

The Influence of Platinum on the Maintenance of α - Al_2O_3 as a Protective Scale

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The influence of externally located platinum on the isothermal stability of α - Al_2O_3 scales formed at high temperatures has been examined. It has been observed that a nickel-base alloy forms an external scale of α - Al_2O_3 during oxidation at 1200°C, but this scale breaks down isothermally, enabling a faster-growing Cr_2O_3 -rich scale to develop. However, in the presence of platinum metal alongside the specimen in the furnace hot zone, the breakdown of the α - Al_2O_3 scale is postponed for a substantial period of time. It appears that platinum, as the volatile species PtO_2 , is incorporated into the growing α - Al_2O_3 scale where it either influences the stress relief mechanism at temperature or reduces oxidation growth stress generation and thus significantly enhances the isothermal stability of the scale.

KEY WORDS: α - Al_2O_3 ; platinum; oxidation; adhesion.

As an adherent and coherent scale of α - Al_2O_3 is an important feature in protecting certain high-temperature materials, there have been numerous investigations into the high-temperature oxidation of alloys which tend to form such scales. Many of these studies have involved the presence of platinum in the furnace hot zone, e.g., platinum specimen suspension wires, platinum/platinum-13% rhodium thermocouples, and the use of platinum markers. In all cases the platinum was considered to be inert. However,

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evidence has accumulated over the years that the presence of platinum in the hot zone affects the isothermal stability of α -Al₂O₃ scales.

In these present studies, flat specimens of various single-phase and duplex iron-base and nickel-base alloy α -Al₂O₃ formers were oxidized in air or oxygen at 1100 and 1200°C. Following transient oxidation, a typical nickel-base alloy formed an α -Al₂O₃ scale during oxidation at 1100 and 1200°C, but on further oxidation this scale broke down isothermally and gave way to a Cr₂O₃-rich scale. The breakdown was evidently due to mechanical failure of the α -Al₂O₃. The presence of platinum, as a piece of foil 25 mm × 25 mm × 0.05 mm alongside the specimen in the furnace hot zone, postponed markedly the breakdown of the α -Al₂O₃. Such α -Al₂O₃ scales were maintained for at least 24 hr at both 1100 and 1200°C. This result is to be compared with breakdown after 1 hr at 1100°C and after 2 hr at 1200°C in the absence of platinum. It should be noted, however, that the presence of platinum did not maintain the α -Al₂O₃ permanently. For example, breakdown had occurred after 48 hr at 1100°C. Furthermore, although the α -Al₂O₃ was maintained isothermally in the presence of platinum for times shorter than this, the scale lifted from the specimen surface and some spallation occurred on cooling to room temperature.

There appears to be a memory effect associated with the phenomenon, in that a specimen oxidized for 2 hr at 1100°C in the presence of platinum maintained a protective α -Al₂O₃ scale for a further 8 hr after the platinum was removed.

Figure 1 shows that the platinum-stabilized α -Al₂O₃ formed at 1200°C is highly convoluted, the convolutions being due to the mechanism of growth¹ of the α -Al₂O₃. The variation in thickness is due to the effect of sectioning convolutions and the best indication of the true scale thickness is the thinnest region shown in Fig. 1. A scanning electron micrograph of the platinum-stabilized α -Al₂O₃ formed at 1100°C (Fig. 2) also illustrates the highly convoluted nature of the oxide, although there appears to be no preferred orientation for the convolutions. The cracks, formed on cooling from the oxidation temperature, predominate in the convolutions. It can also be seen from Fig. 2 that there are whisker-like protrusions from the surface of the oxide. Protrusions of this type have been observed previously² on α -Al₂O₃ and have been explained in terms of a dislocation pipe diffusion mechanism.³ However, they are considered to play no part in the maintenance of the α -Al₂O₃ scale.

Electron microprobe analysis showed that the platinum-stabilized α -Al₂O₃ scale formed after 24 hr at 1200°C contained approximately 1.2 wt.% (0.12 at.%) platinum. There was a slight indication that the platinum concentration was higher towards the outer surface of the oxide,

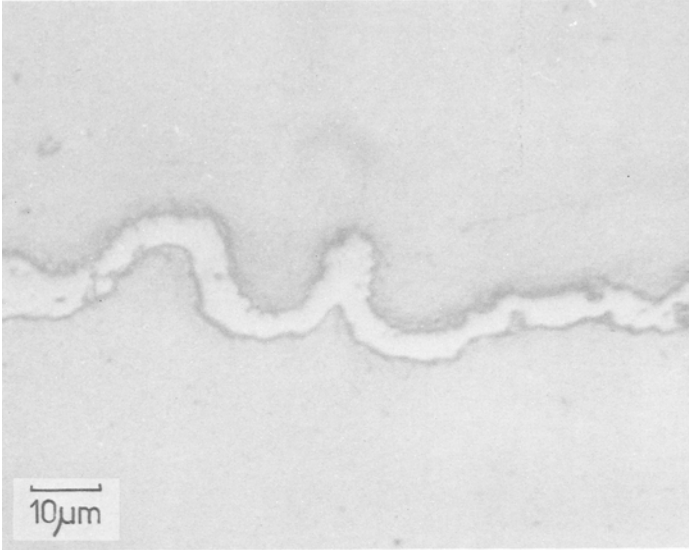


Fig. 1. Cross section of α - Al_2O_3 scale formed after 24 hr at 1200°C in the presence of platinum. The metal surface would be toward the bottom of the photograph.

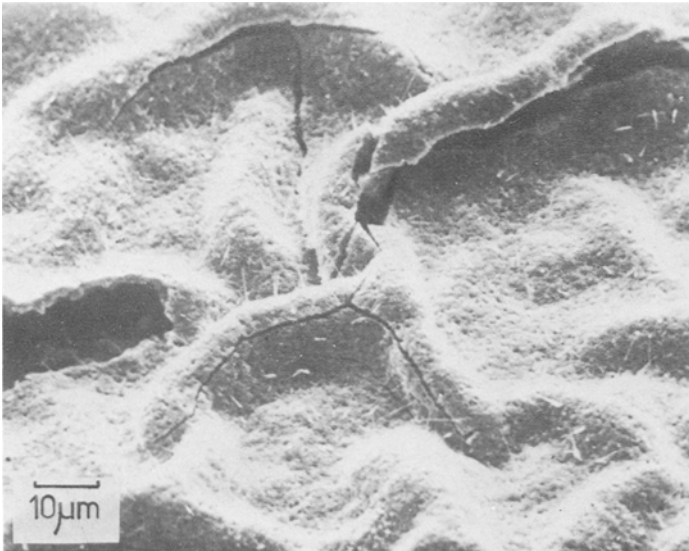


Fig. 2. Surface of α - Al_2O_3 scale formed after 24 hr at 1100°C in the presence of platinum.

although the scale was too thin for quantitative distributions to be determined.

Any explanation at this point must be tentative, but clearly involves the transfer of platinum in the gas phase. The evidence for this is the observation that a specimen, oxidized under conditions such that the flow rate was sufficient for any platinum in the gas phase to be flushed away from the specimen, did not maintain an α - Al_2O_3 scale. Also, platinum wires suspending oxidizing specimens in a flowing oxygen or air stream at 1100 and 1200°C in a thermobalance lost weight.¹ Furthermore, two separate investigators^{4,5} oxidized the same alloy at 1200°C using a platinum suspension wire, and the alloy formed an α - Al_2O_3 scale. However, breakaway oxidation was observed in one investigation but not in the other. In the latter case⁵ the direction of gas flow would have tended to pass any platinum in the gas phase over the specimen, whereas in the former case⁴ the gas flow would have flushed any platinum away from the specimen. Finally, α - Al_2O_3 scales sometimes tend to be retained on the specimen adjacent to platinum support wires when they are lost from other regions. Now, the transfer of platinum in the form of PtO_2 has been investigated⁶ and is described by Chaston⁷ in terms of a high-temperature phase change of PtO_2 solid directly to PtO_2 gas. It is suggested, therefore, that the platinum, as the volatile species PtO_2 , is incorporated into the α - Al_2O_3 .

At first sight it is tempting to suggest that the PtO_2 influences the α - Al_2O_3 in much the same way as would rare-earth additives to the alloy, except that in this case the additive comes from the gas phase. However, although it cannot be ruled out that the α - Al_2O_3 does receive some modification to its growth mechanism, substructure, etc., the platinum effect seems much less dramatic than the rare-earth effect. In view of the lifting and spalling of the α - Al_2O_3 on cooling in the present case, it seems unlikely that the stabilization of the α - Al_2O_3 is due to a significant increase in adherence between the alloy and the oxide. Furthermore, the platinum-stabilized α - Al_2O_3 formed in a highly convoluted manner and the basis of a suggested mechanism for the main yttrium effect is that it prevents the lateral growth of the oxide which gives rise to the convoluted scale morphology.¹ The device of introducing an intervening platinum layer between an aluminide coating and its substrate⁸ appears to improve the stability of α - Al_2O_3 scales, and may be related to the present effect.

As noted earlier, the failure of the α - Al_2O_3 scale, leading to the formation of oxides such as Cr_2O_3 , or in extreme cases iron- or nickel-containing oxides, as appropriate, is considered to be mechanical rather than due to any chemical conversion of the scale, resulting from aluminum depletion in the alloy substrate. This is in agreement with other workers.^{4,5} The possible effects of the platinum therefore appear to be that it either

influences the stress relief mechanism at temperature via an enhanced diffusional creep process or enhanced grain-boundary sliding, or alternatively that it reduces oxidation growth stress generation. Despite the reservations noted above, the latter may arise by a mechanism similar to that proposed to explain the effect of yttrium. The precise nature of the effects of platinum on the grain size of the α -Al₂O₃ and finer substructural and other features remain to be elucidated.

It is concluded that the observations described in the present note indicate that the presence of platinum in the furnace hot zone can significantly enhance the high-temperature isothermal stability of α -Al₂O₃ scales. It would be interesting to examine any possible effects of platinum on other oxides, e.g., Cr₂O₃, but it is nevertheless clear that caution should be exercised when placing platinum in the furnace hot zone alongside oxidizing specimens. The effect does not seem to be strong enough to be used in retaining protective α -Al₂O₃ scales in practical applications except perhaps ephemerally by facilitating platinum incorporation in the oxide formed on alloy surfaces to ensure improved performance during commissioning or running-in processes.

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