Open Archive Toulouse Archive Ouverte (OATAO)
OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: http://oatao.univ-toulouse.fr/
Eprints ID : 2448

To link to this article:
URL : http://dx.doi.org/10.1149/1.2769265

To cite this version: Delmas, Mathieu and Vahlas, Constantin (2007) Microstructure of Metallorganic Chemical Vapor Deposited Aluminum Coatings on Ti6242 Titanium Alloy. Journal of The Electrochemical Society (JES), vol. 154 (n° 10). D538-D542. ISSN 0013-4651

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@inp-toulouse.fr
Microstructure of Metallorganic Chemical Vapor Deposited Aluminum Coatings on Ti6242 Titanium Alloy

Mathieu Delmas and Constantin Vahlas*

Centre Interuniversitaire de Recherche et d’Ingenierie des Matériaux (CIRIMAT-CNRS-INPT-UPS), ENCIACET, 31077 Toulouse Cedex 4, France

DOI: 10.1149/1.2769265

Al-based alloys are used in aeronautics as a protective layer against the excessive oxidation of turbines blades. In this work, Al coatings were deposited by metallorganic chemical vapor deposition on Ti6242, a commercial titanium alloy, with Pt as a sublayer or codeposited to ensure this protection, eventually forming platinum aluminides. Continuous Al coatings were deposited on bare Ti6242, using both trisobutylaluminum and dimethylhexylamine alane as precursors. The same operating conditions applied on a platinum sublayer lead to discontinuous layers mainly containing whiskers. The introduction of a surfactant, namely, ethyl iodide, in the input gas improves the coating morphology by providing nearly whisker-free continuous films, suitable for oxidation protection. Codeposition of Pt and Al results in reduced growth rate and yields layers with lower Pt content and with specific morphology. This behavior is attributed to the competition between Al and Pt compounds on the growing surface.

Experimental

Depositions were performed on 2 mm thick, 15 mm diam Ti6242 disks. Substrates were used as received, i.e., with 600 grit surface polishing. Prior to deposition, they were etched in boiling Turco, cleaned ultrasonically in deionized water and finally degreased in acetone. Some disks were coated with a Pt film before Al deposition. A specially designed setup (the detailed description of the setup can be found in Ref. 2) was used for the CVD experiments. It allowed entire coating of coupons in a single run. It is recalled here that it consists in a vertical cold wall reactor in which the sample is maintained vertically by the two wires of an S-type thermocouple. Temperature is monitored by using a dual-wavelength pyrometer (Williamson), with ±1 ° accuracy. Trisobutylaluminum (TIBA, 95% pure, Strem Chemicals), 99% pure dimethylhexylamine alane (DMEA, EPICHEM), and 99% pure trimethyl(methylcyclopentadienyl)platinum(IV) [(MeCp)MePt] (Strem Chemicals) were used as liquid aluminum and platinum precursors, respectively, without further purification. TIBA and DMEA are aluminum precursors yet widely used in microelectronics. Decomposition of [(MeCp)MePt], in the presence of H2 was reported to provide essentially pure platinum films.

The precursors’ bubblers were loaded into a glove box. They were immersed in thermostatted water baths to ensure fixed vapor pressure and, together with the flow rate of the bubbling gas, to control the compounds’ molar fraction in the gas mixture entering the reactor. Three 99.998% pure N2 lines were used: two for bubbling through the Al and Pt precursors and one for the dilution of the input gas. Before entering the reactor, the dilution line was combined with a 99.999% pure H2 line for Pt deposition. Gases through all four lines were fed through computer driven mass flow controllers. The gas inlet circuit was made of stainless steel and wrapped with heating elements both before and after the bubblers to ensure efficient gas-liquid contact in the bubblers and to avoid premature condensation of the precursors. The gas phase was evacuated at the exit of the reactor by a vacuum pump via a cold trap. Operating pressure was 9330 Pa for deposition from TIBA and 1330 Pa for

*T E-mail: constantin.vahlas@ensicaet.fr

Ensemble des écoles de chimie et de biologie industrielles, ENSICAET, 31077 Toulouse Cedex 4, France


citep@ensicaet.fr
deposition from DMEAA and codeposition. These values are higher than those reported in previous studies for the CVD of Al. They are compatible with the aimed industrial application. Cu and Al CVD deposited films present similar morphological characteristics, due to a Volmer-Weber growth mode. It was reported that the use of ethyl iodide as a surfactant improves copper deposition. Ethyl iodide adsorbs dissociatively upon Al surfaces in the same way as on Cu surfaces. Subsequently, we used iodine as a surfactant during Al deposition upon Pt. This was achieved by introducing a small amount of ethyl iodide in the gas phase during deposition. Tables I and II sum up the conditions used for the films deposition.

Table I. Operating conditions for the deposition of Al using TIBA and DMEAA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flow rate (sccm)</th>
<th>N₂,Al</th>
<th>N₂,Pt</th>
<th>Prec.</th>
<th>C₂H₅I</th>
<th>Reactor</th>
<th>T (K)</th>
<th>P (Pa)</th>
<th>t (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlT1</td>
<td>300</td>
<td>56.6</td>
<td>0.3654</td>
<td>No</td>
<td>623</td>
<td>9330</td>
<td>120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlT2</td>
<td>300</td>
<td>56.6</td>
<td>0.3654</td>
<td>No</td>
<td>623</td>
<td>9330</td>
<td>120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlT3</td>
<td>300</td>
<td>56.6</td>
<td>0.3654</td>
<td>Yes</td>
<td>623</td>
<td>9330</td>
<td>120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AID1</td>
<td>41</td>
<td>3.15</td>
<td>0.1905</td>
<td>Yes</td>
<td>473</td>
<td>1330</td>
<td>75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AID2</td>
<td>41</td>
<td>2.82</td>
<td>0.1704</td>
<td>Yes</td>
<td>473</td>
<td>1330</td>
<td>70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table II. Operating conditions for the codeposition of Al and Pt.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flow rate (sccm)</th>
<th>N₂,Al</th>
<th>N₂,Pt</th>
<th>DMEAA</th>
<th>Me₃(C₅H₅)Pt</th>
<th>C₂H₅I</th>
<th>Reactor</th>
<th>T (K)</th>
<th>P (Pa)</th>
<th>t (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPt1</td>
<td>40.5</td>
<td>1.8</td>
<td>0.0433</td>
<td>9</td>
<td>0.0242</td>
<td>Yes</td>
<td>473</td>
<td>1330</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>AlPt2</td>
<td>40.5</td>
<td>1.8</td>
<td>0.0433</td>
<td>9</td>
<td>0.0242</td>
<td>Yes</td>
<td>523</td>
<td>1330</td>
<td>120</td>
<td></td>
</tr>
</tbody>
</table>

Results

Figure 1 presents the AlT1 (a) and the AID1 (b) samples surface. All SEM micrographs were realized at similar magnifications. Films obtained upon bare Ti6242 using TIBA (sample AlT1) present a continuous base and surface characteristics of Al crystals. The average roughness of AlT1 is 1.7 μm. No preferential orientation could be observed with GIXRD analysis, and the carbon contamination is lower than 1 wt %. Observation of micrograph 1b reveals that the DMEAA based process is different from those observed on AID1 and has no whiskers. The film is continuous and was processed at a growth rate of 1 μm/h. The 300 nm thick Pt sublayer appears as a black, compact strip. AFM measurements prior to Al deposition reveal that it is smooth and covers conformally the surface of the substrate. In addition, this Pt film did not show any scaling or peeling after deposition, even on a mirror-like, 1 μm polished substrate. A crystalline continuous Al film can be observed on the platinum film. The inset on this figure presents the SEM micrograph of the surface morphology (a) and the TEM cross section focusing on the area by the Pt sublayer, of sample AID2; i.e., processed from DMEAA on Pt, by using C₂H₅I. Film AID2 presents small sharp crystals whose shape is different from those observed on AID1 and has no whiskers. The film is continuous and was processed at a growth rate of 1 μm/h. The 300 nm thick Pt sublayer appears as a black, compact strip. AFM measurements prior to Al deposition reveal that it is smooth and covers conformally the surface of the substrate. In addition, this Pt film did not show any scaling or peeling after deposition, even on a mirror-like, 1 μm polished substrate. A crystalline continuous Al film can be observed on the platinum film. The inset on this figure...

Figure 2 presents the Arrhenius plot of DMEAA deposition on Pt. This was achieved by introducing a small amount of ethyl iodide in the gas phase during deposition. All SEM micrographs were realized at similar magnifications. Films obtained upon bare Ti6242 using TIBA and DMEAA, respectively. Figure 3 presents surface and cross section SEM micrographs of sample AlT3. The microstructure of this coating consists of small crystals and only few surface whiskers. This morphology surmounts a continuous Al layer, illustrated in the cross section micrograph.
points out the Pt–Al interface. A 50 nm thick interdiffusion zone is shown to be developed during the deposition of Al; i.e., after 70 min at 473 K. The Pt/Al interface is very reactive,12 the diffusion rate of Pt into Al being several orders of magnitude higher than that of Al into Pt.13 The result of this phenomenon is the formation of platinum aluminides and especially Al2Pt. It thus appears that, as for TIBA processed samples, ethyl iodide assisted Al deposition from DMEA on Pt provides continuous films. Both TIBA and DMEA processed films show very low C contamination and no preferential orientation. Iodine contamination of the surfactant assisted films remains under 1 wt %.

Al–Pt codeposition in conditions AlPt1 corresponds to a growth rate of \( \frac{1}{9262} \text{m/h} \). This value is low compared with the calculated growth rates of Al (6 \( \mu \text{m/h} \)) and Pt (1 \( \mu \text{m/h} \)) in the same conditions. Figure 5 presents a surface SEM micrograph of such a film, processed for 2 h. The Ti6242 surface roughness can be observed thus confirming the conformality and the reduced thickness of the film.

Figure 6 presents a SEM micrograph of the AlPt2 surface. This coating consists of a codeposition performed at 523 K, with a resulting growth rate of 6 \( \mu \text{m/h} \). It can be noticed that the microstructure is close to that of the 473 K processed codeposited sample. AlPt2 presents a higher average roughness of 240 nm and does not show any carbon contamination. The Pt content is about 16 wt %, still lower than the Pt molar fraction in the gas phase, but significantly higher than that of the 473 K deposited coatings.

Despite the low processing temperature, GIXRD patterns of samples AlPt1 and AlPt2 indicate that both films are composed of...
However, DMEAA seems to be very sensitive to the nature of the substrate with those reported in the literature values than Jang’s ones, and modeling of DMEAA decomposition on Al surface resulted in an energy barrier responsible for the diffusion of adatoms across the surface of the system, the balance between the activation energies for nucleation and for growth of Al is shifted towards the nucleation, this resulting in surface smoothening. Second, the presence of I lowers the Ehrlich-Schwoebel barrier, i.e., the energy barrier responsible for the diffusion of adatoms across the surface is about ten times lower than that of Al.

The above observed microstructures can be correlated to the performance of the as processed oxidation barriers. Thermogravimetric tests were performed in dry air on such processed samples, with the test conditions and the obtained results reported in Ref. 1. The link between samples’ morphology and oxidation behavior was established and quantified through the parabolic rate constant of oxidation kinetics, $k_p$ (mg$^2$ cm$^{-4}$ s$^{-1}$), determined by plotting the mass gain vs square root of time. It is recalled that sample AIT1 yields no reduction of the $k_p$ compared with the bare alloy. Also, in the same test conditions samples AID2 and AlPt2 showed an improvement of the oxidation protection, resulting in a $k_p$ ten times lower than that of the bare alloy. This improvement can be attributed to the compactness of these films and their smoother surface morphology with regard to films processed in conditions AIT1.

Conclusion

The deposition of several micrometers thick Al by MOCVD using TIBA and DMEAA on titanium alloy Ti6242 leads to films with a continuous base, no C contamination and no preferred orientation. The deposition rate of platinum drops dramatically. The reduced Pt clusters’ size allows the catalytic properties to appear. During codeposition, Al growth prevents Pt atoms from forming clusters. The presence of I lowers the Ehrlich-Schwoebel barrier, which results in a more compact surface. This improvement can be attributed to the compactness of these films and their smoother surface morphology with regard to films processed in conditions AIT1.

Figure 6. Surface SEM micrograph of sample AlPt2: Al and Pt codeposited on Ti6242 at 523 K.
relations between the microstructure of the deposited coatings and the properties of use, namely protection against oxidation, have been illustrated.

Acknowledgments

The authors are indebted to Yolande Kihn, CEMES, for TEM observations. This work is part of the APROSUTIS project supported by the Réseau National Matériaux et Procédés (RNMP) network (Ministère de la Recherche, opération 02 K0298). It was performed through a grant to M.D. from the French Ministry of Education.

Centre National de la Recherche Scientifique assisted in meeting the publication costs of this article.

References