Noble Metal Aluminide Coatings for Gas Turbines

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Platinum aluminide diffusion coatings act as a remedy against the aggressive environments in which modern nickel-based gas turbine blades operate. Whether as a coating for environmental protection (1) or as a bondcoat for a thermal barrier coating (2), platinum aluminides are used to provide protection for turbine components against the oxidation and hot corrosion conditions generated by a combustion environment. The coating achieves this by promoting the formation of an oxide scale which acts as a barrier between the environment and the component. Ideally, the scale should be alumina-based and be adherent, complete, compact and have a slow growth rate (3). However, these properties, which are central to the performance of the coating, can be undermined by attack from the environment and from damaging elements within both the coating itself and the substrate material, such as sulfur or titanium.

Studies conducted by the Surface Engineering Research Group (SERG) at the University of Northumbria at Newcastle have highlighted potential improvements for platinum aluminides which can be achieved by such means as the optimisation of the coating production process, the addition of noble metals and the addition of active elements.

Effects of the Coating Production Process

Platinum aluminides, produced using a 'high aluminium activity pack' process, provide excellent protection for nickel-based turbine blades. However, as these coatings are formed by an inward diffusion mechanism, the integrity of the alumina scale is particularly susceptible to degradation, as damaging substrate elements are present in the as-processed coating. During service, typically in a rotating turbine blade, these elements will diffuse in an outward direction to the oxide/coating interface where they will act to lower the adhesion of the scale, thus decreasing the effective life of the coating.

However, in contrast, SERG has investigated the potential improvements offered by producing the coating using a 'low aluminium activity, out-of-pack' process (4). A low activity process forms the aluminide by the outward diffusion of nickel from the substrate (5), while the out-of-pack method is similar to a chemical vapour deposition (CVD) process, where the components are suspended above an aluminising pack, the aluminium halide gas being transported over their surface by a carrier gas (6).

The combination of these processes yields a 'cleaner' platinum aluminide, where the presence of damaging substrate elements within the coating is reduced. Upon exposure to a high temperature oxidising atmosphere, the growth of the alumina scale is more controlled, see Figure 1, and the adherence of the oxide scale is improved, due to the reduction of the outward diffusion of elements, such as titanium. Therefore, by designing the coating so that the

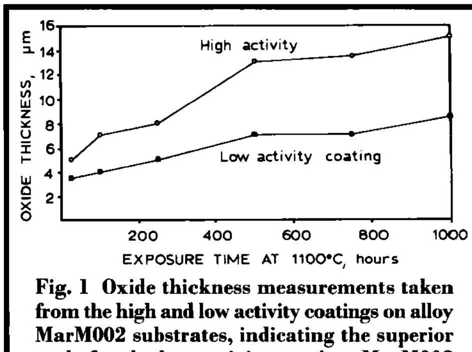

Fig. 1 Oxide thickness measurements taken from the high and low activity coatings on alloy MarM002 substrates, indicating the superior scale for the low activity coating. MarM002 is a nickel-based alloy, containing small additions of titanium and hafnium. It is used extensively in powder form to repair turbine blades damaged by oxidation and hot corrosion

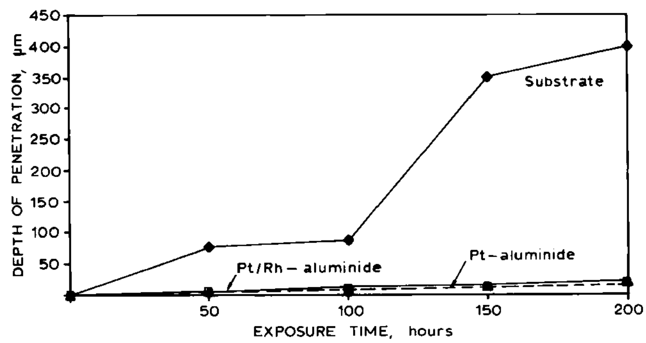

Fig. 2 The depth of attack produced after hot corrosion testing at 900°C. The Pt- and Pt/Rh aluminides on MarM002 substrates are shown to provide excellent protection against the environment

outward diffusion of damaging elements is hindered, the effective life of the coating can be extended.

Addition of Active Elements

The benefits of adding active elements to overlay coatings are well documented in the literature (4). The inclusion of elements, such as yttrium and hafnium, has a number of beneficial effects, for example, decreasing the oxide growth rate, enhancing the mechanical properties of the oxide and acting as sulfur getters (7). Equally, investigations of the addition of active elements to β-NiAl intermetallics have revealed similar benefits (8). Together with the Centro de Fisca Nuclear, Portugal, SERG has investigated the effects of the ion implantation of yttrium and hafnium into a platinum aluminide at a dosage of between 1×10^{15} and 9×10^{15} ions cm^{-2} (9). The effects of the additions on coating performance were inconclusive, but the work highlighted the importance of coating and substrate composition with respect to coating life.

Platinum-Rhodium Aluminides

The use of other noble metals as an addition with, or as a replacement for, platinum can lead to improved coating performance. For example, rhodium additions have been found to increase the lifetime of coating systems (10). The oxidation and hot corrosion performance of a commercially available platinum-rhodium modified aluminide coating has also been investigated. In a hot corrosive environment, the coating behaved at least as well as a platinum aluminide coating, see Figure 2, while in oxidising ($pO_2 \sim 0.2 \times 10^5$ Pa) conditions, the superior stability of the β-type phase within the platinum/rhodium coating led to enhanced durability of the coating.

Effects of Iridium Additions

The performance of iridium-modified aluminides has rarely been reported in the open literature. Iridium has been reported to exhibit low oxidation rates compared to other refractory metals, and is known to have a low oxygen diffusivity (11). Investigations have also shown that IrAl intermetallics have potential as alumina-formers (12). Therefore, an assessment of the potential benefits of iridium and iridium/platinum additions to a low activity aluminide coating was undertaken (13). It was revealed that, compared to platinum aluminides, the iridium-based coatings were relatively thin (a distinct advantage for turbine applications), they promoted alumina-based scales and also formed effective barriers against the outward diffusion of certain damaging elements, such as hafnium. However, the stability of the coating and the adherence of the oxide were lower than those usually exhibited by a platinum aluminide coating. Therefore, further development of the coating systems is required, so as to fully exploit the benefits of iridium.

Overall, it has been demonstrated that by close control of the composition of the coating and by the addition of other noble metals, the effectiveness of platinum aluminide coatings can be greatly increased.

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Anticancer Properties of Platinum(IV) Complexes

Since Barnett Rosenberg published the first work on the antitumour activity of platinum compounds 30 years ago, platinum-based drugs have made a major contribution to cancer therapy (1). Cisplatin, the first platinum anticancer drug, and the later platinum drugs developed, are widely used to treat lung, ovarian, testicular, head and neck, and bladder cancers and many other tumours (2). It is generally established that DNA is the primary target for platinum anticancer drugs and much work has gone into examining the mechanisms of activity taking place.

Now, scientists in the Netherlands, have investigated the activity of Pt(IV) compounds as antitumour agents to discover whether such compounds are real drugs or, as is widely believed, act as prodrugs, that is they are reduced to Pt(II) before reaching their DNA target (3). A prodrug is a compound converted within the body to its active form. It is used when the active drug is too toxic for direct administration, or is poorly absorbed, or would be broken down before finding its target.

Pt(IV) is kinetically more inert than Pt(II), which means Pt(IV) drugs are more stable to acidic media, so may survive the conditions present in the stomach, and thus can be administered orally. Pt(IV) drugs are of particular interest since they may be toxic to tumours which are normally resistant to cisplatin. Pt(IV) amine complexes, with the chelating ligand *trans*-R,R-diaminocyclohexane and other co-ordinating anions, were reacted with DNA model bases, such as 9-methylxanthine and 9-methylhypoxanthine. The nature of the anions, and of the DNA model base, was found to determine the *in vitro* reactivity of the Pt(IV) compounds. Identical Pt-DNA adducts were detected from reaction with both Pt(IV) and Pt(II), suggesting that the mechanism of inhibition of DNA replication is the same for Pt(IV) and Pt(II). Reaction occurred in all cases, and Pt(IV)-DNA intermediates were found, so reduction to Pt(II) is not a requirement prior to reaction with DNA. They speculate that Pt(IV) may enter the cell by a different mechanism to Pt(II) and so the possibility remains that some Pt(IV) compounds do not act as prodrugs.

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Porous Platinum Nanofibres

A new way to produce nanostructures replicating the structure and shape of a base has been developed by researchers from Toyota Central R&D Labs in Japan. They synthesised platinum (Pt) fibres, reproducing the porous structure and fibrous shape of an activated carbon-fibre (C) base (H. Wakayama and Y. Fukushima, *Chem. Commun.*, 1999, (4), 391–392).

The Pt precursor, $Pt(acac)_2$, and acetone were placed in a vessel with activated C fibres and pressurised under supercritical carbon dioxide. The Pt precursor dissolves, and is adsorbed onto the C. Oxidation then removes the C and reduces $Pt(acac)_2$ to Pt metal, which sinters. Thus control of nanostuctural shape has been achieved and porous Pt fibres of high-surface area with potential catalytic use have been made.