Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

PEG FORMATION BY SHORT CIRCUIT DIFFUSION IN Al_2O_3 SCALES CONTAINING OXIDE DISPERSIONS

H. Hindam and D.P. Whittle

November 1981

DISCLAIMER
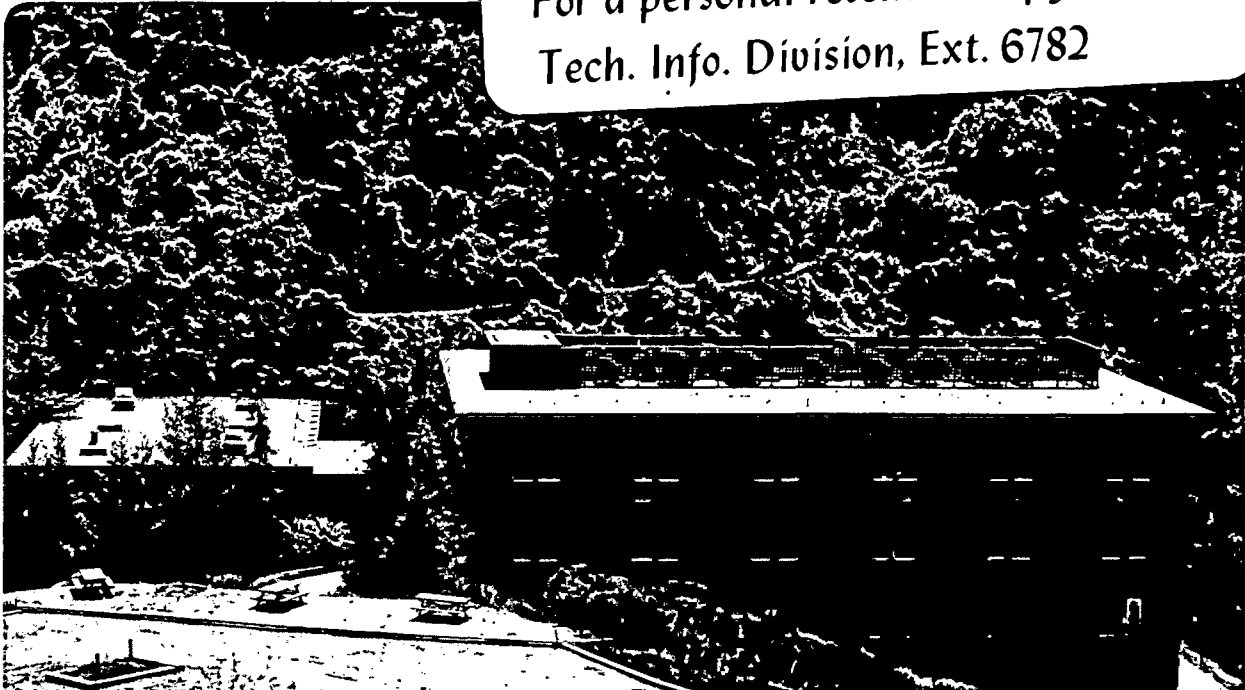
PEG FORMATION BY SHORT CIRCUIT DIFFUSION IN
Al_2O_3 SCALES CONTAINING OXIDE DISPERSIONS

H. Hindam and D. P. Whittle*

Lawrence Berkeley Laboratory, University of California
Berkeley, California   94720

*Electrochemical Society Active Member.

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 Cr_2O_3 and Al_2O_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[1] 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°C for a period of two weeks. The $\alpha-Al_2O_3$ 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 $\alpha-Al_2O_3$ containing dispersed HfO_2 particles (light phase). Unreacted Fe particles are also embeded 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 HfO_2 precipitates incorporated in the scale. Although, the continuity of the 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 HfO_2 stringer completely enveloped by the Al_2O_3 scale.

In attempting to interpret peg formation, it was implicitly suggested[3] that Al_2O_3 grows inward in the alloy encapsulating the internal HfO_2 particles via preferential oxygen diffusion along the supposedly incoherent interfaces between the precipitates and alloy matrix. However, there is no evidence that 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 $\alpha-Al_2O_3$ internal precipitates in dilute Ni-Al alloys diminishes rapidly as temperature is increased in the range of 800-1100°C[4] and becomes negligible at 1200°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].

In the light of the present observations, the following growth model is proposed. The incorporation of HfO_2 as well as unreacted Fe particles in the scale is consistent with the Al_2O_3 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 HfO_2 is expected to be several orders of magnitude greater than in Al_2O_3*, the HfO_2 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 HfO_2 precipitates. The scatter in the data is due, as mentioned earlier, to the difficulty in measuring the true length of the HfO_2 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 $\mu m/\mu m$, 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 HfO_2 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. Al_2O_3 grows very slowly and almost any addition might be expected to locally increase its growth rate. This is not the case for Cr_2O_3 scales, which may well explain why active element additions to Cr_2O_3 forming alloys do not generally lead to appreciable oxide peg development although some improvement in adhesion is usually observed.
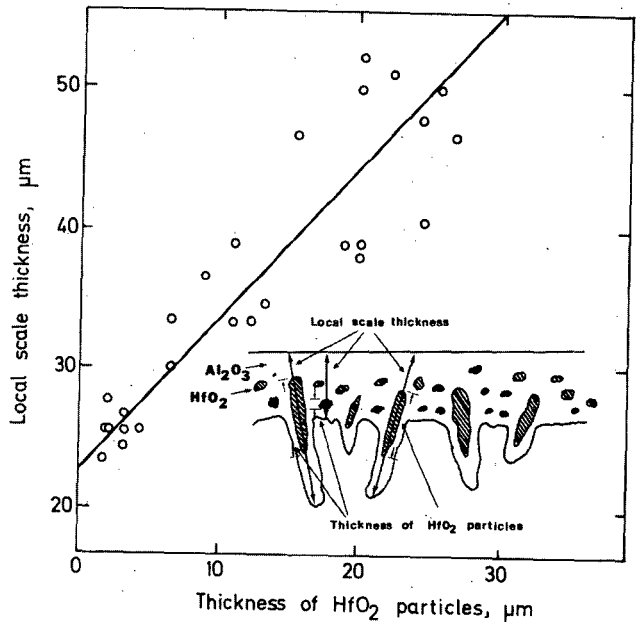
Acknowledgement

References

1. D. P. Whittle and J. Stringer, Phil. Trans. Roy. Soc., London A27, 309 (1980).

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

3. I. M. Allam, D. P. Whittle and J. Stringer, Oxid. Met. 12, 35 (1978); ibid 13, 381 (1979).

4. D. P. Whittle, Y. Shida, G.C. Wood, F. H. Stott and D. B. Bastow, submitted to Phil. Mag. (1981).

5. H. Hindam and D. P. Whittle, paper presented at the 34th Pac. Coast Regional Meeting of the American Ceram. Soc., Newport Beach, CA., October 1981.

---

*The diffusivity of oxygen in pure HfO_2 has not yet been measured. However, it is expected to be within the range of that of oxygen-deficient oxides: $\sim 10^{-9}$ cm^2/sec. in Nb_2O_5(7) and 10^{-7} cm^2/sec. in Er_2O_3(8) at 1200°C. D_0 in polycrystalline $\alpha-Al_2O_3$(9) is $\sim 10^{-15}$ cm^2/sec.

6. D. P. Whittle, D. H. Boone and I. M. Allam, Thin Sol. Films 73, 359 (1980).

7. W. K. Chen and R. A. Jackson, J. Chem. Phys. 47, 1144 (1967).

8. C. D. Wirkus, M. F. Berard and D. R. Wilder, J. Amer. Cer. Soc. 50, 113 (1967).

9. Y. Oishi and W. D. Kingery, J. Chem. Phys. 33, 480 (1960).

10. J. K. Tien and F. S. Pettit, Met. Trans., 3, 1587 (1972); C. S. Giggins, B. H. Kear, F. S. Pettit and J. K. Tien, Met. Trans. 5, 1685 (1974).

XBL 8111-12347

Figure 2. Local scale thickness as a function of thickness of HfO_2 particles.

Figure 1. Section through Al_2O_3 scale formed on Fe-10 Al-1Hf formed at 1200°C showing pegs at alloy/scale interface and HfO_2 particles incorporated into the scale.
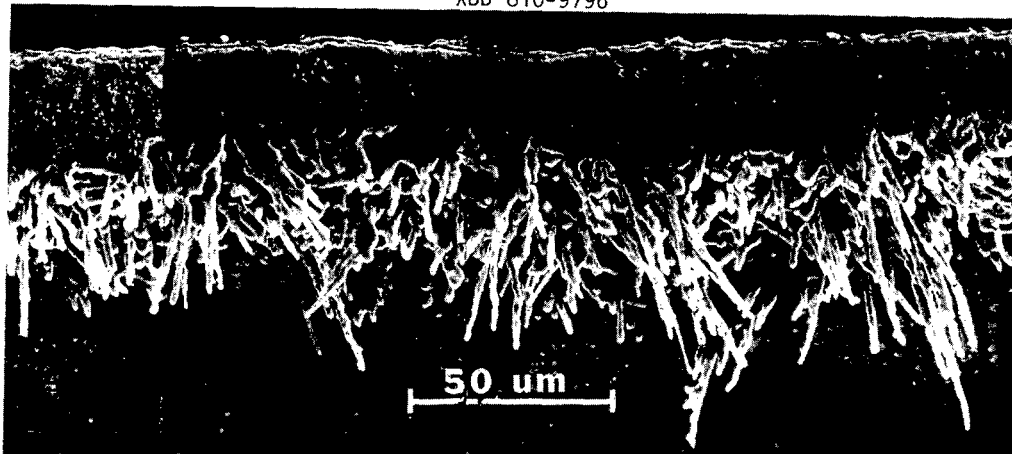
XBB 810-9796

-3-