LOW CYCLE FATIGUE OF PLATINUM ALUMINIDE COATED MAR-M002 NICKEL-BASE SUPERALLOY IN A SULPHIDIZING ATMOSPHERE AT 870°C

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The mechanism of high temperature low cycle fatigue (HTLCF) of platinum aluminide coated MAR-M002 nickel-base superalloy in SO_2 bearing atmosphere was investigated at 870°C. The creep-plasticity mode of the strain range partitioning method (SRP) was used for fatigue loading. A constant strain range of 6.6×10^{-3} was used in argon and Ar + 5vol%SO_2 atmospheres. An accelerated failure was observed in the sulphidizing atmosphere due to the synergistic effect of sulphidation and fatigue loading. The platinum aluminide coating did show resistance to sulphidation, however, once the coating had cracked due to mechanical loading, sulphidation was concentrated in the cracks. The sulphidation mechanism resulted in the crack being filled with the oxides while sulphur was transported via the scale to the oxide scale/substrate interface where sulphidation progressed rapidly which facilitated crack propagation.

INTRODUCTION

The high pressure turbine blades of gas turbines are exposed to a variety of thermal and mechanical loading as well severe environmental conditions. In order to improve the corrosion resistance, coatings are used extensively to protect turbine blades in the hot section of jet engines (Rhys-Jones (1)). The diffusion aluminide coatings are the most extensively used, satisfying more than 90% of the world requirements for protecting blades in gas turbines (Rickerby and Winston (2)). Although aluminide coatings are resistant to oxidation they are susceptible to hot corrosion resulting in relatively high degradation rates (Cocking *et al* (3)). The addition of platinum to aluminide coatings has been shown to improve the oxidation and hot corrosion resistance of these coatings (Goebal *et al* (4)) Farell *et al* (5), Streiff *et al* (6)).

In order for the coatings to perform their function adequately the coating integrity must be maintained under mechanical loading and thermal cycling. The mechanical properties of diffusion aluminide and modified diffusion aluminide coated superalloys

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have indicated that the coating layer displays very brittle properties (Wood and Restall (7), Schneider *et al* (8)). The fatigue properties of the coatings will depend on the ductile to brittle transition temperatures (DBTT) and thermal expansion mismatch. The major problem with the NiAl and $PtAl_2$ intermetallics is their relatively high DBTT which ranges between 868°C - 1060°C for NiAl and 870°C - 1070°C for $PtAl_2$ (Strang and Lang (9)). Working above the DBTT temperature produces a life similar to that of the uncoated alloy (7) while working below this temperature results in an accelerated failure of the coated alloy.

The influence of coatings on the mechanical properties of superalloys have been investigated extensively, however, the effect of the environment on the high temperature mechanical properties of coated superalloys has received less attention. It has been shown that in order for the coatings to be effective under the combination of environment and mechanical loading, cracking of the coating due to the mechanical loading must be avoided (Czech et al (10) , Aghion et al (11)). Cracking of the coating exposes the substrate to the environment and also causes stress concentration points where cracks can be initiated in the substrate. The aim of present research was to determine the effect of sulphidizing environment on the creep-fatigue failure of platinum aluminide coated MAR-M002 at 870°C.

EXPERIMENTAL PROCEDURE

The material was received as unidirectionally solidified MAR-M002 bars. Fatigue samples with a hour glass shaped gauge length (25 mm long) were machined from the bars. The minimum diameter of the specimen was 4 mm at the centre of the gauge length. The gauge length was then coated with a 6-8μm thick platinum layer using an electroplating process. This was then followed by a high temperature low activity pack chrome-aluminising process at 1030°C for 12 hours and an ageing heat treatment at 870°C for 16 hours. Corrosion disc samples were also prepared to perform corrosion tests in the absence of mechanical loading.

HTLCF tests were performed using the creep-plasticity mode of the SRP method (Hirschberg and Halford (12)). This was achieved by using a triangular wave form with the tensile strain rate of 2.6×10^{-4} [sec^{-1}] and compressive strain rate of 66×10^{-4} [sec^{-1}]. The strain range applied was approximately 6.6×10^{-3} , measured across the gauge length of the fatigue sample. HTLCF tests were performed in argon and Ar + 5vol% SO_2 at 870°C. The gaseous mixtures were supplied to the neck of the specimen via a gas mixing system. The gases were concentrated around the neck of the sample using a split cylindrical shell. A slight over-pressure was maintained in the shell in order to prevent contamination of the environment with air. The specimen was stressed inside a split oven furnace via a closed loop servo-hydraulic loading system. The unloaded corrosion disc samples were exposed to Ar + 5%SO_2 at 870°C for five hours. The analysis of the material system and fatigue samples after failure was performed using the scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) and x-ray diffraction (XRD).

RESULTS AND DISCUSSION

Characterisation of the platinum aluminide coating system revealed a coating microstructure consisting of a $PtAl_2$ outer layer, NiAl zone, interdiffusion zone and substrate (figure 1) which was very similar to that described by Streiff *et al* (6). Platinum was present in small quantities in the NiAl zone in solid solution and/or dispersed as $PtAl_2$ particles. The platinum content decreased towards the interdiffusion zone and was totally excluded from this region.

HTLCF of the platinum aluminide coated MAR-M002 sample in inert argon atmosphere produced a life of 1442 cycles. The platinum aluminide coating displayed a very brittle nature forming a network of cracks on the external surface close to the fracture surface (figure 2). It was evident that the $PtAl_2$ layer was prone to brittle failure. The NiAl zone showed a higher resistance to cracking with cracks branching and following a convoluted path (figure 3). The presence of platinum in the NiAl zone altered the mechanical properties of this region when compared to a conventional aluminide coating (11). The higher the platinum content in the NiAl zone the more brittle this region became. This was evident from the "lateral" cracking of the NiAl region with the higher platinum content just below the platinum rich outer zone which resulted in de-lamination of the $PtAl_2$ layer in certain regions. The NiAl region with lower platinum content displayed a "crack blocking" mechanism. This may have resulted from the presence of either discrete particles of $PtAl_2$ or the presence of platinum in solid solution in the NiAl crystal structure which changed the deformation process ahead of the crack tip. A number of cracks had propagated through the coating and stopped at the interdiffusion/substrate interface indicating that the substrate was much more resistant to crack initiation (figure 3).

The platinum aluminide coated sample exposed to HTLCF and Ar + 5%SO_2 experienced an accelerated failure (540 cycles to failure). However, it did show an improvement over aluminide and uncoated samples that were exposed to similar fatigue loading and environmental conditions (11). Figure 4 showed that the fracture surface was covered with corrosion product and the external region close to the fracture also revealed severe cracking of the coating. The sulphidation attack was concentrated in the cracks in the coating while the undamaged regions showed little evidence of sulphidation. Cross-sectional examination revealed that the cracks were filled with corrosion product composed of mainly aluminium oxides and the sulphides were concentrated at the scale/substrate interface (figure 5). The NiAl zone and interdiffusion zone, although more resistant to crack propagation, were very susceptible to sulphidation (figure 5). From the corrosion tests performed on the unstressed samples, it was evident that the coating was resistant to sulphidation. The XRD analysis revealed no significant changes when compared with the as received material. The oxides, Al_2O_3 and Cr_2O_3, and relatively insignificant amounts of Ni_7S_6 was detected.

The mechanism of failure under the combination of mechanical loading and sulphidation can be described as follows: The brittle platinum aluminide phase failed under the mechanical loading resulting in cracks on the surface. This resulted in the stagnation of SO_2 in the cracks. The sulphidation mechanism was such that oxides were formed initially with small amounts of sulphides (due to the oxygen partial pressure being too low). This resulted in the crack being filled with corrosion product and hence protected from the environment since the SO_2 had to be transported via the oxide scale to the scale/substrate interface. However, due to the mechanical loading the oxide was cracked allowing the environment to penetrate the coating. The depletion of the aluminium and chromium from the coating due to oxidation resulted in the formation of low melting point nickel sulphides at the coating/scale interface and crack tip which facilitated the crack propagation in the coating. The lower resistance of the NiAl and interdiffusion zone to sulphidation resulted in severe internal sulphidation and the corrosion proceeded "laterally" along these regions. This resulted in the swelling of the coating and broadening of the crack in the coating. Hence, the stress concentration when the coating was penetrated was lowered when compared to that observed in the aluminide coating (11). The cracks in the substrate had initiated where the coating was penetrated and once the cross-sectional area had reduced sufficiently. Although it was observed that the crack in the coating was blunted due to sulphidation, the synergistic effect of sulphidation and fatigue loading resulted in an accelerated crack propagation.

CONCLUSIONS

The coating had failed in a brittle manner due to the combination of the test temperature being close to the lower end of the DBTT and the strain used for the HTLCF tests being too high. Although the coating did show evidence of resistance to sulpidation, accelerated failure was observed due to the combination of premature cracking of the $PtAl_2$ layer and severe sulphidation attack ahead of the propagating crack tip. The susceptibility of the NiAl and interdiffusion zone to internal sulphidation resulted in the swelling of the coating which would eventually lead to de-lamination of the coating from the substrate given sufficient time. It was evident that the cracking of the $PtAl_2$ layer played the most influential role in the corrosion-fatigue properties of the coated alloy.

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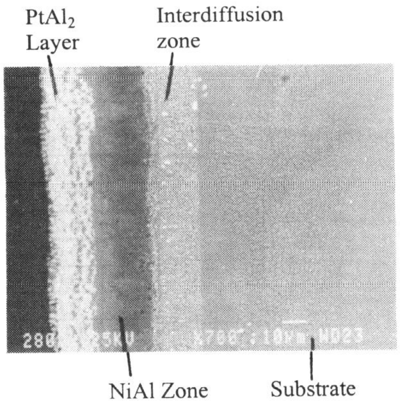


Figure 1: Microstructure of platinum aluminide coated MAR-M002

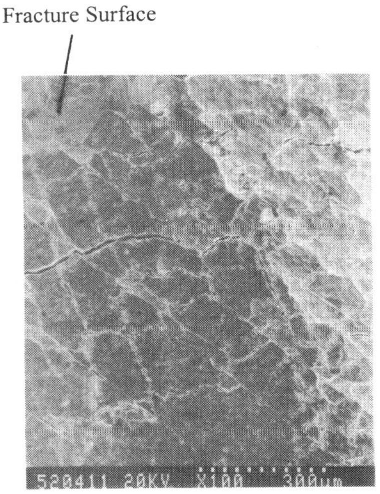


Figure 2 : Fractography after HTLCF in argon atmosphere

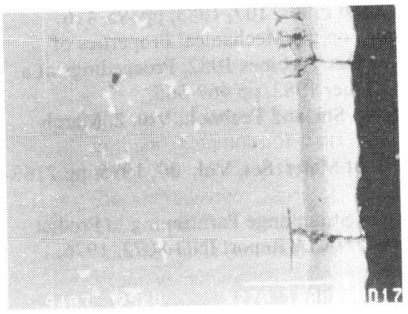


Figure 3: Longitudinal cross-section after after HTLCF in argon

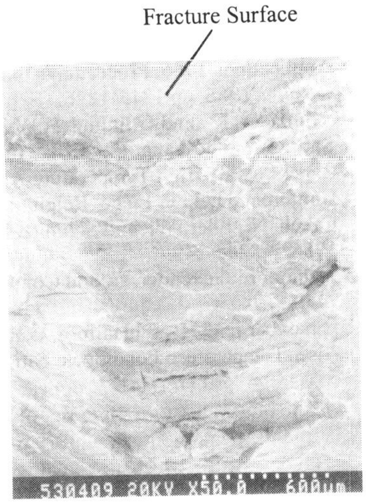
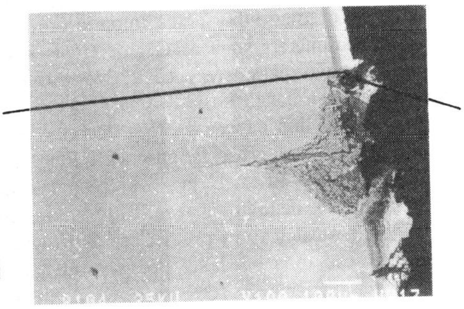


Figure 4: Fractography after HTLCF in in Ar + 5%SO_2

	wt %
Al	6.70
Cr	12.50
Co	6.94
Ni	36.28
Ti	0.56
Zr	0.14
Hf	2.87
Ta	1.14
W	5.97
Pt	1.09
O	0.00
S	25.81



	wt%
Al	37.19
Cr	1.42
Co	2.44
Ni	13.81
Ti	0.38
Zr	1.56
Hf	0.21
Ta	0.00
W	0.00
Pt	0.00
O	39.05
S	3.97

Figure 5: Cross-section showing internal sulphidation and damage to the coating after HTLCF in Ar + 5%SO_2