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PEG FORMATION BY SHORT CIRCUIT DIFFUSION IN \( \text{Al}_2\text{O}_3 \) SCALES CONTAINING OXIDE DISPERSIONS

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It is well established that the addition of active elements (Y, Ce, Hf, Th, etc.) or dispersoids of the respective oxide phases improves the oxidation behavior of \( \text{Cr}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \) forming alloys and coatings. The beneficial effects include: enhancement of selective oxidation leading to curtailment of the transient stage and rapid development of a protective scale, alteration of its growth rate and improvement in the adhesion of the scale to substrate. The latter effect, which represents significant practical importance for alloy protection, is the most dramatic and has received considerable attention. A recent review\(^{11}\) has summarized the various observations and interpretations of this phenomenon. Whilst there is no general consensus view on the mechanism of scale adhesion, the formation of inwardly growing oxide pegs, which mechanically key the scale to substrate is recognized as a pertinent factor.

The purpose of this communication is to present recent observations and advance a mechanism for peg formation. A detailed model accounting for the development of such a tortuous alloy/scale interface and its implications on scale adhesion are the subject of a comprehensive future publication\(^2\).

Alloy specimens with nominal compositions (wt.\%) Fe-10Al and Fe-10Al-1Hf were oxidized in air at \( 1200^\circ\text{C} \) for a period of two weeks. The \( \alpha-\text{Al}_2\text{O}_3 \) scale formed on the Hf-free alloy spalled readily upon cooling revealing a relatively planar alloy/scale interface exhibiting oxide free cavities\(^2\). The structure of the tenaciously adherent scale formed on the Hf-containing alloy is shown in Figure (1). The upper micrograph is a deep-etched section while the lower one was obtained using conventional sample preparation procedures. The scale consists of \( \alpha-\text{Al}_2\text{O}_3 \) containing dispersed \( \text{HfO}_2 \) particles (light phase). Unreacted Fe particles are also embedded in the scale (arrows). Unlike the Hf-free alloy, the alloy/scale interface is highly irregular due to the development of a profusion of inwardly growing pegs. It is evident that the growth of these protrusions is closely related to the distribution of the \( \text{HfO}_2 \) precipitates incorporated in the scale. Although, the continuity of the \( \text{HfO}_2 \) particles cannot be adequately revealed in a two dimensional section, it can be seen occasionally that a well developed peg consists of a \( \text{HfO}_2 \) stringer completely enveloped by the \( \text{Al}_2\text{O}_3 \) scale.

In attempting to interpret peg formation, it was implicitly suggested\(^3\) that \( \text{Al}_2\text{O}_3 \) grows inward in the alloy encapsulating the internal \( \text{HfO}_2 \) particles via preferential oxygen diffusion along the supposedly incoherent interfaces between the precipitates and alloy matrix. However, there is no evidence that \( \text{HfO}_2 \) is precipitated internally in the alloy ahead of the scale. Furthermore, recent measurements indicate that the relative contribution of boundary diffusion to the growth of \( \alpha-\text{Al}_2\text{O}_3 \) internal precipitates in dilute Ni-Al alloys diminishes rapidly as temperature is increased in the range of 800-1100\(^\circ\text{C}\)\(^4\) and becomes negligible at 1200\(^\circ\text{C}\)\(^5\), the temperature at which peg formation is predominant. Nevertheless, other interfaces such as between well oriented two phase Co-Cr-Al-Y alloy coating prepared by electron beam physical vapor deposition (PVD) might be effective for oxygen transport\(^6\).

Keywords: Alloy, Oxidation, Diffusion.
In the light of the present observations, the following growth model is proposed. The incorporation of HfO₂ as well as unreacted Fe particles in the scale is consistent with the Al₂O₃ growth on Hf-containing alloys being controlled by inward oxygen diffusion, most probably along grain boundaries and other structural imperfections. Since the diffusivity of oxygen in HfO₂ is expected to be several orders of magnitude greater than in Al₂O₃, the HfO₂ precipitates within the scale act as short circuit diffusion paths for oxygen transport leading to preferential localized scale thickening in the neighborhood of these particles.

Figure (2) demonstrates that the scale thickness measured parallel to the local growth direction at random positions, as shown in the inset, increases linearly with increasing thickness of the HfO₂ precipitates. The scatter in the data is due, as mentioned earlier, to the difficulty in measuring the true length of the HfO₂ stringers. A least squares fit to the data gives a linear correlation factor of 0.88 and the gradient of the best fit line is 0.98 μm/μm, consistent with the very large difference in oxygen diffusivities in the oxides.

Once the concept of peg formation being caused by localized variations in the scale growth rate is accepted, a number of other important conclusions are evident. The distribution of the internal oxide particles, which are eventually incorporated into the scale, is important, as implied in earlier hypotheses (1,3,10). If the particles are too uniformly distributed, then localized variations in scale thickness tend to be smoothed out and the oxide protrusions will not penetrate very far into the alloy. A simple calculation shows that with 1% active element in the alloy produces approximately 2 vol. % oxide in the scale. If this is uniformly distributed as, for example, 2 μm diameter spherical particles, then these would be 8 μm apart. This would be a poor distribution, since the resulting pegs would only penetrate about 20% thicker than the total scale thickness. The factors governing the microstructure and distribution of HfO₂ in the scale need to be examined.

The advanced model implies that differences in transport rates through the oxide of the active element and the host scale should be critical. Accordingly, the following generalizations can be made. Al₂O₃ grows very slowly and almost any addition might be expected to locally increase its growth rate. This is not the case for Cr₂O₃ scales, which may well explain why active element additions to Cr₂O₃ forming alloys do not generally lead to appreciable oxide peg development although some improvement in adhesion is usually observed.

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References

2. H. Hindam and D. P. Whittle, to be published.


Figure 1. Section through Al₂O₃ scale formed on Fe-10 Al-1Hf formed at 1200°C showing pegs at alloy/scale interface and HfO₂ particles incorporated into the scale.

Figure 2. Local scale thickness as a function of thickness of HfO₂ particles.
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