



This is an author-deposited version published in: <http://oatao.univ-toulouse.fr/>
Eprints ID: 4877

To cite this document: Béguin , Jean-Denis and Adrian, D. and Petit, J.A. and Rivière, J.P. and Vahlas, Constantin and Vaillant, S. *Improvement of salt corrosion resistance of titanium alloys by PVD and CVD coatings.* (2007) In: 20 th International Conference on Surface Modification Technologies, 25-29 Sep 2006, Vienna, Austria.

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@inp-toulouse.fr

Improvement of salt corrosion resistance of titanium alloys by PVD and CVD coatings

J.D. Béguin, D. Adrian & J.A. Petit,
LGP-ENIT, Tarbes, France, jean-denis.Beguin@enit.fr
J.P. Rivière
LMP-UMR6630-CNRS, Poitiers, France
C. Vahlas
CIRIMAT-ENSIACET, Toulouse, France
S. Vaillant
DT/DMTA/EAP-Turboméca-Groupe SAFRAN, Bordes, France

ABSTRACT: The corrosion resistance of two kind of coating systems was investigated to protect a Ti-6242 titanium under hot salt stress corrosion conditions: PVD silicon coatings and CVD alumina coating. All these coatings were tested under hot Salt Stress Corrosion (SSC) with a constant static mechanical stress and cyclic temperature conditions, and have been brought near to the real industrial work conditions. Although all coated specimens were damaged in salted area, both SiC and Al₂O₃ coatings showed no SSC rupture during 100 h, while Si_xN_y lifetime under SSC conditions was increased by a factor 2 compared to non-coated one. As well as these interesting quantitative results, coated specimens exhibit a good adherence on titanium substrate.

1 INTRODUCTION

The use of the Ti-6242 titanium alloy was largely developed in compressor section in aero engines, because of its good specific mechanical resistance, high toughness and structural stability. However, under severe conditions, the presence of salt combined with strong mechanical stress at high temperature, can lead to an untimely failure: It is the well-known hot salt stress corrosion phenomena. Consequently, it is necessary to improve the corrosion resistance by a protective coating, with respect to initial mechanical performance of the substrate. In this study, SiC, Si_xN_y, Al₂O₃ coatings were investigated to protect a titanium alloy substrate under SSC conditions. At first unloaded coated samples were corroded with salt deposit without mechanical loading at 540°C during 100 h to characterize salted damaged areas and corrosion products by Energy Dispersive Spectroscopy (EDS) and X-Ray Diffraction (XRD). Afterwards salted samples were evaluated using a creep test bench. High temperature cycling was performed in a mobile furnace under tensile loading. The salt deposit was formed by dipping calibrated droplets of saline solution onto the coated sample surface.

2 MATERIALS AND EXPERIMENTAL PROCEDURE

Experiments are performed on flat samples (10mm diameter) for salt exposure without mechanical loading, and cylindrical samples (4.5mm diameter, 45 mm length), for salt stress corrosion test bench. The tested material is Ti-6242 with duplex microstructure (α coarse grain, in a β transformed matrix). Flat surface samples were ground using a 600 grit abrasive SiC paper before surface treatment. The salt deposit is obtained by depositing a calibrated droplet of saline solution on sample surface. Saline solution was prepared with natural sea salt. The salt crystallisation was achieved in an oven for 5 minutes at 110°C. This procedure allows to obtain repeatable deposit. Flat samples have been placed in furnace with air circulation. Cylindrical samples were evaluated using a creep test bench. Thermal cyclic conditions 520°C/24h and free air cooling 150°C/1h, were applied four times (100 h total duration), under 450 MPa tensile stress.

2.1 Silicon coatings: SiC and Si_xN_y

These coatings were deposited by a PVD technique with an assisted ion beam bombardment (120 keV energy Ar^+ ions) under $5 \cdot 10^{-3}$ Pa, for the first 40 nm, to create a chemical gradient composition by an ionic mixing between the coatings and the substrate, in order to improve their adherence (Rivière 2005). These dense coatings were very dense and of amorphous structure; their thicknesses are respectively $0.4 \mu\text{m}$ for Si_xN_y and $0.33 \mu\text{m}$ for SiC .

2.2 Alumina coating

This coating was processed by metal organic chemical vapor deposition (MOCVD) at atmospheric pressure (Valhas 2006). The corresponding process involves two reactors operating in series. The first one ensures high, reliable, and reproducible flux of vapors of aluminium acetylacacetate ($\text{Al}(\text{acac})_3$) precursor through sublimation in fluidized bed. The fluidized bed sublimator is connected at its exit to a vertical, resistively heated CVD reactor. Samples were maintained welded on a regulation thermocouple, which is positioned close to the sample along the central axis of the reactor. Preliminary experiments were performed in sublimation conditions 393K, with nitrogen as fluidizing gas. More details on the setup are provided. Sublimation conditions ensure feeding of the CVD reactor with 0.19 sccm $[\text{Al}(\text{acac})_3]$. An additional gas line was used to feed the CVD reactor with 100 sccm of oxygen bubbling through a H_2O bath maintained at 100°C . Deposition temperature was fixed at 580°C in order to maintain the microstructural integrity of the Ti6242 alloy. 300 nm thick amorphous alumina films were deposited in 3 h runs. Films are smooth and do not contain any heteroatoms, namely carbon.

3 CORROSION RESISTANCE OF COATED SPECIMENS

3.1 Salt attack without tensile stress

Salt coated specimens ($10.5 \text{ mg}/\text{cm}^2$) were heated at 540°C for in a tubular furnace during 100h. In order to confirm the degradation mechanism, salted samples were observed means optical microscopy after distilled water immersion to eliminate residual salt. The observation of corroded area for SiC and Si_xN_y coatings showed that pitting corrosion is the principal mode of degradation, while an accelerated oxidation occurred at and near the salt deposit for the SiC coating. Corrosion degradation of Al_2O_3 coating was not significant (Fig.1).

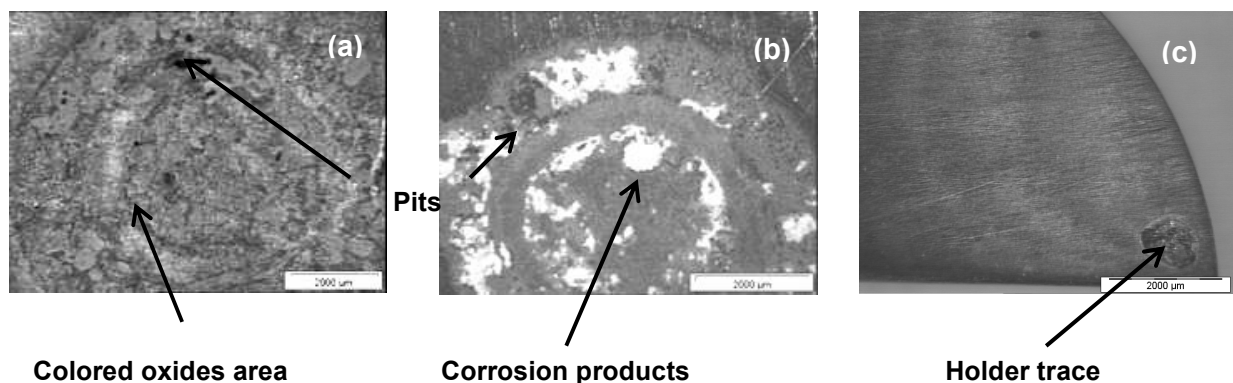


Figure 1: Surface morphology of water washed surface of SiC (a), Si_6N_4 (b) and Al_2O_3 (c) after salt attack at $540^\circ\text{C}/100\text{h}$.

3.2 Salt attack under tensile stress (SSC conditions)

Pre-oxidation of SiC and Si_xN_y coated specimens were conducted in air at 600°C under dry air for 100h, to increase oxide barrier thickness, in order to improve salt corrosion resistance. Salted samples were evaluated using a creep test bench under 450 MPa tensile stress at 520°C during 100 h. Salt deposit was formed by dipping calibrated droplets of saline solution

onto samples (120 μg or 2,1 mg/cm^2 approximatively). Initially, non-coated Ti-6242 specimen was evaluated in the same condition for reference (Fig. 2).

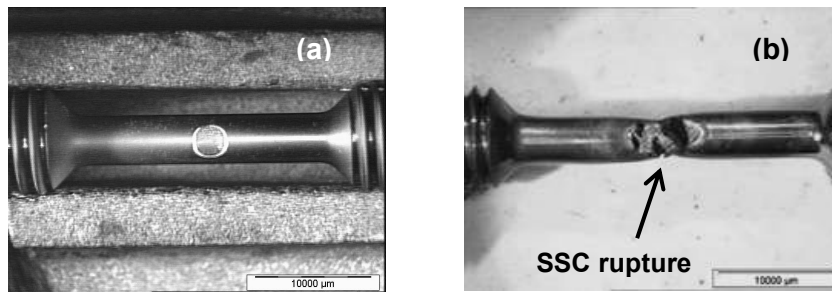


Figure 2: Calibrated salt deposit on creep specimen before test (a), non-coated Ti6242 specimen after test (b).

Under these conditions, lifetime of non-coated specimen was about 39 h. All coated specimens were damaged in salted area (Fig.3), but the results showed no SSC failure for both SiC and Al_2O_3 coatings during 100 h and an increase of lifetime for Si_xN_y coating (96 h).

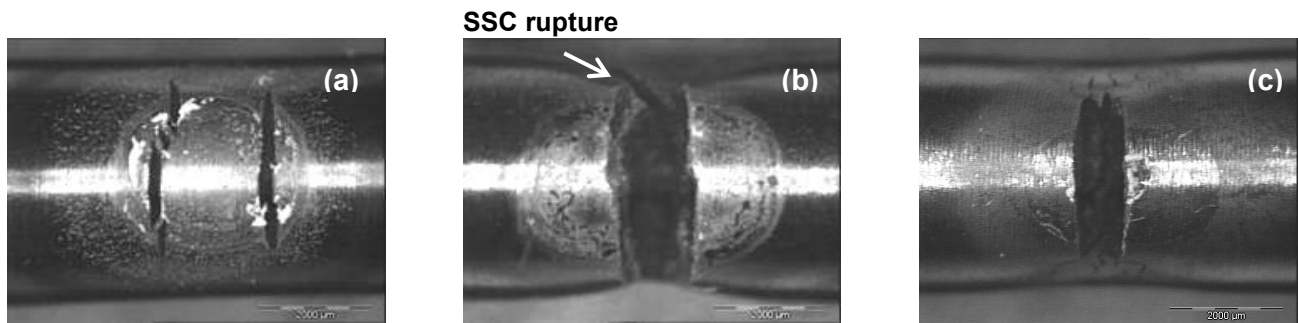


Figure3: SiC coated sample: No SSC failure during 100 h (a), Si_xN_y coated sample: SSC failure for 96 h (b), Al_2O_3 coated sample: No SSC failure during 100 h (c).

After SEM examination of Al_2O_3 cracking, it was clear that the main damage origin was thermomechanical and not SSC phenomena (Fig.4). It was due to a local imperfection like machining ridges on Ti-6242 sample surface, and/or low thickness of Al_2O_3 coating, which increases local stress under these severe conditions.

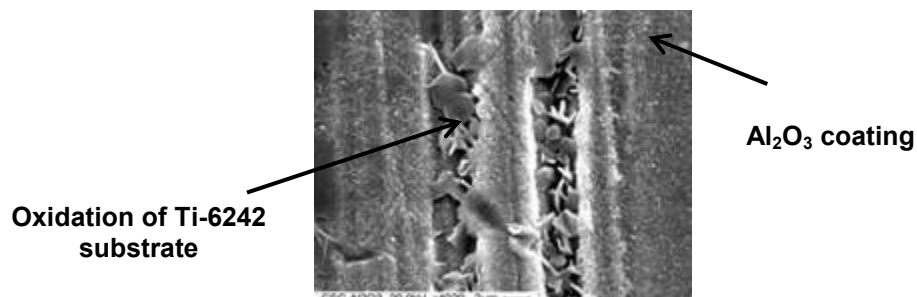


Figure 4: Mechanical degradation of Al_2O_3 starting from a superficial Ti-6242 defect in salted area.

4 THERMOCHEMICAL DEGRADATION OF COATED SPECIMENS

S.E.M observations of corroded areas, for both silicon coatings exhibited a non-uniform degradation with pits and cracks and corrosion products. X-ray maps (Fig.5) showed that Na, O and Si were the major chemical elements.

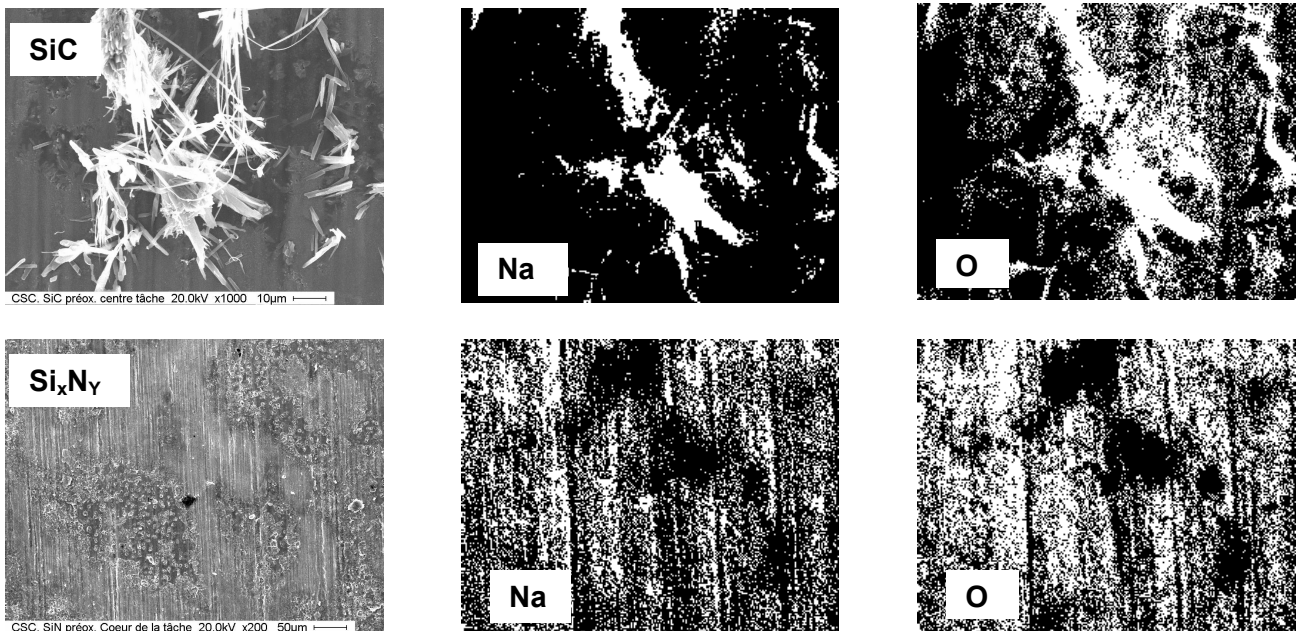


Figure 5: X-ray map on corroded silicon coatings.

To complete these analyses, corrosion products were examined using an X-ray diffractometer under a low incidence angle (3° and 5°) with a pipe collimator to focus the incident beam ($800\ \mu\text{m}$) on corroded area. In spite of a low crystallinity of corrosion products, the main detectable phases were sodium silicates and silicon oxides, with remaining NaCl phases (Fig.6).

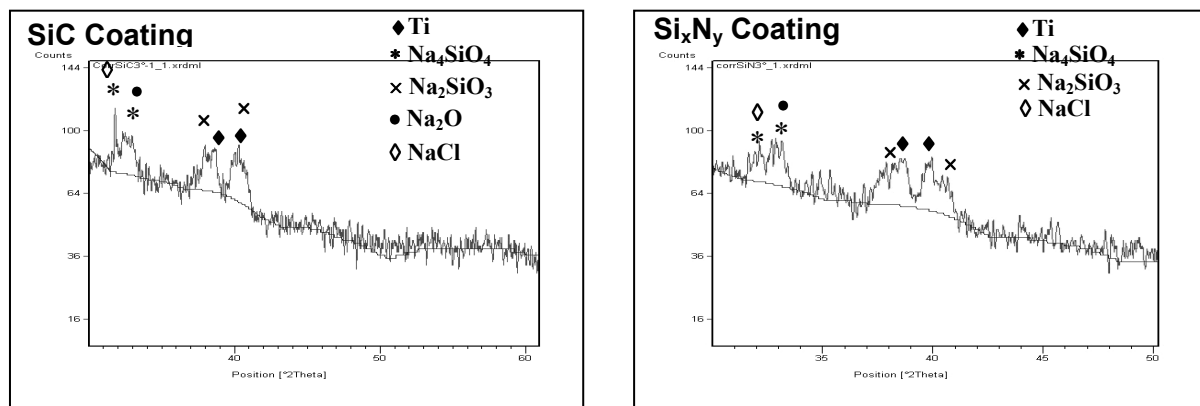


Figure 6: X-ray diffraction spectra under low incident angle (3°) on corroded silicon coatings.

In the case of the Al_2O_3 coated sample, S.E.M observations exhibited no visible pits with a small amount of corrosion products (Fig.7). Combining XRD and EDS analyse, corrosion products contained sodium aluminate (NaAlO_2) and spinel phase (MgAl_2O_3 type). The main difference compared to silicon coatings was the chemical reaction with the Mg element present in sea salt. This element seems to play an important role in the corrosion process. In this case again, no rich Cl products were detected by XRD and EDS analyse.

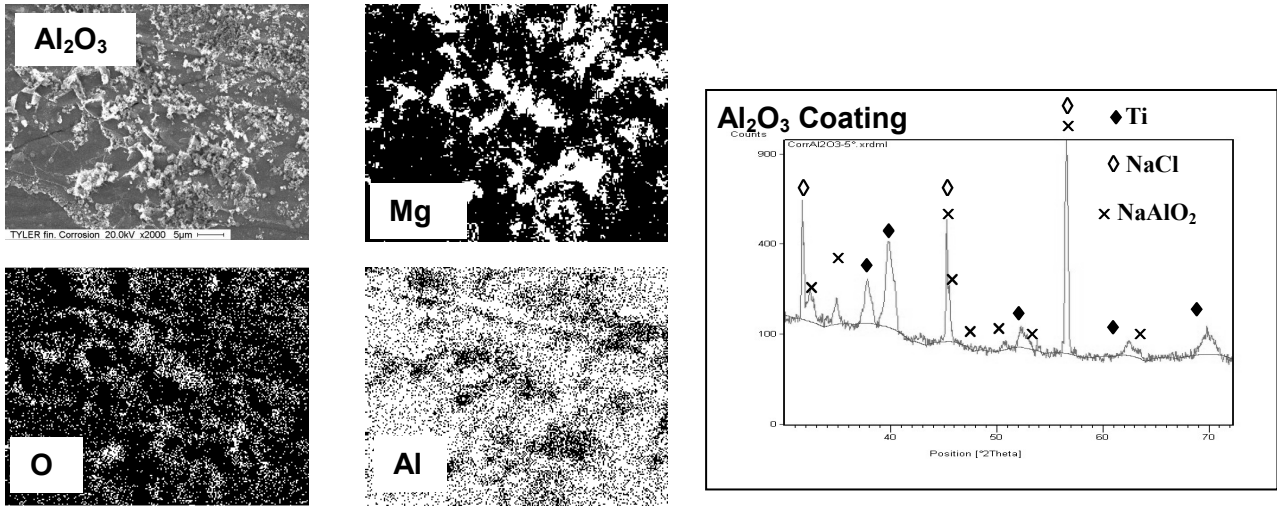


Figure 7: X-ray map and XRD analysis (low incident angle 5°) after salt attack of Al₂O₃.

5 DISCUSSION

5.1 Silicon coatings

Similar corrosion phenomena were observed for both silicon coatings, when the samples were coated with NaCl after exposure to dry air at high temperature. This leads to a sodium silicate formation (Pickrell 1994). The possible reactions to produce sodium silicate are the following:

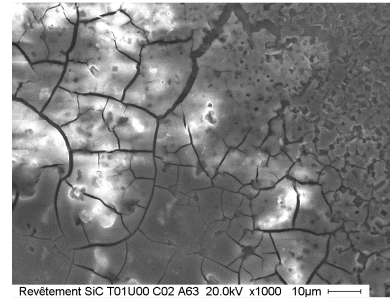
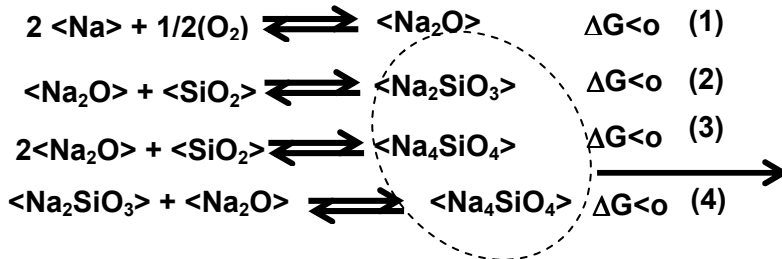
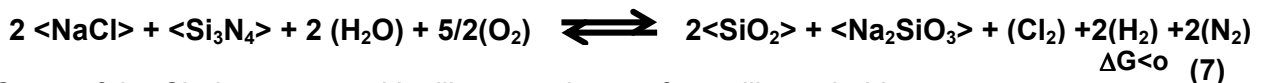
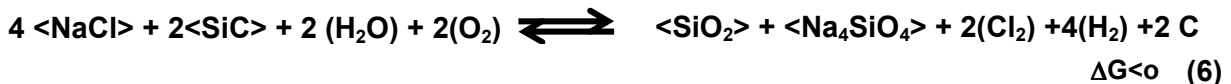
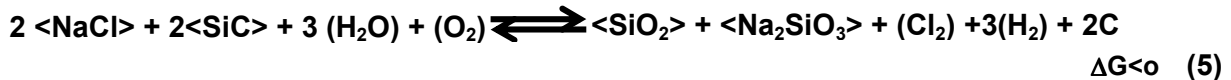
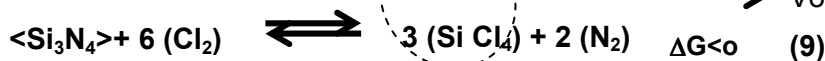
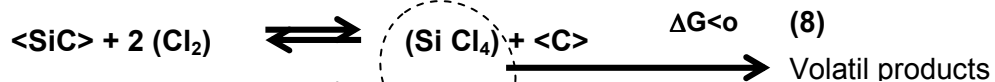


Figure 8: Surface morphology of SiC coating after salt attack for 100 h at 540°C.

Discontinuous sodium silicates layer was contributed to the formation of some cracks and breakdown of SiO₂ (Guangming 2005) in the corroded area, because of volume change (Fig.8). Cracks could serve as short path to lead to a serious hot corrosion of SiC or Si_xN_y coating (Si₃N₄ for simplification) and the following reactions can occur at 520°C:



Some of the Cl₂ then reacts with silicon coatings to form silicon chloride:



Volatil products

5.2 Alumina coating

Chemical analysis combined with thermodynamic calculation showed that sea salt can react with Al₂O₃ coating (Zheng 2003) to form sodium aluminate (Yao 1995) and spinel phase which may occur at 520°C according to following reactions:



6 CONCLUSION

Corrosion resistance of PVD-SiC and Si_xN_y and CVD-Al₂O₃ was evaluated under severe conditions. Lifetime of all coated specimens under SSC conditions were significantly improved by a factor 2.5 compared to uncoated specimen. Silicon coatings were more damaged than Al₂O₃ coating. The formation of sodium silicate seems to be the key factor in the overall corrosion reactions. The Al₂O₃/Ti6242 system showed the best salt attack resistance. It only appeared as small clusters without pits presence. Surface defects of Ti6242 substrate seem to be the principal cause, by initiating corrosion phenomena after a mechanical damage of Al₂O₃ layer, under tensile sollicitations.

7 BIBLIOGRAPHIES

- Guangming, L., Meishnan, L., Yanchun, Z., (2005) Influence of the hot corrosion of Ti₃SiC in the mixture of Na₂SO₄-NaCl melts. *Corrosion science*; (artcle in press).
- Pickrell, G.R., Sun, T., Brown, J.J., (1995) High alcali corrosion of SiC and Si₃Ni₄. *Fuel processing technology*; 44, 213-236.
- Rivière, J.P., Pichon, L., Drouet, M., Galdikas, A., Poquillon, D., (2005) Silicon based oxidation resistant coating on Ti6242 alloy corrosion by dynamic ion mixing. *Surface and coatings technology*; (article in press).
- Valhas, C., Caussat, B., Senocq, F., Gladfelter, W.L., Aloui, L., Moersch, T., (2006) An original device for the delivery of vapors to a deposition apparatus based on the sublimation in a fluidized bed. *Chem. Vap. Deposition*; submitted.
- Yao, Z., Maeek, M., (1995) NaCl induced hot corrosion of a titanium aluminide alloy. *Material Science and Engineering*; A192/193, 994-1000.
- Zheng, C., Wu, N.Q., Mao, S.X., (2003) Effect of Al₂O₃ averlay on hot-corrosion behaviour of yttria-stabilized zirconia coating in molten sulphate-vanadate salt. *Thin solid film*, 443, 46-52.

Keywords:

6242 alloy; corrosion protection; PVD silicon coatings; Interfacial ion dynamic mixing; MOCVD alumina coating; organo-metallic precursor; Salt deposit; thermochemical degradation; Hot salt stress corrosion; oxychloridation; chloridation, oxididation.