

**HIGH TEMPERATURE CORROSION FATIGUE OF PLATINUM COATED
MAR-M002 NICKEL-BASE SUPERALLOY**

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The corrosion fatigue behaviour of platinum coated unidirectionally solidified MAR-M002 was investigated in air, argon and Ar + 5%SO₂ atmospheres at 870°C. The neck of the fatigue samples were coated with 4-6µm of platinum by an electroplating process. The coated fatigue samples were exposed to a constant creep-fatigue loading with creep in tension and plastic compression. Due to the interdiffusion between platinum and the alloying elements, the corrosion resistance of the alloy was not influenced significantly when compared to uncoated MAR-M002. Although the coating provided adequate protection in oxidation environment, it was susceptible to sulphidation attack. The combined effect of creep-fatigue loading and sulphidation attack resulted in an accelerated failure.

INTRODUCTION AND EXPERIMENTAL PROCEDURE

Nickel base superalloys used as blade materials of gas turbines are exposed to extremely severe corrosive environments and mechanical loading. In order to obtain practical lives for these components coatings have been used extensively to improve the corrosion resistance. Aluminide coatings were one of the first and most widely used coatings for the hot section of gas turbine engines. As the operating temperatures of jet engines increased the corrosive environments became more severe and this spurred the development of the overlay coating and a cheaper alternative, the modified aluminide coatings (Rickerby and Winston (1)). Platinum modified aluminides have since received the most attention.

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The addition of platinum to aluminides significantly improves the high temperature corrosion properties over the conventional aluminide coating (Cocking et al (2), Meier and Pettit (3) and Streiff and Boone (4)). Platinum does not participate in the corrosion reaction directly but enhances the diffusion properties of aluminium at the surface improving the self healing properties of the coating (Fountain *et. al.* (5)). Taking into account the relative inactivity of platinum it was decided to investigate the high temperature low cycle fatigue (HTLCF) properties of pure platinum coated MAR-M002 nickel base superalloy at 870°C.

The substrate was received as unidirectionally solidified MAR-M002 bars with the following composition in weight %: Cr 8.9, Co 10.4, W 10.2, T 1.88, Al 5.2, Ti 1.35, Fe 0.16, Hf 1.9, C 0.35, Zr 0.23, Nb \leq 0.1 and Ni making up the balance. The fatigue samples, with a hour glass shaped neck, were turned from the bars. A 4-6 μ m thick platinum coating was applied to the neck by an electroplating process. This was followed by a simulated coating heat treatment , 12 hours at 1030°C, and an aging heat treatment at 870°C for 16 hours.

The fatigue samples were subjected to high temperature creep-fatigue loading following the strain range partitioning method (Hirschberg and Halford (6)). The loading cycle consisted of creep tension and plastic compression. A constant strain range of approximately 0.66×10^{-3} was used. The tensioning strain rate was 2.6×10^{-4} [sec⁻¹] while the compressive rate was 66×10^{-4} . The fatigue tests were performed in air, argon and Ar + 5%SO₂ at 870°C. The environment was concentrated around the neck of the sample using a split cylindrical shell into which the gases were introduced. The specimens were enclosed in a split oven furnace and loaded via a standard closed loop MTS hydraulic mechanical testing system.

RESULTS AND DISCUSSION

Characterization of the coating revealed a platinum rich outer layer and a γ' denuded region adjacent to this layer (figure 1). The coating thickness including the γ' depleted zone was measured to be approximately 15 μ m. Aluminium content in the γ' denuded zone was significantly lower than the substrate as a result of the formation of platinum aluminide phases and the effect of platinum enhancing the diffusion of aluminium to the outer surface (Fountain *et. al.* (5)). The platinum rich layer was made up of two distinct regions identified by their shading: the grey region and the white region. These regions showed distinct difference in their elemental composition. The both regions were made up essentially of Ni and Pt with some smaller amounts of other alloying elements being present. The grey region showed a lower aluminium content and higher Ni, Cr, Co and W content than the white region with Ni being the major constituent. In the white region the Al content was higher and the Pt was the major constituent. This indicated that the grey region was made up of Pt dissolved in nickel and intermetallic phases of Pt containing Cr, Co, and W while the white region can be regarded as essentially a Pt-Ni alloy with the presence of the substrate alloying elements in it. X-ray diffraction analysis produced a spectrum with a number of broad peaks. This indicated that there was incomplete transition of phases and

the presence of small crystallite. The phases present in the coating was : Pt₂Al, CrPt, Cr_{2.5}Pt_{1.5}, Cr₂Pt, Cr₃Pt and CoPt.

Cracking of the coating layer was observed in all environments, however, the high temperature low cycle fatigue (HTLCF) of platinum coated MAR-M002 indicated an accelerated failure in the Ar + 5%SO₂ environment. The mode of crack propagation in the coating was independent of environment with the crack propagation path being "twisted" and propagating preferentially in the grey region of the coating. The thickness of the coating was found to have increased in all the environments tested due to the diffusion and interaction of Pt and the substrate. The volumetric content of the white region diminished as a result of the high temperature exposure and environmental interaction.

HTLCF tests performed in argon atmosphere showed no evidence of environmental interaction. Cracking of the coating was observed on the external surface close to the fracture. The interaction of platinum with the substrate resulted in the formation of brittle phases which embrittled the alloy surface. The crack propagation in the coating was twisted and propagated through the grey region in the coating. Once the coating was breached the crack propagation in the substrate was transdendritic and relatively straight with a sharp crack tip. There was no evidence of environmental interaction along the crack edge and the failure was due to pure mechanical loading.

Fractography analysis after HTLCF in air revealed fine discontinuous circumferential cracks in the coating on the external surface close to the fracture. EDS analysis of the fracture surface showed a high oxygen, Ni and Cr content manifesting the presence the oxides. The external surface showed an increase in the aluminium content with significant amounts of nickel also being present. The higher aluminium content on the external surface was probably as result of the effect of platinum enhancing the diffusion of aluminium which facilitates the formation of Al₂O₃. Cracks through the coating in air atmosphere showed a similar morphology to that observed in the argon atmosphere. Crack propagation in the substrate was transdendritic and branched due to the formation of brittle oxide phases at the crack tip (Aghion *et. al.* (7)). Analysis of the corrosion product in the crack showed that it was made up of a mixture of oxides with the major constituents being Cr and Ni. X-ray diffraction analysis of a platinum coated MAR-M002 sample exposed to air at 870°C for 5 hours revealed the following oxide phases present: NiCr₂O₄, Al₂O₃, Ti₂O₃ and NiO.

Fractography analysis of a platinum coated sample after HTLCF in SO₂ bearing atmosphere revealed the presence of dark corrosion product on the fracture surface (figure 2). It was evident that two cracks propagated simultaneously to failure. Crack propagation occurred in the "smooth" region and final failure occurred in the coarse region. Peeling of the coating and severe localized sulphidation attack, resulting in swelling of coating was observed (figure 3). Cross-sectional examination showing the fracture surface/coating intersection showed the peeling away of the coating (figure 4) from the substrate. The γ' denuded zone was susceptible to sulphidation attack due to the depletion of aluminium from this region. As a result the corrosion process proceeded most rapidly in this region resulting in delamination of the coating from the substrate. The grey region in the coating was sensitive to sulphidation, with internal sulphidation in these regions being very evident resulting in "porous" regions filled with the sulphides of Ni and Cr. The sulphidation attack

of the of the γ' depleted zone resulted in a "porous" region with the "pores" being filled with sulphides of Ni and Cr. There was no evidence of oxygen present in the corrosion product in these "pores", hence, indicating that sulphur was transported more readily through the coating than oxygen. Exposure of a platinum coated sample to Ar + 5%SO₂ at 870°C revealed the formation of the following oxides and sulphides: Cr₂O₃, Al₂O₃, Cr₅S₈, Cr₂S₃, CrS₄, CrS, NiS, Cr₇S₈ and Ni₃S₂. There was no evidence of Pt participating in the corrosion reactions.

CONCLUSIONS

1. The presence of platinum coating does not alter the substrate corrosion properties significantly as result of the platinum diffusing and interacting with the alloy.
2. Although platinum modified surface did provide adequate protection in oxidation, it was vulnerable to internal sulphidation attack.
3. The corrosion fatigue properties was limited in the sulphur containing environment, particularly due to the internal sulphidation of the coating and sulphidation attack of the γ' denuded zone adjacent to the platinum rich layer.

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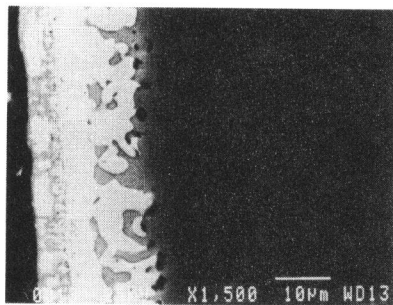


Figure 1: Characterization of platinum coated MAR-M002.

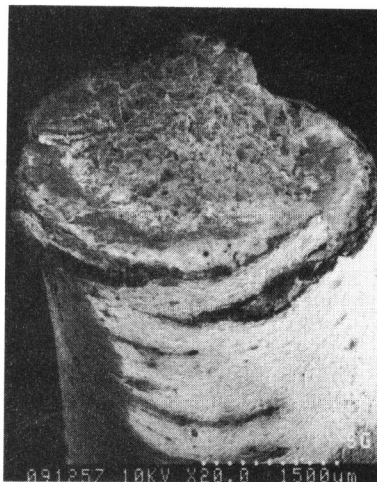


Figure 2: Fractography of platinum coated MAR-M002 after HTLCF in Ar + 5%SO₂.

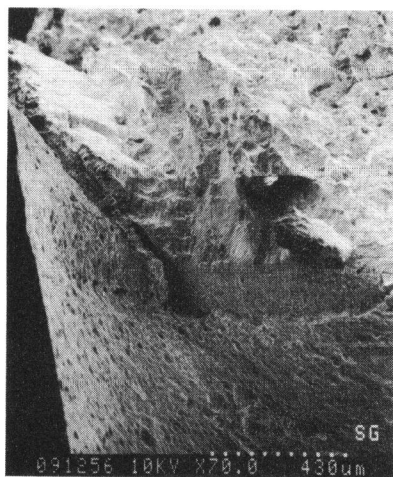


Figure 3: Fractography after HTLCF in Ar + 5%SO₂ showing peeling of coating

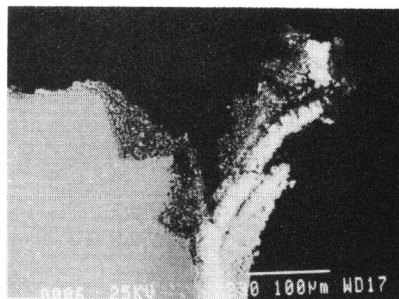


Figure 4: Cross-section of platinum coated MAR-M002 after HTLCF in AR + 5%SO₂