Platinum Aluminide Coatings for Oxidation Resistance of Titanium Alloys

By I. Gurrappa
Defence Metallurgical Research Laboratory, Kanchanbagh PO, Hyderabad-500 058, India

Titanium alloys are used in the manufacture of gas turbine aircraft engine compressor section components, which in use are exposed to high temperatures and corrosive environments. The platinum aluminide coatings described here have been developed to protect titanium alloys from oxidation and alpha case formation and can thus significantly improve the life of the alloys. The coatings showed a very low weight gain and alpha case formation did not occur during the entire period of exposure. The superior performance of the coating is due to the formation of a protective, adherent and continuous alumina scale on its surface. The results clearly suggest that this platinum aluminide coating is a prospective coating material to protect the titanium alloy components both from oxidation and alpha case formation.

The development of a wide range of titanium alloys for use in the compressor section of modern gas turbine engines has resulted in an improvement in aero gas turbine engine performance. The need for higher engine efficiencies necessitates the use of higher operating temperatures and this in turn has driven the development of a family of high strength creep resistant alloys, culminating more recently in the IMI 834 alloy (1). Figure 1 illustrates the mechanical arrangements within a modern gas turbine engine containing multishafts, various stages of turbines and compressor sections. Modern gas turbines tend to use exclusively titanium alloys in the compressor, and nickel superalloys in the combustor and turbine sections. In older engines, prior to suitable titanium alloy manufacturing techniques, steels were generally used for the compressor. In general, titanium alloys readily absorb oxygen, leading to oxidation and alpha case formation. (Alpha case is a brittle alpha phase, similar to case hardening, which forms on surfaces during heating in oxygen-containing atmospheres at temperatures > 500°C, and which can act as a crack initiator. It is responsible for rapid mechanical failure in service. Most titanium alloys allow easy crack propagation.) Alpha

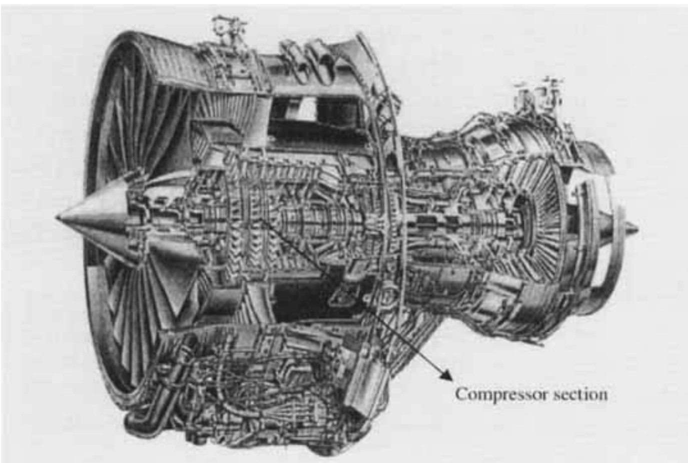

Fig. 1 Mechanical arrangements of a modern gas turbine engine showing the compressor sections where titanium alloys are used

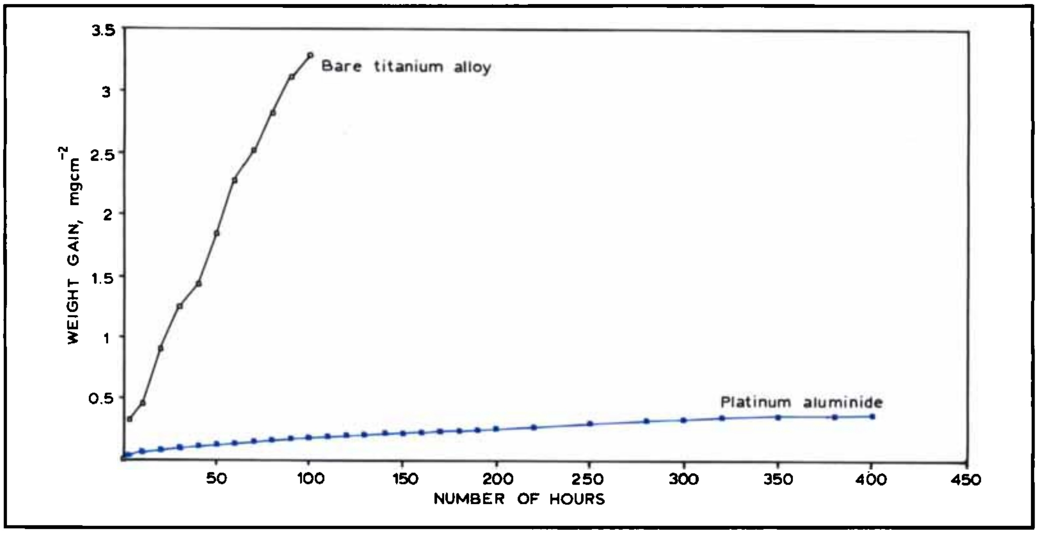

Fig.2 Cyclic oxidation kinetics at 800°C of the titanium-based alloy, IMI 834, with and without a platinum aluminide coating. The superior performance of the coating reduces the weight gain of the titanium alloy

case formation severely limits the high temperature capability of the alloys in terms of their mechanical properties. For titanium alloys to be utilised more effectively at higher temperatures, the ingress of oxygen must be reduced, if not prevented completely. Recent results on bare IMI 834 alloy at different temperatures have revealed that the thickness of oxide scale and depth of alpha case are proportional to the temperature to which they are exposed (2). Another important observation is that alpha case formation increases significantly at and above 800°C. This stresses the need for protective coatings to avoid oxide scale growth and to prevent alpha case formation.

Surface modification techniques have been examined by many researchers as a method for limiting oxygen ingress (3–6). However, the inherent low ductilities of the ceramic coatings they proposed and the lack of stability of metallic coating systems at high temperatures are areas of great concern, restricting their application. A new approach is to develop oxidation-resistant coating systems based on the use of a high melting point intermetallic layer which will act as a diffusion barrier.

The aim of this paper is to report the development of a platinum aluminide coating for the protection of the near-alpha titanium alloy, IMI 834, to increase the range of operating temperatures of such alloys in relation to gas turbine engine compressor applications. To achieve this an attempt has been made to produce an adherent and protective platinum aluminide coating on IMI 834 alloy. The performance of the coating has been evaluated from weight gain data as a function of time, and subsequently scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) techniques have been employed to understand the nature, composition and protective properties of the oxide scales that formed during exposure to elevated temperatures.

Experimental Procedure

A process route has been developed for the deposition of platinum aluminide coating on the substrate alloy, IMI 834 (in weight per cent: Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.35Si-0.06C). The platinum aluminide coating was produced on IMI 834 samples by electrochemically depositing a layer of platinum, ~ 5 μm thickness, followed by a diffusion treatment at 700°C for two hours under an argon atmosphere in order to obtain good metallic bonding between the platinum and substrate. Aluminium was then deposited over the platinum by a high activity pack aluminising route for two hours at 700°C under an argon

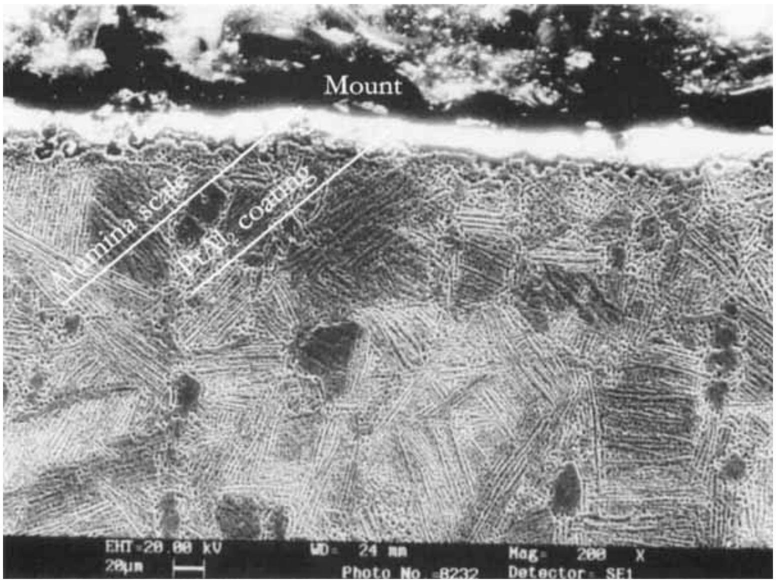

Fig. 3 Scanning electron micrograph showing the presence of a protective alumina scale on the surface of the platinum aluminide coating after oxidation at 800°C in air for 400 hours

atmosphere. Subsequently, the samples (in triplicate) underwent a diffusion treatment at 700°C for four hours under an argon atmosphere, in order to obtain good bonding between the substrate and intermetallic layer.

Cyclic isothermal oxidation studies were carried out in air at 800°C for 400 hours. Weight gain was monitored initially every 3 hours. In effect, the specimens were held at 800°C for 3 hours and then allowed to cool at room temperature in air for one hour so as to observe any rapid weight gain. Subsequently weight gain was monitored every 10 hours: the specimens were held at 800°C for 10 hours and then cooled to room temperature in air for one hour. The oxide morphologies were investigated by SEM and EDS to determine the compositions of the oxide scales. Microhardness measurements were made to understand the effect of the coating.

Results

Oxidation Behaviour of Coated Specimens

The oxidation behaviour of bare titanium alloy and platinum aluminide coated samples is illustrated in Figure 2. By comparison with the uncoated specimens at constant temperature (800°C), only a very low weight gain was observed for the platinum aluminide coated samples. Protection therefore appears to have been effective for the entire exposure period of 400 hours as the platinum aluminide coated samples showed the lowest rate of weight gain. Significant weight gain was observed from the beginning of the experiment for the bare alloy. From the results it is clear that the platinum aluminide coated alloy showed a remarkable improvement in oxidation resistance over the uncoated titanium alloy, IMI 834.

A SEM, see Figure 3, shows the presence of a continuous, protective and adherent aluminium oxide scale on the surface of the coating after cyclic oxidation at 800°C for 400 hours. It appears that the platinum aluminide coating promotes the formation of a continuous alumina scale which is responsible for allowing only the very low weight gain seen during the oxidation. Analysis of the oxide scale by EDS confirms the presence of protective scale rich in aluminium in association with smaller amounts of platinum on the surface of the coating. This protective layer formed during the exposure of the coating to the oxidising environment is the major contributing factor towards the excellent oxidation behaviour and significantly reduced weight gain shown by the alloy. This type of coating is well known for providing excellent protection against oxidation for nickel-based superalloys used in gas turbine engine applications

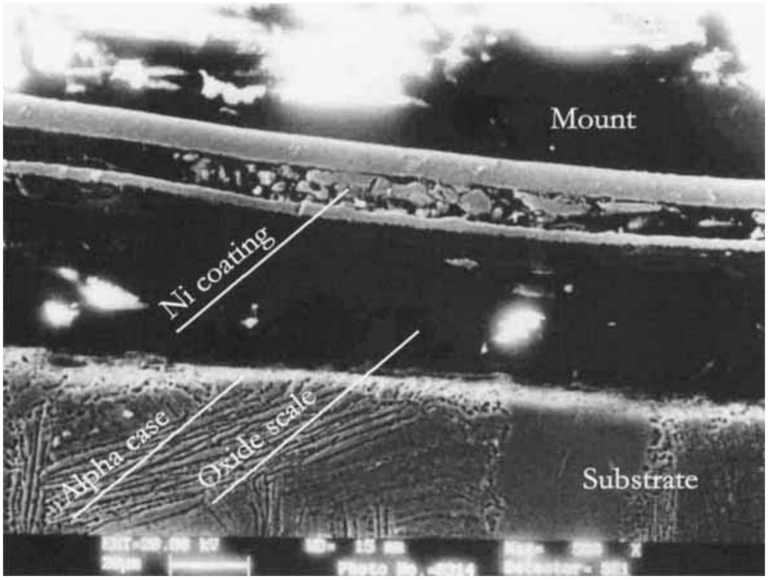

Fig. 4 Scanning electron micrograph showing the formed alpha case region and the extensive oxide scale on the surface of titanium alloy after cyclic oxidation at 800°C in air for 100 hours

(7). However, the coating method for the titanium alloys is different from that used for the nickel-based superalloys.

SEM/EDS

A SEM of a cross-section of an uncoated titanium alloy after cyclic exposure at 800°C for 100 hours is shown in Figure 4. A non-protective thick titania scale in association with tin, zirconium and silicon oxides, can be seen beneath the nickel coating. The oxygen-dissolved region, that is the alpha case, is clearly visible beneath the oxide scale after only 100 hours of exposure. The platinum aluminide coated titanium alloy did not show any alpha case formation and non-protective oxide scale was not present, even after 400 hours of exposure, see Figure 3. These observations clearly demonstrate the superior performance of the platinum aluminide coating in eliminating alpha case and in preventing oxide scale formation.

Microhardness Measurements

Microhardness profiles as a function of depth, for uncoated and platinum aluminide coated alloy specimens, after exposures of 100 hours and 400 hours, respectively, at 800°C, are illustrated in Figure 5. The microhardness data of the bare titanium alloy, IMI 834, showed an alpha zone of about 40 μm depth after exposure of only 100 hours. The extent of this surface embrittlement would be sufficient to cause significant loss of ductility and failure by surface cracking under load (8). However, the microhardness measurements of the platinum aluminide coated specimens showed no detectable hardened zone even after 400 hours of exposure. This indicates that the platinum aluminide coating effectively prevented the formation of alpha case, even during the prolonged exposure of 400 hours at 800°C.

Discussion

Figure 2 clearly demonstrates the effect of platinum aluminide coatings in reducing the weight gain of titanium alloy, IMI 834. For the uncoated alloy, the weight gain is significantly high: 3.4 mg cm^{-2}, after 100 hours at 800°C. This is attributed to the oxidation and also to the formation of alpha case, that is, the oxygen dissolved region in the titanium alloy (2). It was also established that the oxygen dissolved region is significantly deep: 40 μm at 800°C. The platinum aluminide coated alloy had a weight gain of only 0.1 mg cm^{-2} after 100 hours of exposure and about 0.4 mg cm^{-2} after 400 hours of exposure. This weight gain is extremely low and is ~ 34 times less than that of the uncoated alloy.

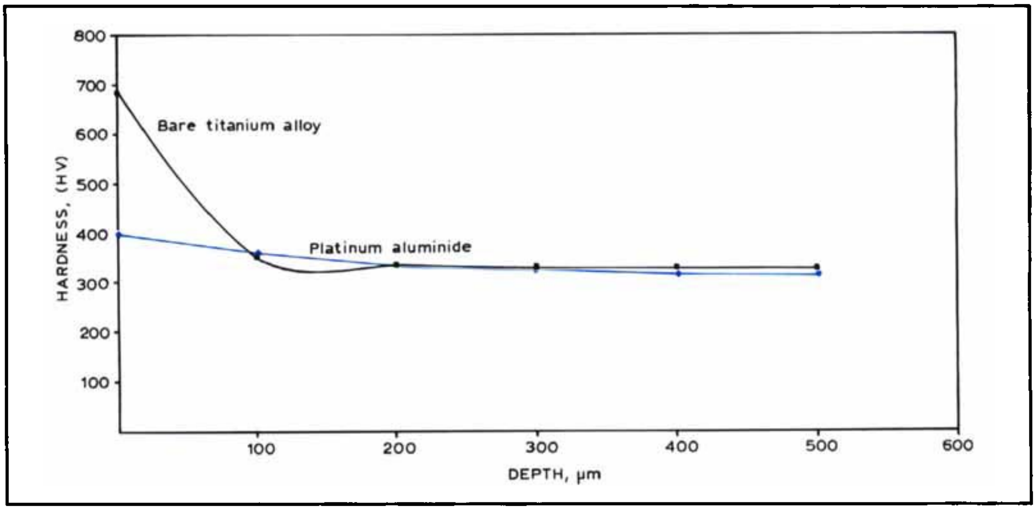

Fig. 5 Microhardness profiles of bare titanium alloy after cyclic oxidation at 800°C for 100 hours, and of platinum aluminide coated titanium alloy after cyclic oxidation at 800°C for 400 hours. There is an extensive hardened zone for the uncoated alloy but not for the coated alloy

From the microhardness data (Figure 5) it is clear that the uncoated titanium alloy when exposed to oxidising atmosphere exhibits a surface hardness as high as 700 HV due to the formation of alpha case. The platinum aluminide coated alloy shows a surface hardness of only 400 HV, which is slightly higher than the uncoated parent titanium alloy. The hardness values clearly showed that the platinum aluminide coating eliminated the formation of alpha case by effectively preventing the ingress of oxygen into the titanium alloy. SEM results show the presence of a uniform and adherent alumina scale, which clearly has a protective role, on the surface of the oxidised platinum aluminide coated alloy after 400 hours at 800°C (Figure 3). This protective scale is responsible for the significant reduction of weight gain and elimination of alpha case formation.

The platinum aluminide coating was deposited onto the titanium alloy by a combination of electrodeposition and pack aluminising techniques, and subsequently protected the alloy surface from oxidation which is a major limitation to using these materials at temperatures of 600°C and higher. The platinum aluminide coating effectively eliminates alpha case formation and also provides excellent oxidation resistance to IMI 834, even at 800°C, which is a temperature generally considered to be highly aggressive and not commonly experienced during service. The normal maximum operating temperature of the modern compressor components is about 590°C, at which temperature the platinum aluminide coating protects the titanium alloy from oxidation in an excellent manner. If a coating is effective at severe high temperatures then it may be assumed to be effective at much lower temperatures. Therefore, it is one of a number of promising coatings which could be applied to titanium alloy components intended for use in gas turbine engine compressor components. Platinum aluminide coatings were originally developed to protect nickel-based superalloys used in turbine engine components against oxidation up to temperatures of 1100°C and higher, and are regarded as being stable and as able to prolong significantly the life of the components (9–12). The results reported here clearly demonstrate that these coatings are useful for titanium alloys and for protection against high temperature oxidation. The main factor contributing to this behaviour is the presence of platinum, which effectively promotes continuous alumina scale formation during high temperature exposure (11). The effect of incorporating platinum into the coating to form a high melting point platinum aluminide layer is the same irrespective of the method of application (electrodeposition or sputtering technique).

Although platinum aluminide coatings have not yet been applied to compressor components (run at temperatures of ~ 300 to 500°C) made from titanium alloys, the present results clearly show the superior performance of such coatings even at very high temperatures. The results also indicate that there is excellent compatibility between the coefficients of thermal expansion of the substrate and the platinum aluminide coating, so this may not pose a problem in coating actual components.

Hot corrosion can be a life limiting factor in gas turbine components, especially where aircraft fly at low altitudes across salt-laden seas. It is therefore desirable that any coating developed should have sufficient hot corrosion resistance, under the aircraft operating conditions, to enhance component durability against both oxidation and hot corrosion. Hot corrosion tests on platinum aluminide coatings applied on nickel-based superalloys have reported good performance under aggressive environments (13–14). Recently, the superior performance of platinum aluminide coatings in combating both oxidation and hot corrosion for nickel-based superalloys was confirmed (11). Platinum aluminide coatings therefore appear to be a possible coating material to protect titanium alloys from oxidation and hot corrosion, and to prevent alpha case formation.

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References

1 D. F. Neal and M. J. Weaver, 'IMI 834: A new high temperature capability titanium alloy for engine use', International Symposium on Air Breathing Engines, American Institute of Aeronautics and Astronautics, 3–8th September, 1989, Athens

2 I. Gurrappa and A. K. Gogia, Proc. 5th National Convention on Corrosion, New Delhi, Nov. 1999, pp. 210--219

3 H. L. Du, P. K. Datta, J. S. Burnell-Gray and G. B. Lewis, *J. Mater. Sci.*, 1995, **30**, 2640

4 D. W. McKee and K. L. Luthra, *Surf. Coat. Technol.*, 1993, **56**, 391

5 S. Fujishiro and D. Eylon, *Met. Trans.*, 1980, **11A**, 1259

6 R. K. Clark, J. Unnan and K. E. Wiedemann, *Oxid. Met.*, 1987, **28**, 391

7 D. Punola, D. Sikkenga and M. M. Sutton, *Adv. Mater. Processes*, 1995, **148**, 29

8 I. Gurrappa, *J. Mater. Sci. Lett.*, (submitted)

9 G. W. Goward, *J. Mater. Sci. Technol.*, 1986, **2**, 194

10 R. G. Wing and I. R. McGill, *Platinum Metals Rev.*, 1981, **25**, (3), 94

11 G. Fisher, W. Y. Chan, P. K. Datta and J. S. Burnell-Gray, *Platinum Metals Rev.*, 1999, **43**, (2), 59

12 G. Fisher, P. K. Datta, J. S. Burnell-Gray, W. Y. Chan and J. C. Soares, *Surf. Coat. Technol.*, 1998, **110**, 24

13 R. Bauer, K. Schreider and H. W. Grunling, *High Temp. Technol.*, 1985, **3**, 59

14 W. T. Wu, A. Rehmel and M. Schorr, *Oxid. Met.*, 1984, **22**, 59

The Author

I. Gurrappa is a Research Scientist in the Surface Engineering Group of the Defence Metallurgical Research Laboratory, Hyderabad, India. His research interests are the development of coatings for oxidation and hot corrosion resistance, the degradation mechanisms of different materials and coatings under high temperature corrosion conditions, evaluation of materials for biomedical applications, development of biocompatible coatings for biomaterials and protection of marine structures by cathodic protection technology.

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