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Anodization of evaporated aluminium on Ti–6 wt% Al–4 wt% V

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Evaporated aluminium on Ti–6 wt% Al–4 wt% V alloy was anodized in phosphoric acid and other electrolytes. The anodic oxide formed was characterized by various techniques and it was found that a duplex oxide forms in which titanium has diffused through the aluminium oxide film and appears at the surface and throughout the film.

1. Introduction

Anodization as a surface preparation for adhesive bonding is well established for aluminium alloys [1]. The phosphoric acid anodization (PAA) provides and extremely bondable and durable [2] surface finish and has been adapted for production of large panels [3, 4]. The suitability of PAA as an adhesive bonding preparation has been shown to be due to, among other things, the porous structure of the anodized oxide [5]. A programme developing new processes and evaluating established methods of surface preparations for titanium and titanium alloys has been carried out in this laboratory [6]. The PAA as used for aluminium alloys was one of the methods tried as a surface preparation for titanium alloys. No advantages of PAA compared to chemical etches such as the phosphate fluoride treatment was observed. Details of these comparisons will be shown separately. An adaptation of the PAA method was developed in which aluminium was vacuum evaporated onto the titanium alloy surface and then anodized according to PAA specifications, as well as under varying conditions of voltage and concentration. Anodized films were evaluated by Ion Scattering Spectrometry (ISS), Secondary Ion Mass Spectrometry (SIMS), Auger Electron Spectrometry (AES) and Scanning Electron Microscopy (SEM).

2. Experimental procedure

About 100 nm of pure aluminum was vacuum evaporated from a commercial UHV evaporator using a helical tungsten boat. Approximate thicknesses were measured using a quartz crystal oscillator. The Ion Scattering Spectrometer equippped with Secondary Ion Mass Spectrometry was the commercial model 520 (3M Co., St. Paul, MN). The Auger Electron Spectrometer was the commercial model 540 thin film analyser (Physical Electronics, Inc., Eden Prairie, MN). Anodizations were carried out both in quiet and stirred solutions using a filtered d.c. power supply.

3. Results and discussion

The surfaces of the as-evaporated films were characterized by several methods prior to annodization. An ion scattering spectrum and a secondary ion mass spectrum from one of the evaporated films before annodization is shown in Fig. 1. The ISS data is typical of thin natural oxide films on aluminium and the elemental analysis as provided by the positive SIMS spectrum shows primarily aluminium with large impurities of sodium and potassium present. Neither the ISS nor SIMS spectrum show titanium to have diffused to the surface. It is interesting to note, however, that fluorine does appear in the possitive SIMS spectrum, indicating that, probably, diffusion of fluorine through the aluminium film takes place from the titanium surface which had been treated with HF/HNO_3 prior to vacuum deposition of the aluminium. AES data as shown in Fig. 2 shows just aluminium and oxygen to be present on the surface with a small carbon impurity. The carbon disappeared rapidly on ion etching indicating probable atmospheric contamination.

Several different anodization solutions were

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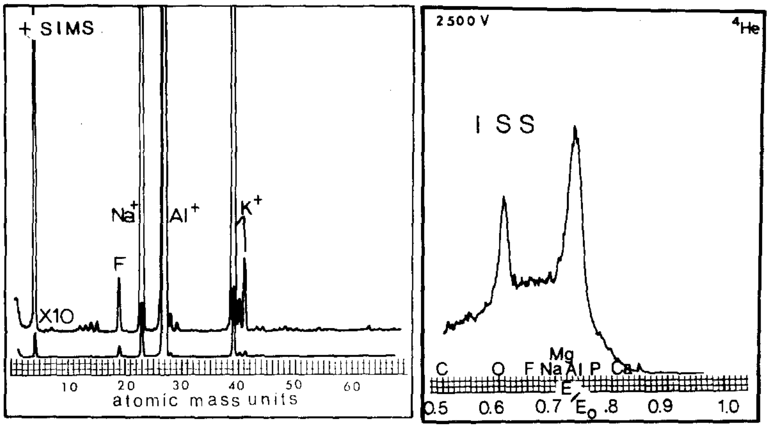

Figure 1 ISS and SIMS data for the aluminium evaporated film on Ti–6 wt% Al–4 wt% V.

used in this work. When the anodization was carried on 0.1 M H_3PO_4, it was not possible to stir the solution since stirring caused uneven and rapid anodization or sparking at the meniscus. In order to carry out anodizations with the stirred solution it was necessary to decrease the concentration of the solution to 0.05 M H_3PO_4. Fig. 3 shows the surface characterization data on a specimen anodized in an unstirred solution of 0.1 M H_3PO_4. Similarly, Fig. 4 shows the AES spectrum for the same anodized specimen. All of the surface characterization methods showed that the anodized film is not just Al_2O_3, but contains significantly large amounts of titanium. It was suspected that this would be the case, even before the analysis was carried out, because, during annodization, the surface films assumed the typical characteristic colours seen in anodized titanium. These colours when compared to some of the titanium not covered by aluminium did not show exactly the same colours but colours within the same family. This may indicate that the thickness of the oxides in the area covered by aluminium is different or it may indicate that the differences in the index of refraction play a part in the changes in apparent colour of the films.

The elemental profiles of these films were also obtained. A 2000 eV argon ion beam slowly erodes away the surface while the crater is being sampled by the electron beam. The result then is a plot of the elemental constituents present against time as the surface is sputtered away. Such a plot is shown for the original aluminium evaporated on titanium in Fig. 5. The surface is first sampled with only the electron beam. This is represented by the area on the time scale between 0 and the arrow. The arrow signifies the turning on of the argon ion beam. It is seen that the

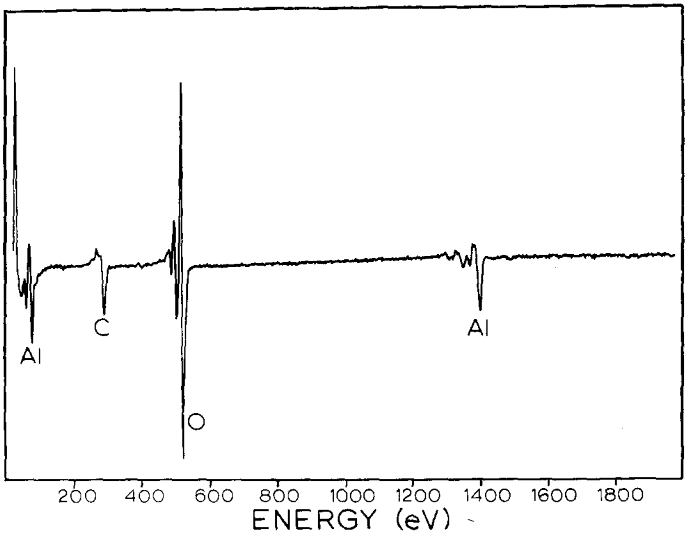

Figure 2 AES data for the evaporated aluminium film on Ti–6 wt% Al–4 wt% V alloy.

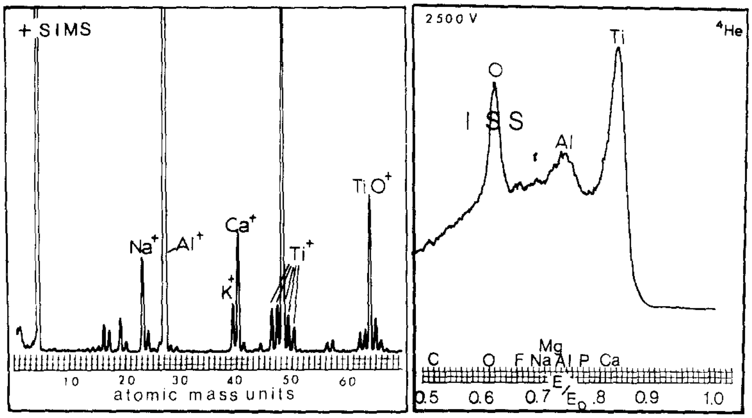

Figure 3 ISS and SIMS data for the duplex oxide formed during anodization of aluminium on Ti–6 wt% Al–4 wt% V alloy.

carbon impurity on the surface disappears quite rapidly. The thin natural oxide film on the aluminium is eroded, as seen here by a decrease in oxygen and the increase in aluminum. Then as the interface is approached, the aluminium intensity begins to drop rapidly accompanied by an increase in titanium intensity. It appears that the carbon content increases near the interfacial region probably indicating that the titanium was contaminated before deposition. Also there is a large oxygen concentration increase at the interface probably due to partial oxidation of the titanium between preparation time and the time that the aluminium deposition was carried out. No appreciable diffusion of aluminium and titanium is seen, however, in this elemental profile. Fig. 6 shows the elemental profile obtained by AES for the sample anodized in 0.1 M H_3PO_4 at 10 volts. Significant mixing is now seen with appreciable amounts of titanium at the surface decreasing somewhat in the region of the original interface and then rising to the bulk concentration. Aluminium is seen throughout the film. Large quantities of phosphorous are observed all the way through the film, the concentration following closely that of oxygen.

This duplex oxide was obtained for all of the electrolytes which were tried in this work. Among these were NaOH, NaH_2PO_4, phthalic acid and other mixtures. In addition to the phenomena already described, when fluorine was present in the electrolytes the fluorine was retained in large quantities in the anodized film and is seen in the SIMS spectra of Fig. 7. It appears that the fluorine has combined with some of the constituents of the anodized film. These fingerprint SIMS spectra,

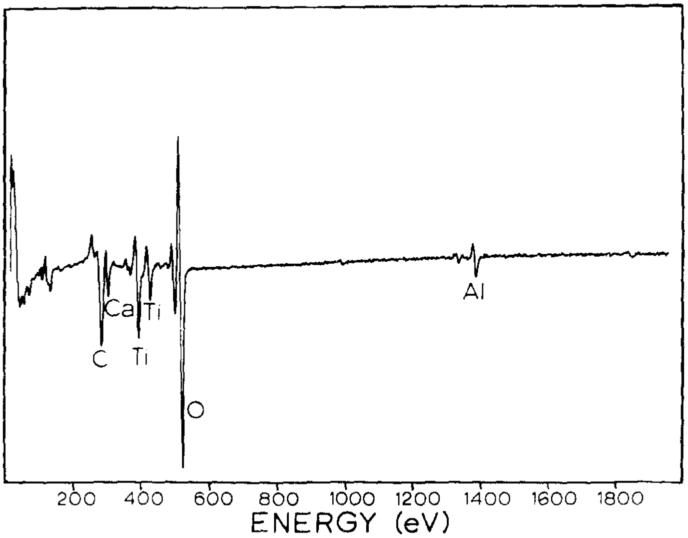

Figure 4 AES data for the duplex oxide formed by anodization of aluminium on Ti–6 wt% Al–4 wt% V alloy.

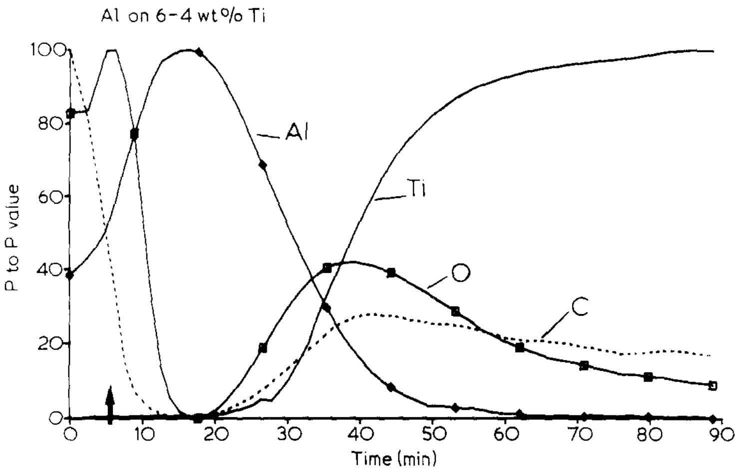

Figure 5 The elemental profile with depth obtained by Auger electron spectrometry with argon ion etching.

in which clusters appear, suggest compound formation but do not necessarily mean that these species were present on the surface. However, from spectra of pure compounds that have been obtained, it appears that these clusters do indicate that some chemical combination has taken place on the surface. SEM investigation of these oxide films indicated that they did not have a similar porous structure to that observed on PAA films on aluminium alloys. More porous appearing films could be obtained by anodization at mugh higher voltages; but the sparking and uneven anodization began to create problems.

Simple bondability tests utilizing the lap shear technique showed that the duplex oxide forms a strong bond. It is doubtful, however, that the production problems of evaporation of aluminum or titanium followed by the annodization procedure would be practical. No long-time durability tests such as the wedge opening test under high temperature and humidity have been carried out as yet.

4. Conclusions

When an aluminium film on titanium is anodized, the titanium diffuses through the aluminium oxide film to form a mixed anodic oxide. Diffusion does not occur during the initial vacuum evaporation step. Films formed in phosphoric acid at low voltages do not show the porous structure associated with similar PAA films on aluminium alloys. However, these duplex films do show mixing of

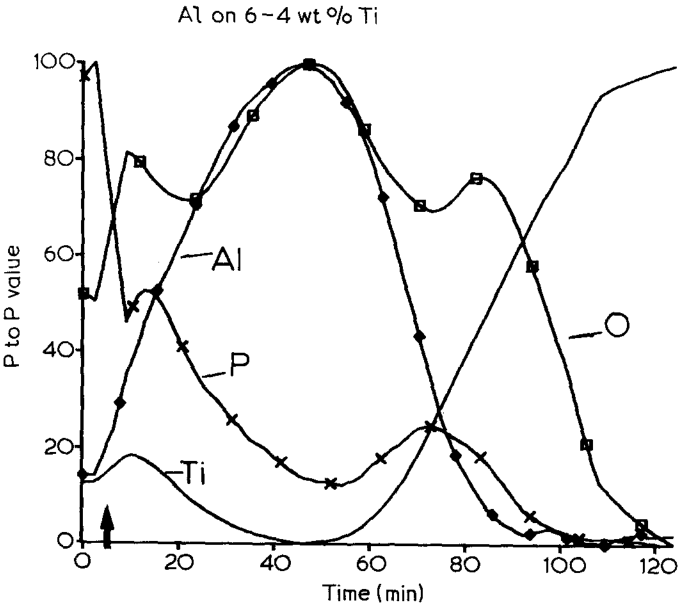

Figure 6 The elemental profile with depth obtained by AES and argon ion etching for the duplex oxide formed by anodization of evaporated aluminium on Ti–6 wt% Al–4 wt% V alloy.

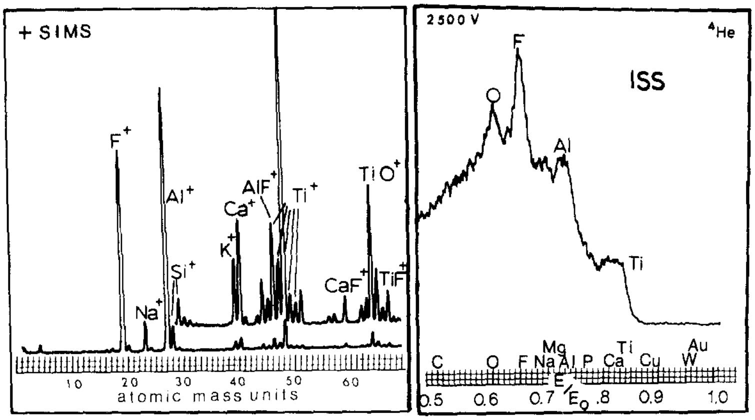

Figure 7 ISS and SIMS data for the duplex oxide formed by anodization of an evaporated aluminium film on Ti–6 wt% Al–4 wt% V alloy in a dilute hydrofluosilicic acid electrolyte at 10 volts.

aluminium and titanium along with a large inclusion of phosphate ion. Films formed in other electrolytes such as hydrofluosilicic acid includes much fluorine in the oxide and on the surface and appears to combine chemically with other elements in the oxide film. No advantage for adhesive bonding of these duplex oxides is envisioned, but they could be useful for other technologies.

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