7}$ to $10^{-6}$ atm. Other diffusion data for Cr diffusion in single crystal Cr$_2$O$_3$ at 1300°C in H$_2$/H$_2$O mixtures over a very limited range of effective oxygen pressure ($10^{-16}$ - $5 \times 10^{-16}$ atm.) were not conclusive (38).

An important implication of the above is that the Cr diffusion rate in Cr$_2$O$_3$ increases with decreasing oxygen pressure, and experimental evidence to support (or contradict) this are sorely needed. Increase in the sintering rate of Cr$_2$O$_3$ as the oxygen partial pressure is decreased is also consistent with an increased transport rate, although usually this is of the slower moving species, oxygen (41-44).

Of course, if the Cr transport rate does increase with decreasing oxygen pressure, then the important cation lattice defects are not vacancies, as seems to be commonly accepted in literature discussions, although the basis for this seems rather obscure, or at least tentative. Kroger (45) has comprehensively reviewed all the evidence and is unable to differentiate between $V^{	ext{III}}_{\text{Cr}}$ or $\text{Cr}^{	ext{III}}_1$ as the migrating species. Kofstad (4) favors the latter, which would explain the approximate independence of growth rate on oxygen pressure. Recent measurements (6) of the growth of Cr$_2$O$_3$ on pure Cr as a function of $P_{0_2}$ using CO/CO$_2$ mixtures, shown in Figure 7, confirm this.

Thus, using a point defect equilibrium given by

$$\frac{3}{2} \text{O}_2^X + \text{Cr}_2^X = \text{Cr}^{	ext{III}}_1 + 3\text{e}^- + \frac{3}{4} \text{O}_2$$

which give a dependence of the equilibrium concentration of Cr interstitials, $[\text{Cr}^{	ext{III}}_1]$ on $P_{0_2}$ as

$$[\text{Cr}^{	ext{III}}_1] \propto P_{0_2}^{-3/16}$$

and assuming that Hagel and Seybolt's diffusivities refer to a $P_{0_2}$ equal to the dissociation pressure of Cr$_2$O$_3$/Cr, Kofstad calculates the growth constant of Cr$_2$O$_3$ from the relationship

$$K_p \text{ (cm}^2 \text{s}^{-1}) = 2 (\alpha+1) D_{\text{Cr}}^*$$

where $D_{\text{Cr}}^*$ is the diffusion coefficient of Cr at the Cr$_2$O$_3$/Cr phase boundary
(Hagel and Seybolt's measurements). This has been converted into a gravimetric rate constant and is the line plotted in Figure 6.

At the risk of repetition, it is important to stress that the parabolic rate constants derived from independent diffusion measurements correspond to the upper limit of the experimental measurements. This is unusual (see for example the discussion of $\text{Al}_2\text{O}_3$ later). In most oxide systems the concern is usually with some type of short circuit diffusion process making the growth process faster than expected from lattice diffusion, with oxide grain boundaries usually serving as the short circuit paths. In this system the scale has a much finer grain size (see later) than the samples used for the diffusion studies: yet the apparent growth rate is much slower. It must be remembered, of course, that these conclusions are very tentative, being based on only two studies on diffusion in $\text{Cr}_2\text{O}_3$, and it is perhaps premature to prolong the discussion further. However, the dependence of the growth rate of $\text{Cr}_2\text{O}_3$ on some parameter, which may be grain size, is extremely important and will be referred to again, after the data for $\text{Al}_2\text{O}_3$ are present. It is abundantly clear, however, than detailed studies of the defect and transport properties of $\text{Cr}_2\text{O}_3$ are desperately needed.

$\text{Al}_2\text{O}_3$ - Figure 7 summarizes the parabolic rate constants for the growth of $\text{Al}_2\text{O}_3$ on binary or ternary Al containing alloys, some of which contain active element additions. Before discussing the figure in detail, some comments on the data: as with the $\text{Cr}_2\text{O}_3$-forming alloys, some of the gravimetric data may include the transient oxides formed in the early stages of oxidation. Secondly, some investigators comment that the growth of the $\text{Al}_2\text{O}_3$ is not strictly parabolic, and consequently, an 'apparent' $K_p$ has been plotted: this is based on weight change at maximum exposure time, or the equivalent in scale thickness. Nevertheless, in spite of these reservations, all the data fall in a scatter band of about 16. (Scale thickness after corresponding exposure times only vary by a factor of about 4x). This is quite remarkable, when the wide range of alloy compositions which are included is considered.

No direct correlation between alloy composition or system and growth constant is possible. Furthermore, the addition of active elements has no major influence on the growth rate (although see later). Variations within
the scatter band, are presumably related to subtle variations in the grain size (and morphology) of the Al₂O₃ scale, and the possible incorporation of dopants (Fe, Ni, Co, or Cr, or active elements Y, Hf, Ce, Th, etc.) modifying the defect structure. Both these points are discussed presently, but first it should be pointed out that it is probably of little practical significance. An Al₂O₃ scale growing at the rate indicated at the upper limit of the scatter band would only be 20 µm thick after 1000 h at 1100°C. As a consequence, in terms of oxide thickness, or consumption of Al from the alloy, this is not important. If, however, a faster growth rate implies an earlier onset of breakaway (i.e., loss of protection) then it is rather critical.

It is not possible to make a comparison between measured and calculated parabolic rate constants, as was attempted for Cr₂O₃, since the pressure dependency of transport in Al₂O₃ is not known, and, as indicated presently, the contribution of grain boundary diffusion to growth rate is generally accepted to be of primary importance. Nevertheless, following Smialek (59), the scale may be envisioned as a moving boundary of fixed composition, and thus, its boundaries follow a parabolic law and

\[ x^2 = D_{eff} t = K_x t \]

i.e. \( D_{eff} = K_x \)

where \( x \) is the scale thickness, \( D_{eff} \) an "effective" diffusion coefficient, and \( K_x \) the parabolic growth constant in terms of scale thickness. This latter parameter is obtained from the gravimetric constant using the molecular volume of Al₂O₃ (3.98 cm²/g, mole) and the ratio of weight of oxygen in Al₂O₃ to weight of Al₂O₃ (\( \frac{3/2 \cdot M_{O_2}}{M_{Al_2O_3}} = 0.235 \)). The \( K_x \)'s or \( D_{eff} \)'s from Figure 8 are plotted as a band in Figure 9.

Independent studies of diffusion in Al₂O₃ have only been conducted at temperatures outside the range of oxidation studies: 1670-1905°C for Al (60) and 1200-1780°C for oxygen diffusion (61-63). This should be borne in mind when considering the other data presented in Figure 9: they all represent extensive extrapolation. The one study of Al diffusion (60) indicated similar values for the diffusion coefficient in polycrystalline or single crystal material, and thus, no significant grain boundary contribution.
Extrapolated values are shown as a single line in Figure 9. Oxygen diffusion is at least two orders of magnitude slower in single crystal Al₂O₃ than in polycrystalline material, although there is considerable disagreement between the measurements of the various groups (61-63). (These differences will not be discussed in detail here but in essence they have been variously ascribed to differences in purity of the Al₂O₃ single crystals, or a non-equilibrium (higher) concentration of defects (V₀   implied) remaining in un-preannealed samples from low P₀₂ environment during crystal growth or sintering.) Extrapolation of the single crystal data (characteristic of lattice diffusion) are shown as a band on Figure 9.

The grain boundary contribution to diffusion in Al₂O₃ has been assessed by Smialek (59). This is achieved by comparing data obtained from polycrystalline and single crystal material. An effective diffusion coefficient, D_eff, is defined, when if grain boundaries represent the major short circuit diffusion path, then

\[ D_{\text{eff}} \approx (1-F)D_L + FD_{gb} \]

where \( D_L \) and \( D_{gb} \) are the lattice and grain boundary diffusion coefficients respectively, and \( F \) is the effective volume fraction of grain boundaries. For an array of square grains, it can be shown that,

\[ F = \frac{2\delta}{GS} \]

where \( \delta \) is the grain boundary width and \( GS \) is the grain size. Furthermore, if \( D_{gb} \gg D_L \) and \( F \gg 0.1 \), then

\[ D_{\text{eff}} \approx \frac{2\delta D_{gb}}{GS} \]

The vertically hatched band marked oxygen grain boundary in Figure 9 correspond to \( D_{\text{eff}} \) calculated, and extrapolated, from a combination of the measured diffusivities in poly- and single-crystalline Al₂O₃, using the lower branch of the single crystal data. A value of \( \delta \) of 100 Å (seems to be generally accepted) and a grain size of 0.1 μm has been used. The spread of values corresponds to the experimental spread in the two sets of original data (61-63). Extrapolated values of actual direct measurements (64) of grain boundary oxygen diffusion in Al₂O₃ full within this band.

Finally, the fourth band on Figure 9, diagonally hatched area, correspond to \( D_{\text{eff}} \) calculated in the same manner as above, but using extrapolated data
from the higher branch of the single crystal data (note that this also corresponds to a lower apparent activation energy), for which it will be recalled that it was suggested (60) that the higher diffusivities were due to a higher than equilibrium concentration of defects ($V_0^\cdot$) remaining in the sample from the low $P_{O_2}$ environment encountered during crystal growth or sintering. The samples were not annealed prior to the diffusion studies; however, the original authors attributed the higher diffusivities to unintentional doping (impurities) of the $Al_2O_3$ powder. The band of data come from using grain sizes in the range 0.1-5 μm; a constant grain boundary width of 100 Å was used.

It is fairly evident then from Figure 9, that the effective diffusivities from scale growth measurements can only correspond to a short circuit diffusion process (0.1-5 μm is a typical range of grain size for $Al_2O_3$ scales), and even then, only to the somewhat untypical results, supposedly characteristic of a high vacancy content. Smialek (59) suggests that the $Al_2O_3$ which grows on alloys also contains excess (cf. equilibrium) vacancies, as evidenced by the formation of pores within the growing scale. Elegant transmission micrographs support this view, with more pores forming at the oxide/gas interface where the flux of vacancies, due to the continually growing scale, is greatest.

It appears reasonably conclusive, then, that some type of short circuit diffusion process, via grain boundaries, is responsible for the observed growth rates being higher than independent diffusion measurements would suggest. Equally it would seem that oxygen is the more mobile species, at least in fine-grained $Al_2O_3$ scales; but it must be remembered, that the 'conclusion' (if it can be called such) that Al lattice and grain boundary diffusion rates is based on a single determination at very high temperature (1670-1905°C). Thus, it seems perfectly reasonable that the extrapolated line in Figure 9 for Al diffusion is too low, and that both Al and O diffusion may contribute to scale growth. (This point is returned to when the scale morphologies are discussed.) In part substantiation of this, the extensive studies of Krüger and his co-workers (65) on $α-Al_2O_3$, both nominally pure and doped with various donors and acceptors have apparently reached the conclusion that the intrinsic disorder in the Schottky type. This conclusion was arrived at by deriving the energy of formation of both
Schottky and cation Frenkyl defects using the experimental data and an estimated expression for the constant of intrinsic electronic excitation and comparing these with those calculated by Dienes et al. (66), or later by James (67), on the basis of the different types of disorder. Reasonable correspondence with the calculated value for Schottky disorder, which is also the smallest, indicates that this is the dominant intrinsic type of disorder.

The ionic defect concentrations, and thus, the transport properties are of course strongly affected by aliovalent acceptors or donors, and oxygen pressure. Particularly, the concentration of \( V_0 \) (or \( A1_i \) if the conclusion of negligible Frenkyl-type disorder is incorrect) is increased in the presence of acceptors, and of \( V^+ \) (or even less likely \( O_i \), under the same proviso as above) in the presence of donors.

Chemical diffusion studies in polycrystalline \( \text{Al}_2\text{O}_3 \) have also indicated a significant contribution of grain boundary diffusion (68). According to Kröger et al. (68), the oxygen pressure dependence of the rate of diffusion indicates that neutral interstitial oxygen is the major mobile species at the grain boundaries, although, this is not universally accepted (69).

**MORPHOLOGY OF THE PROTECTIVE SCALES**

As alluded to earlier, the growth of kinetics of both \( \text{Al}_2\text{O}_3 \) and \( \text{Cr}_2\text{O}_3 \) are very dependent on the microstructure of the scale, and vice versa. The microstructure, in turn, is closely related to the mechanism of scale growth, and in particular, the dominant diffusing species. Furthermore, all these features are critically affected by the presence of active elements and stable oxide dispersions.

Unlike the previous section, it is more appropriate here to discuss scales of \( \text{Al}_2\text{O}_3 \) and \( \text{Cr}_2\text{O}_3 \) in parallel, since there are many common features of growth morphology. Essentially five features are worthy of discussion. These include: (a) grain size and distribution through the scale; (b) oxide ridge development; (c) convoluted scale development; (d) void or cavity formation at the alloy/scale interface; and (e) the morphology of the alloy/scale interface.
Scale Grain Size and Distribution

Figure 10 shows a fracture section through the Cr$_2$O$_3$ scale on an Fe-18% Cr-1% Ti alloy oxidized at 1000°C (70). The grain size is relatively fine, < 1μm, and uniform through the scale. Contrast this with Figure 11, which shows a similar fracture section through an Al$_2$O$_3$ scale formed on a Co-15% Cr-8% Al alloy at 1100°C (71). In this latter, there is considerable variation in grain size across the section, with sub-micron size grains in the outermost part of the scale and relatively large, 1-5μm, columnar grains in contact with the alloy. These scale morphologies are fairly typical of Cr$_2$O$_3$ and Al$_2$O$_3$, respectively, formed on any of the alloys discussed in the previous section. The presence of active element or dispersed oxide additions, however, do have a tendency to reduce to overall grain size of the scale, and this has been attributed (33) to the dispersed oxides providing more nucleation sites on the original alloy surface for initial oxide formation. The presence of the additives, does not alter the variation in grain size in the scale, or lack of it in the Cr$_2$O$_3$ case.

It has been maintained (72, 73) that the morphology exhibited by Al$_2$O$_3$ scales is consistent with the scale growing by inward oxygen diffusion. The outer fine grains represent the initially nucleated oxide, whilst the inner columnar grains are formed during the later stages of growth when the overall thickening rate of the scale is low. Loss of contact between scale and alloy (see later) may also contribute to the uninhibited growth of the inner grains when they are no longer restrained by the alloy (46) and this effect could be exaggerated by Al vapor transport from the alloy to the inner surface of the scale.

A completely different view of the scale growth mechanism could also fit the same morphological pattern, and it could be equally argued that the scale grows instead by cation diffusion outwards. The outer fine grains would then represent the newly formed grains on the surface, while the inner, larger grains, these formed at an earlier stage, for which there has been a longer time for grain growth to occur. Smialek (59) and Hindam and Smeltzer (54) have documented grain growth in Al$_2$O$_3$ scales formed on Ni-Al alloys: the latter show that at 1300°C, the average grain size increases
from about 3 μm after 1 day exposure to about 9 μm after 14 days. Wood et. al. (74) have gone into considerable details in speculation of the grain structure development. Seven types of grains are classified, but the details will not be reproduced here.

**Oxide Ridge Development**

The development of oxide ridges must be differentiated from the formation of convoluted scales, in that the latter refers to the morphological features the scales develop, usually after detachment from the alloy surface, and are considered in a later section. Here oxide ridges refer to localized variations in actual scale thickness. Figure 12 shows an example for Cr₂O₃ formed on Cr, from the work of Caplan et.al. (7,12). According to them, the nodular regions of oxide are polycrystalline and grow by two-way transport of cation diffusion outward and oxygen ion inward along oxide grain boundaries. The thinner oxide is monocrystalline and grows by lattice cation diffusion outward. Considerable compressive stress develops within the polycrystalline oxide, since the two-way transport causes new oxide to be formed within the body of the scale. This does lead to substantial wrinkling of the scale layer by plastic deformation, the consequences of which are discussed later. It suffices to point out here that this irregular growth is essentially due to the presence of short circuiting grain boundaries in parts of the scale, and their absence in others. However, no explanations are offered as to why there should be these differences in grain morphology, although there is some allusion to the effects of surface preparation, and favorable grain orientations in the metal substrate.

Generally, it should be pointed out that gross variations in Cr₂O₃ scale thickness are not generally observed in alloys. The scale is relatively fine-grained over the entire surface (see Figure 10 earlier). There is one exception, although for a different reason. Stringer et.al. (25,29,33,34) studied the oxidation behavior of Ni and Co-based alloys containing various oxide dispersions. Nodules of Cr₂O₃ grew in some locations, whilst in others the Cr₂O₃ was relatively thin. The nodular regions were associated with areas of the alloy devoid of the oxide dispersion. The alloys were prepared by mechanical alloying which apparently was not able to produce a completely homogeneous alloy. As indicated earlier (Figs. 4 and 5) the
presence of a dispersed oxide reduces the growth rate of the scale. It is also suggested (33) that it alters the growth mechanism from predominantly cation diffusion outwards to anion inwards, the dispersion blocking short circuit paths - dislocation pipes - for Cr diffusion, whilst increasing the number of short circuit paths for anion transport - grain boundaries, due to the smaller oxide grain size.

Oxide ridge development is also observed with Al$_2$O$_3$ scales (51, 54, 58, 75) especially during the early stages of growth. Again, the mechanism postulated relates to the nodular region containing large densities of short circuiting grain boundaries acting as easy paths for inward oxygen transport. The presence of these polycrystalline ridges could be influenced by the alloy substructure or be induced by faulted regions in the initially formed γ-Al$_2$O$_3$ film when it transformed to α-Al$_2$O$_3$. This conversion is accompanied by a 14.3% reduction in volume.

**Convoluted Scale Development**

Figure 13 shows the convoluted scales which can develop on Cr and Cr$_2$O$_3$-forming alloys, from the work of Caplan et.al. (7). The lower micrograph shows a multi-layered convoluted scale formed when the detached oxide repeatedly cracks open and allows the oxidizing gas access to the bare metal and re-formation of another layer of oxide. This is generally only the case for pure Cr and alloys very rich in Cr: with diluter alloys, the formation of the first Cr$_2$O$_3$ layer usually depletes the alloy surface of Cr such that if the detached oxide cracks, and it usually does, base metal oxidation takes place.

Detached Al$_2$O$_3$ scales also develop convolutions. However, there are important differences. Firstly, the Al$_2$O$_3$ scales seem to be able to adopt much more tortuous morphologies without cracking. Indeed, they seem much less prone to cracking all together, and multiple layers of Al$_2$O$_3$ are rarely, if ever, observed. Equally though, because of the slower growth rate of Al$_2$O$_3$ compared to Cr$_2$O$_3$, and the generally faster interdiffusion rate in Al-containing alloys than in Cr-containing systems, the Al-depletion behind a growing Al$_2$O$_3$ scale would be relatively slight. As a consequence, even a moderate Al level in the alloy should permit re-formation of a second layer of Al$_2$O$_3$ should the first formed, but detached layer crack. Breakdown of
Al₂O₃ is thus not as commonly observed as with Cr₂O₃ scales.

A popular mechanism for the development of a convoluted morphology in both Cr₂O₃ (7) and Al₂O₃ (3, 48, 76) is the lateral growth mechanism, an idea originally put forward by Rhines et al. (77) for NiO growth. This has been elaborated in some detail by Wood et al. (48). Essentially, they suggest that for Al₂O₃, in addition to inward oxygen diffusion down the Al₂O₃ grain boundaries, outward diffusion of Al occurs, probably along line defects in the oxide. Reaction between the inward and outward diffusing species results in the formation of oxide within the existing scale layer. Hence, lateral growth of the oxide occurs as oxidation proceeds, leading to the rapid development of high compressive stresses and consequent localized detachment and buckling of the scale. Based on this model, they attribute the increased adherence of the scale due to Y-additions to the prevention of lateral growth of the oxide: incorporation of Y into the scale suppresses the cation contribution to scale growth. In their more recent review (3), they claim this is consistent with the views, and work, of Kröger (45) who suggests that Y acts as a donor, presumably because of its large ionic radius. This donor activity compensates the iron acceptors in Al₂O₃: Fe, and thus, by reducing the concentration of interstitial Al ions without markedly increasing that of Al vacancies, explains how Al transport outward is stifled. There is also some evidence to suggest that doping enhances plastic deformation of Al₂O₃, particularly creep. Hollenberg and Gordon (78) found that doping polycrystalline Al₂O₃ with either Fe²⁺ or Ti⁴⁺ resulted in the creation of either Al-ion interstitials or vacancies, both of which enhanced the cation diffusion rate and increased the creep rate. In the case of Cr₂O₃, Kofstad (4) has suggested that its ability to deform is enhanced at low oxygen potentials. This is in accord with the rate-limiting factor in creep being the diffusion of the minority defects—oxygen vacancies. On the basis of their proposed defect model, the defect concentration would be increased as the oxygen partial pressure is decreased.

An alternate view of scale buckling was proposed earlier by Pettit (46), and this attributed the phenomenon to the growth of large oxide crystals at the underside of the scale where it was detached from the alloy. These impinge on one another and cause scale buckling. The large Al₂O₃ crystals
grow only at these locations where the alloy supplies Al vapor sufficiently fast and oxide grain growth is not restricted by a retarding substrate.

Void and Cavity Formation at the Alloy/Scale Interface

When the surface scale is removed from the alloy, in many cases unintentionally during cooling from the oxidation temperature, the exposed alloy surface shows a number of slightly concave craters having a smooth, sometimes thermally etched, appearance, and representing areas where oxide and metal were not in intimate contact during the oxidation. Elsewhere, the surface exhibits oxide grain 'imprints', where the scale had maintained alloy contact. Howes (79) was probably the first to observe this phenomena; however, subsequently, it has been observed for virtually all Al$_2$O$_3$ and Cr$_2$O$_3$ scales grown on alloys not containing active elements. Figure 13 shows a typical example of the surface of an Fe-Cr alloy after removal of the Cr$_2$O$_3$ scale (6). The voided area approximates to virtually 50% of the surface.

The presence of these voids or cavities between scale and substrate does not seemingly affect the growth rate of the surface scale, as discussed earlier. The voids can, however, have a relatively dramatic effect on the adhesion of the surface scale to the substrate. Indeed, the elimination of these interfacial voids by active element or oxide additions to the alloy - a universally accepted experimental observation - is frequently quoted as one of the mechanisms by which such additions improve alloy/scale adherence (2, 3, 33, 34, 46-48, 52, 57, 58, 74, 76, 80-90): not necessarily the only mechanism - see later. It is thus relevant to consider then the two interrelated phenomena: (i) how do the voids form? and (ii) how are they eliminated by the active element or oxide additions? Both these subjects are somewhat controversial, and the various arguments are only reproduced briefly.

Broadly, there are two views of void (or cavity) formation. The first relates to the continued condensation of point defects (vacancies) into microscopic voids and their subsequent growth into cavities. These are not observed with addition-containing alloys because the active element atoms themselves or the stable oxide dispersions provide alternate sites for vacancy condensation (91) - the so-called vacancy sink model. The question
does arise, however, as to the source of the vacancies. Before it was sus­pected that the growth direction of \( \text{Cr}_2\text{O}_3 \) scales in the presence of additions might have changed, then the outward diffusion current of metal ions from the alloy to the oxide and across the scale produces a countercurrent of vacancies. However, if the growth direction is changed, the vacancy source must be elsewhere: \( \text{Al}_2\text{O}_3 \) grows primarily by oxygen transport anyway.

Kuenzly and Douglass (52) have suggested it might arise from a Kirkendall effect in the alloy substrate, associated with the selective removal of one of the alloy components, and the unequal flux of the more noble components away from the alloy/scale interface. In view of the very slow rates of scale growth, however, particularly for \( \text{Al}_2\text{O}_3 \), such a vacancy flux would be quite small.

There is a further possible source of vacancies: vacancy formation and subsequent development of interfacial voids may be confined to the early, transient stages of oxidation when the faster growing base metal oxides, \( \text{NiO}, \text{CoO} \), etc., are being formed. Thus, since the active element of stable oxide additions reduce this transient period, there are fewer vacancies to eliminate. Gibbs has suggested (92), although not in this context, that the scale may not relax completely on to the receding alloy substrate, and thus, removal of any alloying component into the scale, irrespective of the growth direction of the scale, can be considered as a flux of vacancies into the alloy.

The second major view of void or cavity development centers around the development of growth stresses within the oxide, particularly if there is formation of oxide within the scale itself, as discussed in the last section. The tendency towards formation of a convoluted morphology results in localized loss of scale adhesion and cavity formation at the interface. Stringer (93) has suggested, however, that if new oxide is formed within the scale layer whilst it is still adherent to the alloy, then the stress developed will discourage further oxide from forming in that location - Le Chatelier's principle.

Clearly, there is still considerable controversy surrounding the develop­ment of both convoluted scale morphologies and the partial, and eventually complete, detachment of the scale in both \( \text{Cr}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \)-forming systems.
Most of the controversy relates to whether the voids and convolutions are the cause, or the result of the loss of adhesion. Nevertheless, it is important not to lose sight of the facts: active element or oxide dispersion additions prevent both from occurring.

**Morphology of the Alloy/Scale Interface**

Finally, perhaps the most dramatic difference produced by active element or oxide dispersion additions, at least with Al$_2$O$_3$-forming alloys, is the modification to the alloy/scale interface. Figure 15 compares an Fe-10% Al and a similar alloy containing 1% Hf. In the former case, the Al$_2$O$_3$ scale spalled readily upon cooling revealing a relatively planar alloy/scale interface, whereas with the Hf-containing alloy, there is a profusion of oxide pegs penetrating into the alloy. These have been dramatically revealed by deep-etching away a substantial portion of the underlying alloy. The pegs are principally Al$_2$O$_3$, although the scale does contain dispersed HfO$_2$ particles (light phase) and indeed when polished sections are prepared, the pegs can be seen to consist of a HfO$_2$ stringer completely enveloped by the Al$_2$O$_3$ scale.

The observation of a highly convoluted alloy/scale interface is not of course new; it is nearly always seen with Al$_2$O$_3$ forming alloys containing active elements. Many authors (2, 3, 33, 34, 46-48, 52, 57, 58, 74, 76, 80-85, 95) attribute the improvement in alloy/scale adhesion to the formation of these pegs and recently Allam et.al. (73) have rationalized the differing extents of the beneficial effects for Y, Hf and other additions in terms of the distribution of the pegs along the interface.

Of course, it has never been maintained that oxide peg formation is the only mechanism by which the active element addition improves scale adhesion, but it is certainly the most dramatic in Al$_2$O$_3$-forming systems. Recently (96), attempts have been made to quantify the effect by following the propagation of cracks in the scale (or at the interface) induced by microhardness indentations. Figure 16 shows an example for the scale shown in Figure 15. Substantial lateral cracking of the Al$_2$O$_3$ scale has taken place, without any loss of contact between scale and alloy. Indeed, crack propagation appears to be blunted at the interface.
The question that remains to be answered then, is why such a tortuous alloy/scale interface forms. Earlier, it was implicitly suggested (72, 73) that \( \text{Al}_2\text{O}_3 \) grew inward in the alloy encapsulating the internal \( \text{HfO}_2 \) particles via preferential oxygen diffusion along the supposedly incoherent interfaces between the precipitates and the matrix. However, in the light of further evidence, it has now been suggested (84) that the \( \text{HfO}_2 \) precipitates within the \( \text{Al}_2\text{O}_3 \) scale act as short circuit diffusion paths for oxygen leading to preferential localized scale thickening in the neighborhood of these particles. Scale thickness measurements parallel to the local growth direction at random positions through the scale show there is a linear correlation between the local scale thickness and the thickness of the \( \text{HfO}_2 \) precipitates.

This model implies of course that any stable addition which forms an oxide in which the oxygen diffusivity is substantially higher than in \( \text{Al}_2\text{O}_3 \) will produce a similar effect, although the distribution of the oxide particles in the \( \text{Al}_2\text{O}_3 \) is also important. Figure 17, from the work of Tien and Pettit (47), shows a similar close correspondence between the \( \text{Sc}_2\text{O}_3 \) particles in the \( \text{Al}_2\text{O}_3 \) scale and the development of a convoluted alloy/scale interface. Again, the available diffusion data for \( \text{Sc}_2\text{O}_3 \) indicate oxygen transport rates orders of magnitude faster than in \( \text{Al}_2\text{O}_3 \). \( \text{ZrO}_2 \) would be expected to act similarly, and using weight gain data of Kahn et.al. (56), the amount of oxide formed after 100 h at 1100°C is shown to increase with increase in the Zr level in NiCrAl alloys: Figure 21. Also, included are data for CoCrAlHf and CoCrAlY (72); in the latter case, there is essentially no increase in oxide formation because the Y is primarily confined to the yttride phase present in alloy grain boundaries.

CONCLUDING REMARKS

The close interaction between growth kinetics, scale microstructure and adhesion has been demonstrated. This is probably not of major importance in terms of the growth rate of the protective oxide, especially in the case of \( \text{Al}_2\text{O}_3 \), since even growth at the fastest observed rate, does not correspond to a major loss in material in many instances. The spread of growth rates observed for \( \text{Cr}_2\text{O}_3 \) scales, however, does encompass unacceptedly high rates. Breakdown of the protective scale, especially by mechanical spallation, is
critically dependent on the details of the microstructure, and the ability of active element or oxide dispersion additions to modify this is of clear technological importance. However, without a clear understanding of the mechanism, it is unlikely that the maximum benefit of these effects can be achieved. The work described in the later part of this paper points to the right direction.

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FIGURE CAPTIONS

Figure 1. Schematic reaction kinetics for a protective oxide forming alloy.

Figure 2. Schematic representation of the interaction between kinetics, microstructure and adhesion.

Figure 3. Summary of reported parabolic rate constants for the oxidation of Cr

- Phalniker, Evans and Baldwin (5)  △ Hindam and Whittle (6)
- Caplan, Harvey and Cohen (7)  ○ Lillernd and Kofstad (4)
- Mortimer and Pest (8)  △ Hagel (9)
- Gulbransen and Andrew (10)  □ Cadion and Paidasi (11)
- Caplan and Sproule (12)

Figure 4. Summary of reported parabolic rate constants for the growth of Cr$_2$O$_3$ on binary Cr-containing alloys.

Co-Cr  ★★ Phalniker, Evans and Baldwin (5)
Fe-Cr  ○ Francis and Whitlow (13)
      ○○○○ Tedmon (14)
      ○○○○ Tedmon (14)
      ○○○○ Tedmon (14)
      △ Tedmon (14)
      ○ Felten (15)
      □ Wood and Whittle (16)
      ○ Mortimer and Post (8)
      ● Wallwork and Hed (18)
      ● Moulin, Huntz and Lacombe (19)
      ▼ Giggins and Pettit (20)
      ● Hodgkiess, Wood, Whittle and Bastow (21)
      ● Espevik, Rapp, Daniel and Hirth (22)
      ● Ecer and Meier (23).

Figure 5. Summary of reported parabolic rate constants for the growth of Cr$_2$O$_3$ on alloys containing active elements or dispersed oxides.

Co-Cr  ★ Stringer and Wright (25)
      ★★★ Whittle, El Dahshan and Stringer (26)
Fe-Cr  ○○○○ Gonzel, Whittle and Stringer (27)
      ○ Wood and Bonstead (28)
      □ Wright and Wilcox (29)
      □ Francis and Whitlow (13)
Nagai, Takebayashi and Mitani (30)
Falten (15)

Giggs and Pettit (31)
Davis, Graham and Kvernes (32)
Stringer, Wilcox and Jaffee (33)
Wright, Wilcox and Jaffee (34)
Michels (35).

Figure 6. Comparison of the parabolic growth constants for Cr$_2$O$_3$ with diffusion data (see text for details).

Figure 7. Parabolic rate constant for the growth of Cr$_2$O$_3$ on Cr in Co/CO$_2$ at 1300°K as a function of oxygen potential.

Figure 8. Summary of the parabolic growth constants of Al$_2$O$_3$ on Al-containing alloys

Tien and Pettit (47)
Golightly, Sott and Wood (48)
Amano, Yajima and Saito (49)
Wukusick and Collins (50)
Smialek (51)
Kuenzly and Douglass (52)
Pettit (53)
Hindam and Smeltzer (54)
Pettit (55)
Kahn, Lowell and Barrett (56)
Kumar, Hassallah and Douglass (57)
Felten and Pettit (58).

Figure 9. Comparison of the parabolic growth constants of Al$_2$O$_3$ with diffusion data (see text for details).

Figure 10. Fracture section of Cr$_2$O$_3$ formed on Fe-18 Cr-1 Ti after Goncel et al. (70).

Figure 11. Fracture section of Al$_2$O$_3$ formed on Co-15 Cr-8 Al after Allam (71).

Figure 12. Oxide ridge formation in Cr$_2$O$_3$ on pure Cr after Caplan et al. (12).
Figure 13. Convoluted \( \text{Cr}_2\text{O}_3 \) scales on pure Cr after Caplan et.al. (7).

Figure 14. Cavity formation beneath the \( \text{Cr}_2\text{O}_3 \) scale on Fe-25 Cr after Hindam et.al. (6).

Figure 15. \( \text{Al}_2\text{O}_3 \) scale formed on (a) Fe-10 Al and (b) Fe-10 Al-1 Hf after Hindam et.al. (94).

Figure 16. Crack propagation in \( \text{Al}_2\text{O}_3 \) scales subjected to microhardness indentation (96).

Figure 17. Cross-section of \( \text{Al}_2\text{O}_3 \) scale formed on FeCrAlSc after Tien and Pettit (47).

Figure 18. Wt. gain after 100 h at 1100°C as a function of active element content (NiCrAlZr data from ref. 56; CoCrAlY and CoCrAlHf data from ref. 72).
MAJOR FACTORS

\( t_B \) - time to breakaway: determines effective lifetime

\( ('K_p')_{ss} \) - growth rate (diffusion controlled): must be sufficiently small; may affect \( t_B \)

MINOR FACTORS (unless they influence above)

- Initial transient rate
- Post-breakaway rate
- Healing of protective oxide

Figure 1.
Figure 2.
Figure 3.
Figure 4.

XBL 821-7735
Figure 5.
Figure 6.
Figure 7.
Figure 9.
Figure 12

Cr - Caplan et al

XBB821-265
FeCrAlSc
Tien and Pettit

Figure 17
Figure 18.

Wt. gain in 100 hr at 1100°C mg cm⁻²

at % Hf, Y or Zr

NiCrAlZr
CoCrAlHf
CoCrAlY

XBL 821-7726
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