Electrochemical Behavior of Chemical Vapor Deposited Protective Aluminum Oxide Coatings on Ti6242 Titanium Alloy

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To cite this version:

Grégory Boisier, Monica Raciulete, Diane Samélor, Nadine Pébère, Alain Gleizes, et al.. Electrochemical Behavior of Chemical Vapor Deposited Protective Aluminum Oxide Coatings on Ti6242 Titanium Alloy. ELECTROCHEMICAL AND SOLID STATE LETTERS, 2008, vol. 11, pp.C55-C57. <10.1149/1.2968109>. <hal-00806102>

HAL Id: hal-00806102
https://hal.archives-ouvertes.fr/hal-00806102
Submitted on 29 Mar 2013

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Eprints ID : 2433

To link to this article:
URL : http://dx.doi.org/10.1149/1.2968109

To cite this version: Boisier, Grégory and Raciulete, M. and Samélor, D. and Pébère, Nadine and Gleizes, Alain and Vahlas, Constantin (2008)
Electrochemical Behavior of Chemical Vapor Deposited Protective Aluminum Oxide Coatings on Ti6242 Titanium Alloy. Electrochemical and Solid State Letters, vol. 11 (n° 10). C55-C57. ISSN 1099-0062

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Electrochemical Behavior of Chemical Vapor Deposited Protective Aluminum Oxide Coatings on Ti6242 Titanium Alloy

G. Boisier,* M. Raciulete, D. Samélor, N. Pébere,** A. N. Gleizes, and C. Vahlas†

Institut Carnot-Centre Interuniversitaire de Recherche et d’Ingénierie des Matériaux, ENSIACET, 31077 Toulouse cedex 04, France

The electrochemical behavior at room temperature in a neutral sodium chloride aqueous solution of four types of metallorganic chemical vapor deposited aluminum oxide coatings on commercial Ti6242 titanium alloy was investigated. Polarization and electrochemical impedance curves revealed that porosity free, amorphous alumina coatings provide a two order of magnitude improvement of the corrosion resistance with regard to the bare alloy. Crystallized alumina as well as amorphous Al2O3 (OH) only slightly improve the corrosion resistance of Ti6242. It was demonstrated that metallorganic chemical vapor deposition processed amorphous alumina is a highly promising solution to the protection of titanium alloys against corrosion in salt environments.

[DOI: 10.1149/1.2968109]

Experimental

Sample preparation.— The MOCVD setup consisted of an instrumented horizontal, 2.54 cm in diameter, hot wall reactor and has been previously described. Deposits were performed on Ti6242 disks with diameter and thickness of 15 and 2 mm, respectively. The substrates were polished down to 0.25 μm with diamond paste, which provided mirror-like surface finishing. Aluminum triisopropoxide (ATI, Across Organics) was used as precursor for the deposition of aluminum oxide films. It was melted in its bubbler above 413 K and was kept as a supercooled liquid at 383 K during deposition. Total pressure 0.67 kPa (5 Torr), N2 flow rate bubbling through ATI at 53 standard centimeters per minute (sccm) and dilution N2 flow rate at 653 sccm were kept constant for all experiments. Complementary information on processing conditions for reported experiments is provided in Table I. Sample R19 was postdeposition annealed in a sealed quartz tube in vacuum. Gleizes et al. showed that the adopted conditions provide amorphous (R17), poorly crystallized (R22), and crystallized (R19) alumina films, whereas the lowest deposition temperature (R20) provides amorphous films of formula Al(OH).4

Films thickness was estimated by optical reflectometry using a NC-UV-VIS reflectometer (Ocean Optics) and the Nanocalc software. Calibration of the instrument was performed by using an uncoated Ti6242 sample with the same surface preparation.

Electrochemical tests.— The samples were characterized by voltammetry and electrochemical impedance spectroscopy. A three-electrode cell was used for the experiments: the coated or uncoated Ti6242 coupons as working electrode with an exposed area of 1 cm², a saturated calomel reference electrode (SCE) and a platinum grid as auxiliary electrode. Experiments were performed in a 0.1 M NaCl solution at room temperature without stirring. Electrochemical measurements were carried out using a Solartron 1287 electrochemical interface and a 1250 frequency response analyzer. The impedance diagrams were performed under potentiostatic regulation at the corrosion potential after 1 h of immersion in the NaCl solution and over a frequency range of 65 kHz to 20 mHz with 6 points per decade. The polarization curves were obtained after the impedance measurements from cathodic to anodic potentials. The potential sweep rate was fixed at 0.277 mV s⁻¹. One measurement was realized on each sample. This is not sufficient to unambiguously validate the obtained quantitative information. However, it can be pointed out that the controlled and reproducible microstructure of each film allows, at least, a qualitative ranking of the samples with regard to their electrochemical behavior.

Results and Discussion

Samples with comparable thickness of 200–300 nm were targeted. Estimated thickness values reported in Table I vary between 200 nm and 350 nm. This discrepancy is attributed to the evolution...
of the precursor characteristics during storage and operation\textsuperscript{7} and to the short deposition time used; i.e., between 7 and 8 min, with regard to the duration of the transient regimes of the deposition protocol.

Table I also resumes the differences in composition and crystallinity of the four samples. From infrared spectroscopy, X-ray diffraction, electron probe microanalysis, energy dispersive X-ray analysis, elastic recoil detection analysis, Rutherford backscattering spectroscopy techniques, and thermal gravimetric analysis, it has been shown\textsuperscript{5} that deposition at 623 K from ATI provides amorphous, hydroxylated films whose elemental composition fits the formula \( \text{AlOOH} \). The other three deposits that were prepared above are amorphous, hydroxylated films whose elemental composition fits the formula \( \text{AlO}_x \text{OH} \). Thus, this coating provides the best protection in agreement with the very low current densities measured on the polarization curve (Fig. 1).

It is known that the thickness of the coating influences corrosion performance. For example, Guidi et al.\textsuperscript{8} showed that a 2.40 \( \mu \)m thick, MOCVD processed \( \text{Al}_2\text{O}_3 \) coating ensures better protection against corrosion than a 0.31 \( \mu \)m thick one. In the present study, the thickness variation of the four coatings is less than twofold. Consequently, only the oxide microstructure (crystalline state, chemical composition) and the presence of defects (such as pores) in the coatings are taken into account for a better understanding of the corrosion behavior observed for the different systems.\textsuperscript{9} Both R17 and R20 coatings are amorphous but chemically different (vide supra). The R17 coating prepared at 753 K is composed of \( \text{Al}_2\text{O}_3 \) and is exempt of porosity. The composition of R20 prepared at 623 K is \( \text{Al}_2\text{O}_3 \). Crystallized \( \text{Al}_2\text{O}_3 \) (OH) is known to have a layered structure.\textsuperscript{10,11} Amorphous \( \text{Al}_2\text{O}_3 \) (OH) most likely contains short range layered structure domains rendering coating R20 somewhat porous at the nanoscale. A film prepared in the same conditions has been

<table>
<thead>
<tr>
<th>Sample</th>
<th>R20</th>
<th>R17</th>
<th>R19</th>
<th>R22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition temperature [K (°C)]</td>
<td>623 (350)</td>
<td>753 (480)</td>
<td>753 (480)</td>
<td>1023 (750)</td>
</tr>
<tr>
<td>Deposition time (min)</td>
<td>7</td>
<td>7</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Annealing temperature [K (°C)]</td>
<td>–</td>
<td>–</td>
<td>1073 (800)</td>
<td>–</td>
</tr>
<tr>
<td>Annealing time (min)</td>
<td>300</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Composition</td>
<td>AlOOH</td>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>( \text{Al}_2\text{O}_3 )</td>
</tr>
<tr>
<td>Crystalline state</td>
<td>Amorphous</td>
<td>Amorphous</td>
<td>Crystallized</td>
<td>Poorly crystallized</td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>200</td>
<td>350</td>
<td>320</td>
<td>200</td>
</tr>
<tr>
<td>([Z</td>
<td>_{20 \text{ mHz}} (\Omega \text{ cm})^2])</td>
<td>(3.6 \times 10^5)</td>
<td>(2.3 \times 10^5)</td>
<td>(5.7 \times 10^5)</td>
</tr>
</tbody>
</table>

\( a \) \( P_{\text{total}} = 0.67 \text{ kPa} \) (5 Torr), \( Q_{\text{N}_2, \text{ATI}} = 53 \text{ sccm} \), and \( Q_{\text{N}_2, \text{dilution}} = 653 \text{ sccm} \).

\( b \) \( |Z|_{20 \text{ mHz}}/|Z|_{1023 \text{ K}} = 1.3 \times 10^3 \Omega \text{ cm}^2\).
observed from the electrochemical results. The subsequent decrease of the protection against corrosion as was presently shown to most likely absorb water when maintained in ambient air. Moreover, the presence of the hydroxo groups may lead to reduced chemical stability in chloride-containing aqueous solution with subsequent decrease of the protection against corrosion as was presently observed from the electrochemical results.

Film R19 consists of well crystallized alumina obtained by annealing the as-deposited amorphous structure at 1073 K. In this case, microstructure features, such as grain boundaries, may favor electrolyte penetration thus decreasing the barrier properties of the coating. Film R22 consists of poorly crystallized alumina. Its efficiency against corrosion is comparable to that of R19. However, the impedance diagram for R22 revealed the presence of a time constant in the HF range. This behavior might originate from the intermediary state between amorphous and well crystallized alumina.

Optical microscopy observations were performed to assess the surface damages after the electrochemical tests. These observations (not shown) corroborate the electrochemical results. Film R17 revealed an unaffected surface after the anodic polarization, whereas localized attacks were observed for the R19 coating.

**Conclusion**

Polarization curves and electrical impedance measurements were used to evaluate the corrosion resistance of bare and aluminum oxide coated Ti6242 commercial titanium alloy in a neutral sodium chloride aqueous solution. Crystallized alumina containing coatings provide poor corrosion protection due to the presence of grain boundaries which favor electrolyte penetration through the film. Amorphous AlO(OH) coatings also provide limited corrosion protection due to their lamellar nanostructure and to the presence of reactive hydroxo groups. In contrast, porosity free, amorphous Al₂O₃ insulating coatings allow for a two order of magnitude improvement of the corrosion resistance with regard to the bare alloy. It is demonstrated that MOCVD processed amorphous alumina from ATI is a highly promising solution for the protection of titanium alloys against corrosion in salt environments.

This communication is aimed to establish a preliminary electrochemical characterization of aluminum oxide films of various compositions and microstructures. A higher number of measurements and correlation of the film thickness with the electrochemical impedance spectroscopy and dc characteristics should allow for the consolidation of the results reported.

_Centre National de Recherche Scientifique assisted in meeting the publication costs of this article._

**References**