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ENVIRONMENTAL PROTECTION OF TITANIUM ALLOYS IN CENTRIFUGAL COMPRESSORS AT 500°C IN SALINE ATMOSPHERE

J. D. Beguin, P. Faure, D. Adrian, J. Alexis, J. A. Petit, P. Belaygue and D. Fournier

The use of the titanium alloy Ti-246 (Ti-6Al-2Sn-4Zr-6Mo, wt-%) for gas turbine compressors allows an increase in working temperature and stress level. Under severe service conditions, the material experiences combined high temperature and high mechanical stress and, in saline atmospheres, stress corrosion cracking (SCC) can occur, leading to catastrophic mechanical failure. The present study was performed to evaluate the potential of several surface treatments to protect Ti-6246 alloy, after salt deposit, from hot salt SCC at temperatures $\leq 500^\circ\text{C}$ and 500 MPa static mechanical stress conditions. Shot peening, thermal oxidation and metal-ceramic coatings were investigated. Experimental results confirm the existence of brittle stress corrosion phenomena marked by a low residual elongation of test samples and the presence of oxides on the fracture surfaces. Both shot peening and metal-ceramic coatings increase the hot salt SCC resistance of the alloy. Times to rupture were improved by a factor of 3 for shot peening and by a factor of 10 for metal-ceramic coatings. Inversely, the time to rupture of preoxidised alloys has been halved compared with uncoated alloys. As well as

these interesting quantitative results, structural studies of metal-ceramic coatings showed that they are mechanically and chemically compatible with the titanium alloy substructure and should work under severe thermomechanical stresses and aggressive atmospheres.

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Keywords: saline atmosphere, hot salt stress corrosion cracking, shot peening, thermal oxidation, metal-ceramic coatings, titanium alloy

INTRODUCTION

Titanium alloys are widely used for components such as turbine compressors. Under severe service conditions of high mechanical stress and saline atmosphere (Fig. 1), stress corrosion cracking (SCC) can occur, leading to brittle mechanical rupture. In an earlier study,¹ the possible range for the use of a Ti-6246 alloy was precisely established. At 500°C and 500 MPa with a salt deposit of 0.34 mg cm^{-2} , brittle rupture is obtained for the $\alpha + \beta$ Ti-6246 alloy. Under these experimental conditions, the lifetime of the samples was $< 16\text{ h}$.

If the full mechanical strength of titanium alloys is to be utilised, surface treatments are essential. This work was undertaken to evaluate potential surface treatments for titanium alloy protection to prevent SCC at 500°C . Three types of treatment were investigated: mechanical treatments, together with conversion and metal-ceramic coatings.

EXPERIMENTAL

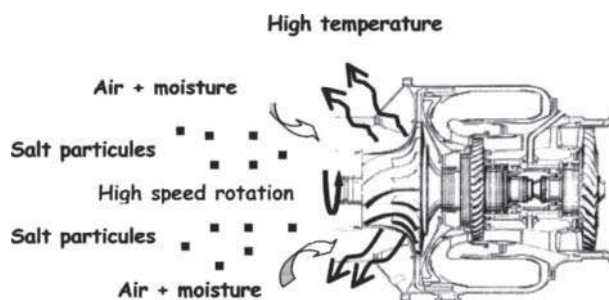
Treated specimens were evaluated using a creep test bench. Thermomechanical evaluation was carried out in a mobile furnace to provide high temperature cyclic conditions under tensile loading (Fig. 2a).

The salt deposit was formed by dipping calibrated droplets of saline solution onto the sample surface followed by crystallisation in an oven for 5 min at 110°C (Fig. 2b). This procedure produced a reproducible deposit.

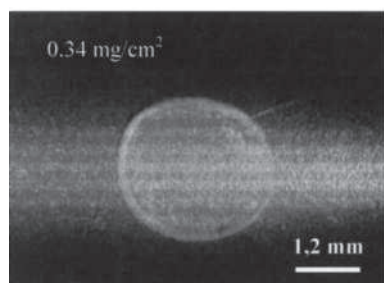
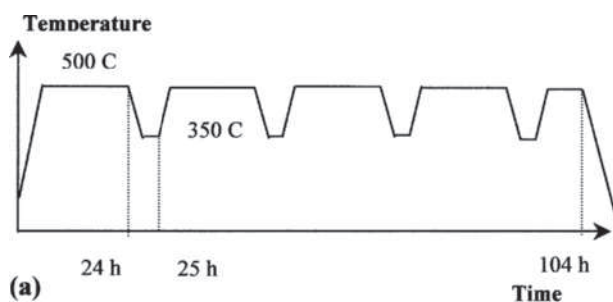
Tests were performed on cylindrical samples 4.5 mm in diameter, machined from a centrifugal compressor. The test material was Ti-246 with a Widmanstätten structure (α platelets in a β transformed matrix). Surface preparation before surface treatment involved mechanical polishing to a $6\text{ }\mu\text{m}$ diamond powder finish.

The surface treatment parameters studied were:

- (i) shot peening: BA 200, F17, 200% recovery
- (ii) thermal preoxidation: 500°C , 24 h in air atmosphere
- (iii) aluminium rich coating: slurry deposition, furnace heat treating at 350°C and glass bead peening
- (iv) 'sealed' metal-ceramic coatings: aluminium rich coating + phosphate/chromium coating by slurry deposition + furnace heat treating at 350°C .



1 Work conditions of gas turbine blade compressor



(b)

2 a Thermal cyclic test conditions; b sample salt deposit

EXPERIMENTAL RESULTS

Treated specimens were evaluated together with untreated specimens under the same severe conditions:

- (i) 500°C in static air
- (ii) salt deposit (0.34 mg cm⁻²)
- (iii) 500 MPa of tensile stress.

Lifetime comparison results of salt coated specimens with salt shot peened or preoxidised specimens appear in Fig. 3.

The data show that both shot peening and metal–ceramic coatings increased the hot salt SCC resistance of the alloy. Times to failure were improved by a factor of 3 for shot peening compared with uncoated alloy, while the metallic–ceramic coating increased the lifetime by a factor of approximately 10. After 100 h, no failure was observed for these coated samples. Inversely, the time to rupture of the preoxidised alloy was reduced by 50%.

To understand the SCC improvements, it is necessary to study the degradation mechanisms of titanium alloys under hot salt stress conditions.

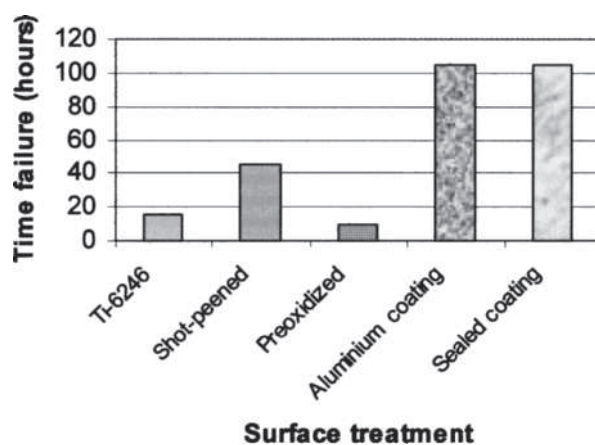
DISCUSSION

Effects of hot salt on titanium alloys

Since severe experimental conditions were applied to the specimens (500°C cyclic, 500 MPa tension stress/0.34 mg cm⁻² salt concentration), rapid hot salt SCC can be anticipated in < 16 h of exposure. The fracture surface was found to exhibit a brittle transgranular rupture with oxidised cracks. The residual elongation was < 2%.

While there is some disagreement as to the exact mechanism involved in SCC, it is generally accepted that hydrogen is the major cause of embrittlement leading to crack initiation and propagation. Generally, two processes are advanced: electrochemical² and chemical.³

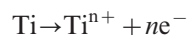
The first stage for the whole process is the mechanical rupture of the passive layer under the salt deposit by tensile stress.



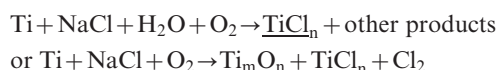
3 Hot salt stress corrosion susceptibility: lifetime of surface treated specimen after salt deposit of 34 mg cm⁻² and exposure at 500°C/500 MPa tensile stress

The second stage is the decomposition of NaCl and the formation of titanium chlorides:

- (i) electrochemical process

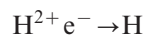


- (ii) chemical process



The third stage is titanium chloride decomposition with hydrogen formation:

- (i) electrochemical process



- (ii) chemical process



The fourth stage is hydrogen embrittlement of the crack tip area.

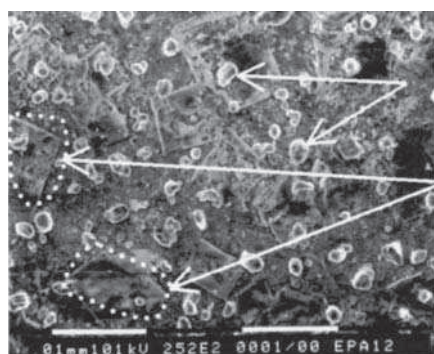
Under dry conditions (500°C) in the present study, a chemical process is more probable than an electrical process. Nevertheless, the presence of atmospheric moisture is necessary for titanium chloride decomposition, in order to generate atomic hydrogen.

Protection by surface treatment

Thermal preoxidation

This treatment displays poor resistance to HSSC.⁴ Its action seems to intensify alloy embrittlement (the time to failure is half that of the untreated alloy).

However, a TiO₂ oxide layer could be a good protective barrier for hydrogen diffusion, but the low thickness (< 1 μm in the present preoxidation conditions) and poor ductility encourages rupture of the passive film under applied tensile stresses under thermal cycling. This reduction in lifetime after treatment could also be attributed to alloy contamination by oxygen under the oxide layer.



Growth of $\langle \text{Al}_2\text{O}_3 \rangle$

Clusters of $\langle \text{MgAl}_2\text{O}_4 \rangle$

4 Oxide morphology on aluminium-ceramic coating in affected salt area

Shot peening

The shot peening treatment brings a compressive stress state at the surface (200 μm deep). The residual compressive stress evaluated by X-ray analysis was 350 MPa. Exposed specimens fail by brittle stress corrosion failure, but time to failure is improved by a factor of 3.⁴

The beneficial action of shot peening is to reduce the stress state by opposing compressive stress to tensile stress present in the corrosion pitting during the corrosion test. It allows the incubation period for crack initiation to be prolonged. The incubation time is dependent on hydrogen absorption. Then the high localised stress field accelerates hydrogen absorption.²

Shot peening seems useful, but its effect can be lessened by thermal stress relaxation after long exposure at high temperature.

Metal-ceramic coatings

Aluminium-ceramic coatings have been used mainly to protect ferrous alloys from oxidation and salt corrosion in turbomachinery applications.⁵ These coatings are used alone or with a phosphate/chromium topcoat (sealed coating) for severe temperature and environmental conditions. Aluminium-ceramic coatings are applied by slurry deposition, dried and thermally cured at 350°C. Its microstructure consists of aluminium particles bonded together by the chromate/phosphate glassy matrix. To improve density, ductility and electric conductivity, coated specimens are glass bead peened. Such coatings will corrode preferentially to steel under corrosion conditions.

The present work was undertaken mainly to evaluate potential metallic-ceramic coating systems for the protection of titanium alloys at high temperatures.⁶ Coated specimens were quantitatively analysed (in wt-%) using a Philips probe microanalyser with an energy dispersive analysis system (LINK).

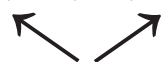
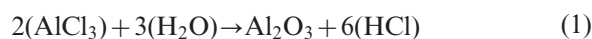
The aluminium slurry deposit presents a significantly high concentration of oxygen near the surface, and at the midthickness it contains 73Al-10P-1.3Mg-3Cr (wt-%) in the glass matrix between boundaries.

The results of microanalysis on the sealed deposit show a high content of oxygen (47%) near the extreme surface, and at the midthickness 26P-9Cr-7Mg-5Si (wt-%) with a homogeneous distribution.

Phase analysis by X-ray diffraction shows a composite layer of Al_2O_3 oxide and the spinel oxide MgAl_2O_4 for the aluminium rich deposit, and a $\text{Cr}_2\text{O}_3/\text{SiO}_2$ composite oxide film for the phosphate/chromium

rich deposit. These results therefore justify the high oxygen contents near the extreme coating surface.

The most serious problem associated with the coating process is the occurrence of coating cracks during thermal curing. Accordingly, the salt attach areas were examined by SEM to detect microcracking. No cracks were observed for the aluminium rich coatings, but severe degradation of the outer layer was revealed, with a significant amount of precipitation as discontinuous particles. The damaged area clearly does not offer protection. In order to explain the chemical mechanism of the precipitation products, an investigation was conducted by X-ray diffraction with a pipe collimator (800 μm diameter) in the salted area. X-ray phase analysis showed that the corrosion products were essentially Al_2O_3 and MgAl_2O_4 . No metallic chlorides were detected. Aluminium oxide precipitation may therefore be explained by pyrohydrolysis of aluminium chloride according to the following reaction



corrosion products

which is thermodynamically probable under the test conditions prevailing ($\Delta G_{500^\circ} < 0$). MgAl_2O_4 spinel oxide formation can be the result of a reaction between oxides (Fig. 4)

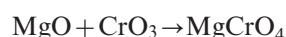


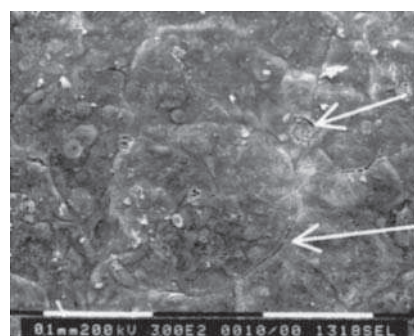
which is thermodynamically probable under the present test conditions ($\Delta G_{500^\circ} < 0$).

Again, it must be emphasised that the presence of moisture is necessary for the oxidation mechanism's protection enhancement. Moisture is also necessary for the production of HCl, which can favour embrittlement.

'Sealed' metal-ceramic coatings with a phosphate/chromium topcoat were shown to exhibit better corrosion resistance than did the aluminium-ceramic coatings. Salt damage is less important. X-ray phase analysis has shown that corrosion products are complex and are made of mixed oxides, MgCrO_4 and MgSiO_3 , and also chromium chlorides and complex sodium phosphates.

Mixed oxides may be the result of reaction between oxide particles formed in the salt area by an oxidation process and a corrosion process according to the following complex scheme



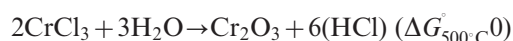


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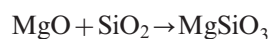
microcracks formed
during thermal cure

5 Oxide morphology on sealed metal–ceramic coating (phosphate/chromium topcoat) in affected salt area

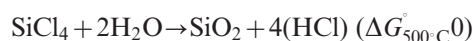
The $\langle \text{CrO}_3 \rangle$ oxidation result of Cr_2O_3 may be formed by chromium chloride pyrohydrolysis



corrosion products



SiO_2 precipitates formed by chromium chloride pyrohydrolysis



corrosion products

In the present study, the presence of microcracks (Fig. 5) which developed during thermal curing after the last slurry deposition could have masked the relative performance of the sealed coatings compared with the non-sealed ones.

Mechanical and chemical compatibility between aluminium rich coatings and the substrate were investigated to study mechanical integrity. Two coated specimens were investigated under creep exposure with thermal cyclic conditions (500°C 24 h/air cooling $350^\circ\text{C}/1\text{ h}$) for 100 h, and then oxidised in air only without stress for 1000 h at 500°C .

The creep exposed specimen tested at high stress (500 MPa) exhibited a few fine cracks, which seem to be due to structural decohesion between aluminium particles. It is worth noting that these test conditions aimed to simulate the most severe conditions possible for this type of application.

Longitudinal cross-sections of the coated creep specimen showed good adhesion between the coating and the substrate. No cracks or decohesion were observed in the interfacial area.

After 1000 h exposure in air under thermal cyclic conditions at 500°C , transverse cross-section examination by SEM confirmed that the coating and substrate were well bonded together. X-ray microprobe analysis of the main element of the coating and the substrate was done to study their repartition. Aluminium and titanium X-ray images show no migration in the coating area adjacent to the substrate. The compositional distribution of the main elements was substantially similar to that measured for unexposed specimens. Therefore, no oxygen penetration was detected in the substrate.

CONCLUSIONS

1. The susceptibility to hot salt stress corrosion of Ti-6246 was established. For use above 450°C , alloy embrittlement followed by crack initiation and propagation leads to rapid failure.

2. In order to improve the potential utilisation of Ti-6246, surface treatments were investigated for the corrosion protection of titanium alloys in the most severe simulated conditions.

3. No protection was obtained by thermal oxidation. Furthermore, oxygen contamination severely degraded the mechanical properties of Ti-6246.

4. A shot peening treatment gave resistance to hot salt SCC, but the effect may be limited for long-term exposure owing to thermal stress relaxation.

5. The most promising treatment seems to be metal–ceramic coatings. They displayed excellent resistance to hot salt stress corrosion and oxygen contamination. Lifetime was improved by a factor of ~ 10 .

6. After 1000 h exposure, neither interdiffusion nor intermetallic precipitation occurred: chemical compatibility between coating and substrate was demonstrated.

7. Metal–ceramic coatings seem to overcome the combined effects of oxidation and hot salt stress corrosion.

8. The most serious problem is still the occurrence of a few microcracks in aluminium rich coatings but, under these severe experimental test conditions, this would correspond to excessive heat from emergency utilisation. However, such damage of coated parts could be repaired by spray deposition.

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