High Temperature Degradation of Nickel Based Alloys

A CONSIDERATION OF THE ROLE OF PLATINUM

By G. J. Tatlock, T. J. Hurd and J. S. Punni

Department of Materials Science and Engineering, The University of Liverpool

The addition of platinum to nickel-based alloys can have a profound effect on their oxidation and hot corrosion resistance. Improvements in gas turbine blade performance in aggressive environments are linked with the protective nature of surface oxides and coatings. However the precise role of platinum in promoting and maintaining this protection is still under active investigation and the results of several recent studies are reviewed here.

Blades within the turbine section of advanced gas turbine engines can operate at temperatures ranging from 650 to 950°C, under highly stressed conditions, and in gas environments which are generally extremely oxidising and which in many cases contain corrosive fuel residues and ingested salts. There is, therefore, a continuing need for both new structural materials and new coating compositions having improved mechanical properties and greater resistance to high temperature oxidation and hot corrosion. Major advances have been made in nickel alloy design over the past thirty years but many of the improvements in high temperature strength have been made at the expense of oxidation and hot corrosion resistance. The chromium content of early forged blades, for example, was gradually reduced below 12 per cent at the expense of resistance to hot corrosion. The switch to higher strength cast materials produced a further drop in chromium level, to about 9 per cent, and led to the extensive use of coatings to provide added protection. This was accompanied by improvements in coating technology and the widespread application of a variety of aluminised coatings and MCrAlY overlays, where M is usually a combination of nickel and cobalt. Although the combination of a high strength blade and a corrosion resistant coating is now the primary route to blade production, the process is still not without its problems. In particular, the adherence of the coating is paramount, since any cracking or loss of coating can lead to a massive attack on the blade substrate. Hence improvements in substrate alloys which enhance the oxidation and hot corrosion resistance, while maintaining or improving their mechanical performance, are still being sought. One such improvement, made at the Johnson Matthey Research Centre, was the production of a range of nickel based superalloys containing platinum group metals (1). It had been known for some time that the addition of platinum to alumina coatings improved their performance (2), and that platinum additions to nickel alloys had proved beneficial (3), but this was the first attempt to produce a commercial product. However the mechanisms for these improvements are still not well understood and this paper reviews the background to these developments and discusses some of the beneficial corrosion resistant properties of nickel based superalloys containing platinum.

The Oxidation of Nickel Alloys

The effect of platinum additions on the oxidation of pure nickel was first investigated by Kubaschewski and von Goldbeck (4). Their results could be interpreted as showing that the oxidation rate constant decreased as the platinum content increased. Thomas also studied the oxidation of nickel-15 per cent platinum in oxygen at temperatures between 850 and 1000°C and showed that the resulting subscale consisted of a platinum enriched matrix (5). This system is often cited—for example (6)—as a classic system where oxide grows by the outward migration of nickel to form a NiO layer on the surface while the platinum is concentrated at the scale/metal interface, with a corresponding reduction in the nickel concentration. For nickel rich alloys the diffusion of nickel is the rate determining step, and can be analysed theoretically to give good agreement with experiment (7).

The situation becomes more complex when other elements are added to nickel-platinum alloys. For example, Felten examined the effect of platinum on the behaviour of a nickel-8 per cent chromium-6 per cent aluminium alloy in cyclic oxidation tests carried out between 800 and 1000°C (3). The addition of 2.5 weight per cent platinum considerably improved the oxide adherence above 1000°C but was less effective at lower temperatures. Increases in the platinum level up to 10 weight per cent produced corresponding improvements in oxidation resistance under cyclic conditions. Nickel-8 chromium-6 aluminium readily forms alumina, and it was suggested that the presence of platinum in sufficient amounts allowed an alumina scale to reform even when modest spalling had occurred.

Similar effects are also observed in other alumina forming systems. For example Felten and Pettit showed that platinum increased the adherence of alumina to platinum-2 aluminium and platinum-6 aluminium alloys (8). An oxide pegging mechanism was suggested in these cases. Allam, Akuezue and Whittle also suggested a pegging mechanism when examining the oxidation behaviour of cobalt-10 chromium-1 aluminium and also cobalt-10 chromium-1 aluminium-1 hafnium alloys containing 1 and 3 weight per cent platinum, respectively (9). It was speculated that the presence of a fine dispersion of $PtAl_3$ and/or $HfPt_3$ may be responsible for the growth of the pegs. Short circuit diffusion of oxygen along the incoherent interface between matrix and dispersoid would enhance oxide formation at certain points and lead to peg formation.

The Effect of Platinum on Oxide Formation

Another unusual property of platinum is its influence on the formation of metal oxides when in close proximity to a sample in an oxidation furnace. This was first suspected when samples suspended from platinum wires behaved differently from those on other suspension systems. Work by Fountain, Golightly, Stott and Wood showed that the presence of platinum foil adjacent to alumina forming alloys altered their oxidation kinetics at high temperatures and led to the incorporation of platinum into the oxide scale (10). Increases in the flow rate of gas through the furnace decreased the influence of the platinum, and hence it was suggested that a gaseous transport mechanism involving volatile PtO_2 was responsible for the incorporation of platinum into the scales. Recent work on nickel-silicon-magnesium alloys at 1100°C has also highlighted the influence of platinum on oxide formation (11). However in this case the oxidation rate of a nickel-4.4 silicon-0.1 magnesium alloy was increased by approximately one order of magnitude in the presence of platinum. Once again a gas phase interaction involving PtO_2 was thought to be involved, although rather than contributing platinum which was incorporated into the growing scale it was suggested that on this occasion platinum removed magnesium from the scale as volatile platinum-magnesium or platinum-magnesium-oxide. The change in the magnesium concentration then had a major influence on the formation of the scale.

The work carried out at Johnson Matthey on platinum containing superalloys also showed that platinum additions can have a major effect on oxidation mechanisms at high temperatures. In a recent study by the authors the behaviour of one such alloy, designated RJM2012, was compared with a similar alloy, IN792 + Hf,

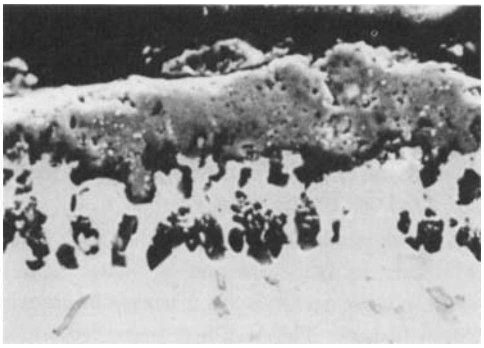

Fig. 1 This cross-section through the surface of a sample of IN792+Hf oxidised in air for 500 hours at 1100°C shows the chromia-rich scale that exhibits poor adhesion, and a line of aluminium-rich internal oxides which is always present below the surface. Further bands of internal oxide are formed when the outer scale spalls ×700

which did not contain platinum. It was found that the presence of 4.5 weight per cent platinum in RJM2012 changed both the oxidation kinetics and the oxide development. Both alloys exhibited oxide spalling at 1100°C following the growth of aluminium rich oxides below the outer scale. In the case of IN792 + Hf, however, these internal oxides continued to form and led to further attack on the superalloy substrate, shown in Figure 1. By contrast, in RJM2012 the internal oxides eventually joined up to form a continuous layer of alumina which inhibited further attack, see Figure 2. Similar behaviour was observed in certain model alloys which contained nickel-12 chromium-6 aluminium-4.5 platinum. Hence it was concluded that a major role of platinum was to change the growth characteristics of the aluminium oxide. Platinum particles were sometimes observed above the alumina layer in the scales, but these were thought to be formed as a result of the change in oxidation mechanism, rather than its cause.

The Influence of Platinum on Hot Corrosion

Little work has been done on the hot corrosion of nickel based superalloys containing platinum. Most studies have concentrated on the behaviour of aluminide coatings containing platinum which have been deposited on a range of nickel based superalloys. For example early work by Lehnert and Meinhardt was aimed at finding a diffusion barrier to reduce the migration of aluminium from a coating into the substrate (2). However this approach proved unsuccessful in the search for an alumina diffusion barrier, but it did produce a marked improvement in the hot corrosion resistance of the coating, with the platinum remaining concentrated in the outermost region of what was a duplex coating. The chemistry and morphology of aluminide coatings on platinum and platinum coated superalloys were studied by Jackson and Rairden (13). They suggested that the platinum coating inhibits the movement of refractory metals to the outer region of the coating, thereby improving the hot corrosion resistance, but that platinum should be viewed as a diffusion medium for aluminium rather than as a barrier to it.

The production and properties of platinum-aluminide coatings have been reviewed by Wing and McGill (14). They showed how a suitable choice of production route can alter the relative amounts of the platinum-aluminium intermetallics in the coatings. The route also has a major influence on the performance of the coated alloys since in some cases volume changes, which occur as the coatings degrade,

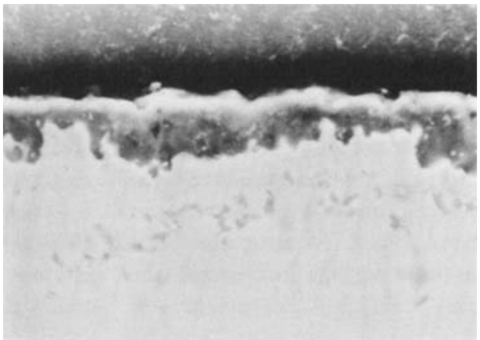

Fig. 2 This sample of RJM2012 has been oxidised in air for 800 hours at a temperature of 1100°C. The original band of aluminium-rich internal oxides have linked together to form a continuous layer. The outer scale then becomes detached, leaving the single protective alumina scale shown here ×700

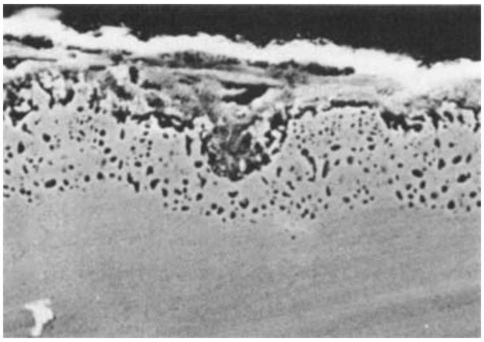

Fig. 3 Broadfront penetration of sulphides into the matrix is shown on this cross-section taken through a sample of IN792 + Hf after hot corrosion testing for 200 hours at 800 °C ×450

can lead to void formation and cracking. Burner rig and engine tests illustrated the improved performance of the coatings and further successful engine tests have recently been reported on platinum containing coatings (15). However examples of crack formation in service have also been described (16).

The influence of platinum on Na_2SO_4 induced hot corrosion of aluminium diffusion coatings has been examined recently by Wu, Rahmel and Schorr (17). Hot corrosion mechanisms are often grouped under two headings: basic fluxing, where oxides such as alumina are dissolved in molten salts as aluminates, and acid fluxing where aluminium is converted into Al^{3+} ions; for example see Goebel and Pettit (18). The results obtained by Wu and colleagues suggest that platinum improves the resistance to basic fluxing, but that there is little difference in the resistance of the platinum containing coatings to acid fluxing. It is suggested that the platinum modifies the structure and composition of the alumina scales or that the platinum rich subsurface layer affords further protection. During the basic fluxing reaction an increase in the oxygen ion activity in species such as Na_2SO_4 adjacent to the alumina layers triggers the conversion of alumina to aluminate, and porosity in the alumina then leads to sulphate penetration and metal attack. Hence modification of the alumina or the subscale region by platinum could inhibit the basic fluxing reaction.

Platinum containing alloys developed by Coupland and his colleagues at the Johnson Matthey Research Centre also exhibit good hot corrosion resistance (19). Salt shower testing and crucible sulphidation tests conducted at 925°C with samples immersed in a 90 per cent sodium sulphate/10 per cent sodium chloride mixture both indicated that additions of up to 10 weight per cent platinum had a marked effect on the corrosion resistance. In order to study this further a detailed comparison was made of IN792 + Hf and a similar alloy containing platinum (RJM2012) after burner rig tests. Although the details of this investigation will be presented elsewhere (20) the results are summarised here.

Burner rig testing was carried out for up to 1000 hours at 800°C on pin samples mounted in a rotating carousel. After only 200 hours there were marked differences in the behaviour of the two alloys and by 600 hours the IN792 + Hf samples were heavily spalled compared to the RJM2012. The degree of attack was also very clearly seen in cross-sections taken through the centres of the pins. After only 200 hours broadfront penetration of sulphides into the matrix was often observed in IN792 + Hf, see Figure 3, while this degree of attack was still not present in RJM2012 after 1000 hours, see Figure 4.

The detailed evolution of the scales on these

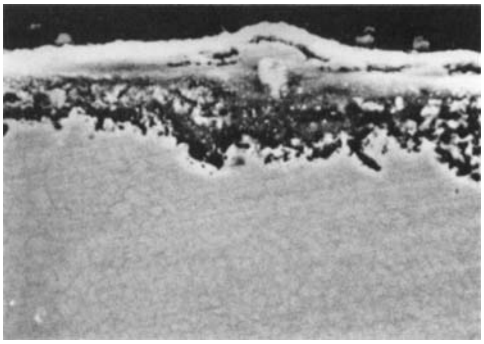

Fig. 4 This sample of RJM2012, a similar alloy containing platinum, has been subjected to hot corrosion testing for 1000 hours at 800 °C. Even after a five-fold increase in time (compared with the sample in Figure 3) sulphide penetration is only just starting ×750

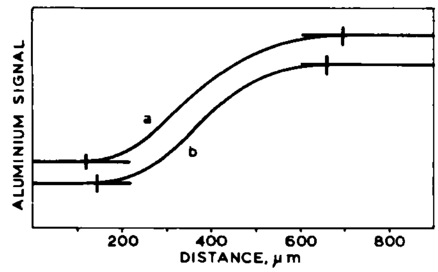

Fig. 5 These aluminium composition profiles across diffusion couples, containing (a) 4.5 per cent platinum and (b) no platinum, show the similarity in the interdiffusion distance. Each curve represents the average of three traverses across the centre section of the couples

alloys is quite complex and will be reported elsewhere. However the major differences in scale formation and development appear, once again, to be connected with the protection imparted by the alumina scale. The oxides formed on IN792 + Hf were much thicker and less protective than those on RJM2012 and rapidly became enriched with porous nickel oxide. On RJM2012, however, the scale remained predominantly rich in aluminium and chromium, and the sulphides formed after 1000 hours were mainly detected at grain boundaries with only very isolated areas of more severe attack. By contrast on IN792 + Hf internal sulphides had formed into broadfront attack after only 200 hours, and after longer times the alloy adopted the classic hot corrosion morphology of a voluminous porous nickel rich oxide layer over massive sulphide penetration. Only slight reductions in the aluminium and chromium levels occurred below the scale in the platinum containing alloy, while the platinum level itself was increased in this region, presumably by a mechanism similar to the case of pure nickel described earlier. In IN792 + Hf, however, below the oxide scale the chromium level had dropped to less than 6 per cent, and this had seriously impeded any "healing" of the alloy after oxide spalling.

Although major differences were apparent in the alloys after only 200 hours, no refractory metals such as tungsten or molybdenum were observed in the scales after these short times. Hence acid fluxing involving MoO_3 or WO_3 appears to be precluded at early times, although sulphite enhanced attack could still have occurred. However the major effect of the platinum on the hot corrosion results appeared to be the promotion of the rapid formation of a protective alumina + chromia layer, which remained adherent and resistant to corrosion attack without the formation of deleterious NiO. In the subscale region chromium and aluminium levels were also maintained undepleted, and hence protective scales could reform if spalling occurred.

The Role of Platinum

It is evident from the foregoing discussion that platinum plays a complex role in both the oxidation and the hot corrosion of nickel based alloys. It appears to promote the formation of alumina scales and it improves their adherence to the substrate. It may also be incorporated into scales either directly by platinum/aluminide coatings, as particles during oxide growth on platinum containing alloys, or through volatile PtO_2 when samples are heated in the presence of the metal. If platinum enhances the formation of a continuous alumina scale on alloys which would otherwise suffer from progressive internal oxidation, then, as discussed in (12), either the platinum speeds up the diffusion of aluminium through the alloy matrix or it slows down the diffusion of oxygen through the mixed surface scales. Alternatively its presence near the metal/oxide interface changes the growth morphology as the internal oxides develop.

Any change in the diffusion rate of aluminium through a matrix when platinum is added can be detected simply with appropriate diffusion couples. Therefore two couples were prepared, the first consisting of nickel-12 chromium/nickel-12 chromium-6 aluminium and the second of nickel-12 chromium-4.5 platinum/nickel-12 chromium-6 aluminium-4.5 platinum. In each case the starting materials were melted in an argon arc furnace. The matching faces of each half of the couples were polished to a 1 micrometre surface finish and then they were held together with tantalum wire. The couples were next wrapped in tantalum foil and sealed in quartz tubes under a vacuum of 10^{-5} torr, before being annealed for 4 days at 1100°C. Subsequently, metallographically prepared sections across the interface revealed clean oxide free welds, although some isolated aluminium rich particles, thought to be internal oxides, were observed near the interface. Aluminium concentrations along lines normal to the interface were measured by electron probe microanalysis, and typical penetration curves are shown in Figure 5. Although the depletion zone of the aluminium did appear to be slightly greater in the platinum containing alloy with a slightly different profile, the magnitude of the difference was similar to the estimated errors and no firm conclusion could be reached. A new couple was therefore made containing twice the amount of platinum, with correspondingly lower nickel content. Unfortunately this increase also had little effect on the diffusion rate. Hence it must be concluded that if platinum is affecting the aluminium diffusion, the change is small and unlikely to be the main factor in accounting for the observed oxidation behaviour.

The precise role of platinum is still not clear. Both the oxidation and hot corrosion results could be explained by the platinum modifying the oxide scales but changes in the scale growth mechanisms in the presence of platinum may also play a part, especially in view of the evidence for the strong interfacial interaction between platinum and alumina.

Platinum is finding an increasing role to play during the design of new cost effective coating systems for turbine blades, and has been shown to have interesting effects on the oxidation and hot corrosion of nickel based superalloys. In both cases, there is a lack of understanding of how platinum is providing these beneficial properties. There is certainly a need for further investigation in order to define the exact role of platinum, and other platinum group elements.

Acknowledgements

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