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# The Stability of Anodized Titanium Surfaces in Hot Water

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Adhesive bonding of titanium structures for high performance aircraft has gained increased attention in recent years, but very little work has been done to determine the stability of bond strength in humid environments or the effect of higher operating temperatures envisioned in future aircraft. In this paper, the stability of an important bond component—the surface oxide—is considered. It is shown that an anodically formed amorphous  $\text{TiO}_2$  layer on Ti-6Al-4V is unstable in pure water at 85°C. Morphological and structural changes in the oxide and possible corrosion of the substrate lead to the formation of an anatase crystallite layer and an increase in the surface oxide mass. Crystallization does not occur when the oxide is heated in vacuum at typical adhesive curing temperatures. The relevance of oxide instability to bond failure is discussed.

## INTRODUCTION

The use of titanium-to-titanium and titanium-to-composite adhesive bonding is expected to play an important role in the design and production of lighter, high performance air and space crafts of the future. The proposed high operating temperatures, around 300°C, present special bonding problems, since it is required that all bond components—adhesive, primer, and surface oxide—remain stable for long periods at these temperatures. Great advances have been made in the area of adhesives and composite materials with the development of high temperature, polyimide base resins. However, until now, the subject of surface oxide stability, especially on titanium, has received considerably less attention.

Studies on both aluminum and titanium surfaces prepared for adhesive bonding<sup>1,2</sup> have shown that oxide morphology and thickness play major roles in bondability. The best surface treatments, such as phosphoric acid anodization (PAA) on aluminum and chromic acid anodization (CAA) on titanium,

create oxides having thicknesses of a few thousand angstroms (depending on anodization voltage) and an extremely porous cellular structure that ends in protruding "fingers".<sup>1</sup> This structure interlocks with the penetrating adhesive or primer, providing a mechanical component that imparts great strength to the bond. If environmental factors affect the oxide structure and morphology, bond strength can diminish considerably. In aluminum, strength deterioration can occur upon exposure to humidity. Venables *et al.*<sup>3</sup> have shown that this situation is caused by a transformation of the original oxide into hydroxide, which is only loosely attached to the aluminum substrate, thereby allowing interfacial failure. It is very important to determine whether oxides on titanium are similarly affected by humidity and, since the operating temperature range for titanium structures may be considerably greater than that for aluminum, the effect of the thermal environment is also of interest.

This paper presents the results of a study on the morphology and structure of titanium oxides exposed to various temperatures and times in "wet" environments. Ti-6Al-4V alloy samples prepared by the CAA treatment<sup>4</sup> were used to investigate the behavior of surface oxides that exhibit the best available morphology for adhesive bonding. To isolate water-induced changes from pure thermal effects, oxides were also heat treated in a vacuum of  $10^{-5}$  torr and were studied with SEM, TEM, and AES.

## EXPERIMENTAL PROCEDURE

### A. Specimen preparation

Ti-6Al-4V coupons (50- $\mu$ m-thick sheet) were degreased in trichloroethylene vapor for 10 minutes and pickled in a solution containing 15 vol.% 70%  $\text{HNO}_3$  and 3 vol.% 50% HF for 30 seconds. After a 2-minute rinse in distilled water, each coupon was anodized in an electrolyte consisting of 5% chromic acid and 1 g/l  $\text{NH}_4\text{F}$ , at 10 V for 20 minutes. The anodized coupons received two 2-minute rinses in distilled water and were dried for 2 to 5 minutes in a hot air flow. Specimens with surface areas of approximately 1  $\text{cm}^2$  were sheared from the coupon. The bare edges lacked an anodic film, but probably were instantly covered with a natural oxide layer. To demonstrate that edge effects did not significantly influence the behavior, some experiments were repeated on totally anodized coupons with identical results.

### B. Water exposure

Each test specimen was placed in a glass tube filled with 20 ml of preheated distilled-deionized water (pH 7). The tubes were plugged with glass stopcocks and placed in heat blocks in a Fisher Isotemp Dry Bath. Exposure conditions

were 60, 70, and 85°C ± 1°C for up to 1100, 500, and 230 hours, respectively. At given intervals, tubes were removed from the bath, the specimens washed ultrasonically in pure acetone, and then dried in a hot air flow.

### C. Vacuum heating

Individual test specimens were vacuum heated in the chamber of an Auger electron spectrometer (AES) unit (Physical Electronics Model 548) at 10<sup>-5</sup> torr. Radiation was supplied by a heating element 0.5 cm away. The specimen was mounted on a rotating stainless steel carousel using two small stainless steel screws. Ceramic sleeves on the screws provided thermal insulation by acting as spacers between the specimen back and the carousel. A small thermocouple touching the specimen back monitored the temperature. Heating and cooling were rapid, at a rate of ~1°C/second. Exposure conditions were 100, 150, and 250°C for 1 hour and 100°C for 24 hours. The oxide mass/unit surface area ("equivalent thickness") was determined by AES depth profiling before and after each heat treatment.

### D. Electron microscopy

A JEOL JEM 100-CX STEM was used for scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A special method of coating SEM specimens with a thin layer of Pt allowed high resolution (30 Å) studies of the titanium oxide in the SEM mode at 50,000× magnification. Details are given in Ref. 1. SEM stereo pairs were obtained on a split CRT screen at a ±6° tilt angle, allowing three-dimensional views of the oxide. For TEM, thin foils were prepared by ion milling. First, the original 1-mm-thick pieces were mechanically thinned to about 5 μm, with the oxide side protected, and then 3-mm diameter discs were punched out of them. Milling was done on the Ti side, with a 5-kV Ar-ion beam hitting the sample at a 17° angle, and lasted from a few hours to a few days. Although the ion beam heated the specimen to nearly 100°C, it is believed that no artifacts were introduced. Stereo views were taken with the specimen tilted ±6° around a tilt axis.

### E. Auger electron spectroscopy

Auger Electron Spectroscopy was used to measure the oxide mass<sup>5</sup> and to detect composition changes and contaminants. The technique also allows a rough evaluation of oxide stoichiometry, which on all our specimens was mainly TiO<sub>2</sub>, at least near the surface. Depth profiles were taken by sputtering the oxide with a 2-kV, Ar-ion beam incident to the specimen surface at a 76° angle with respect to the primary Auger electron beam. The use of this technique on porous oxides is discussed in Ref. 5.

## RESULTS AND DISCUSSION

The oxides were characterized by integrating the SEM, TEM, and AES measurements. The AES depth profiles of the as-treated surface were repeated five times to determine the reproducibility of the equivalent thickness measurement. A typical profile is shown in Figure 1. The information on oxide composition, thickness, contaminants, etc., that can be extracted from this type of profile is discussed in Ref. 5 and will not be repeated here. In general, all profiles exhibit three regions: (I) oxide region, (II) oxide/metal transition region, and (III) metal region. The equivalent oxide thickness is estimated by multiplying the sputtering time taken to reach the middle of region II by a calibrated sputtering rate. Since the calibration is performed on a fully dense oxide with a thin oxide/metal transition region, the equivalent thickness underestimates the real thickness by a factor of 2 to 4 depending on the oxide porosity.<sup>5</sup> However, the method gives a very good indication of the oxide mass/unit area of the surface and can be used to monitor mass changes.

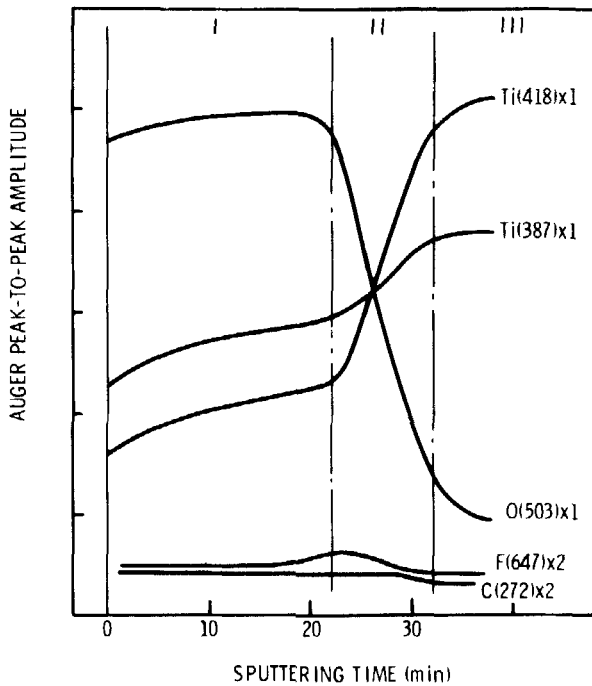


FIGURE 1 AES depth profile of the as-prepared CAA oxide.

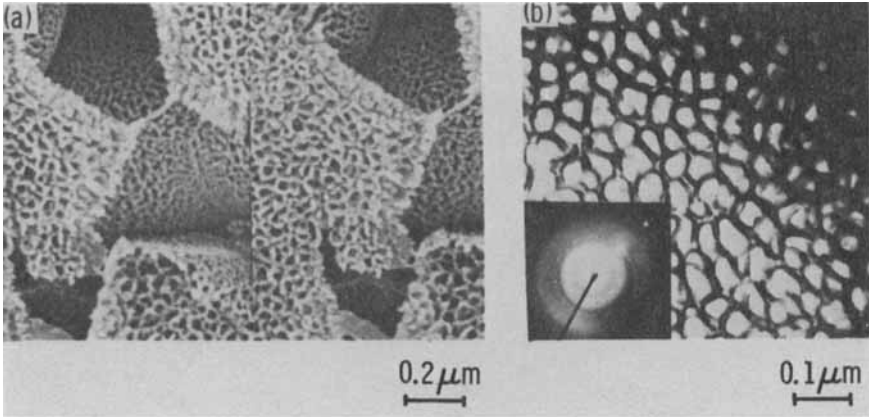


FIGURE 2 As-prepared CAA oxide: (a) SEM stereo view and (b) TEM bright-field and SAD pattern.

Hereafter, for simplicity, we will refer to equivalent thicknesses only. The original oxide was  $1050 \pm 50 \text{ \AA}$  thick, and the reproducibility of the measurement was about  $\pm 5\%$ .

Chromic acid anodization of titanium creates a porous, columnar, cellular oxide, with 100- $\text{\AA}$ -diameter fingers extending 100–200  $\text{\AA}$  above the cells. These fingers are clearly seen in the SEM stereo pair, Figure 2a. On this coupon, the porous oxide covered only 80–90% of the surface. It has been shown that avoidance of smooth areas, which lack porosity, is essential for good bondability.<sup>2</sup> Total coverage can be, and has been, achieved in our laboratory.

Examination of thin foils of this oxide by TEM, Figure 2b, showed a regular array of cells, which matched the SEM view in size and distribution. The crystal structure of these cells was obtained by selected area diffraction (SAD) patterns, one of which is shown in the inset in Figure 2b. It always consisted of two or three concentric halos, which sometimes were accompanied by one or two faint, dotted rings. Halos are characteristic of amorphous materials, whereas rings indicate the presence of a polycrystalline phase, which for this oxide, was not well developed, as shown by the very faint reflections. Correlation with later results and comparison with a standard Al pattern indicated that the two most commonly seen rings were 200 and 220 reflections of a cubic TiO phase that was probably introduced during anodization. However, the amount of this phase, when present, was negligible compared with the total mass of the mostly amorphous oxide. In many original specimens, TiO was not detected at all.

The amorphous character of the CAA oxide is likely to influence its stability

in various environments. Some investigators<sup>6-8</sup> have shown that the amorphous form is the least stable of four  $\text{TiO}_2$  polymorphs found in nature. The other three are crystalline and, in order of increased thermodynamic stability, are named anatase, brookite, and rutile. Rutile is the only phase stable at all temperatures and is the one usually found as the "natural" oxide on exposed titanium surfaces, whereas anatase and brookite transform into rutile at a very fast rate above  $\sim 600^\circ\text{C}$ . Below  $\sim 200^\circ\text{C}$ , their transformation in dry air is so slow that both can be considered practically stable. The transformation kinetics are accelerated markedly by exposing anatase and brookite to water. For example, under hydrothermal conditions, the temperature limit at which the anatase-to-rutile transformation rate becomes significant is lowered to the region of  $100\text{--}200^\circ\text{C}$ .<sup>6</sup> Under such conditions, bulk amorphous  $\text{TiO}_2$  also transforms into rutile following the path: amorphous  $\text{TiO}_2 \rightarrow$  anatase  $\rightarrow$  rutile. The overall process appears to involve dissolution of the original phase and precipitation of the stable one. To see whether a similar transformation occurs in CAA oxide films, we directed our efforts toward characterization of oxides exposed to heat and/or water.

### A. Water-heated oxides

In mechanical testing of adhesive bonds, wedge- and lap-shear stress-durability tests are normally run at  $60^\circ\text{C}$  and 100% relative humidity. Therefore, the three temperatures chosen for water immersions ( $60$ ,  $70$ , and  $85^\circ\text{C}$ ) include the typical test case and more severe temperatures. At present, aircraft operating conditions often are less severe than test conditions, but in the future, as new high temperature adhesives are developed, it is anticipated that some structural components may be exposed to temperatures up to  $300^\circ\text{C}$ .

AES depth profiling on all immersed specimens produced the thicknesses plotted in Figures 3 and 4. In general, the equivalent thickness remained unchanged on the  $60$  and  $70^\circ\text{C}$  immersed specimens, except for very long exposures when there was an apparent decrease, slightly greater than the error band. At  $85^\circ\text{C}$ , however, after an "incubation time" of little change, the equivalent thickness (mass) increased drastically, to about  $1900 \text{ \AA}$  after 72 hours. This increase coincided with the formation of an anatase crystallite layer (see below). The mass increase occurred on all specimens tested from three separate anodization batches, including one in which a wholly anodized coupon was used.

Extensive SEM and TEM work was done on all surfaces and Figure 5 shows some typical structures observed. At  $60^\circ\text{C}$  for up to 1100 hours and at  $70^\circ\text{C}$  for less than 500 hours, *i.e.*, in a period overlapping that of the constant thicknesses, no morphological changes occurred. At  $60^\circ\text{C}$  and 1100 hours, the

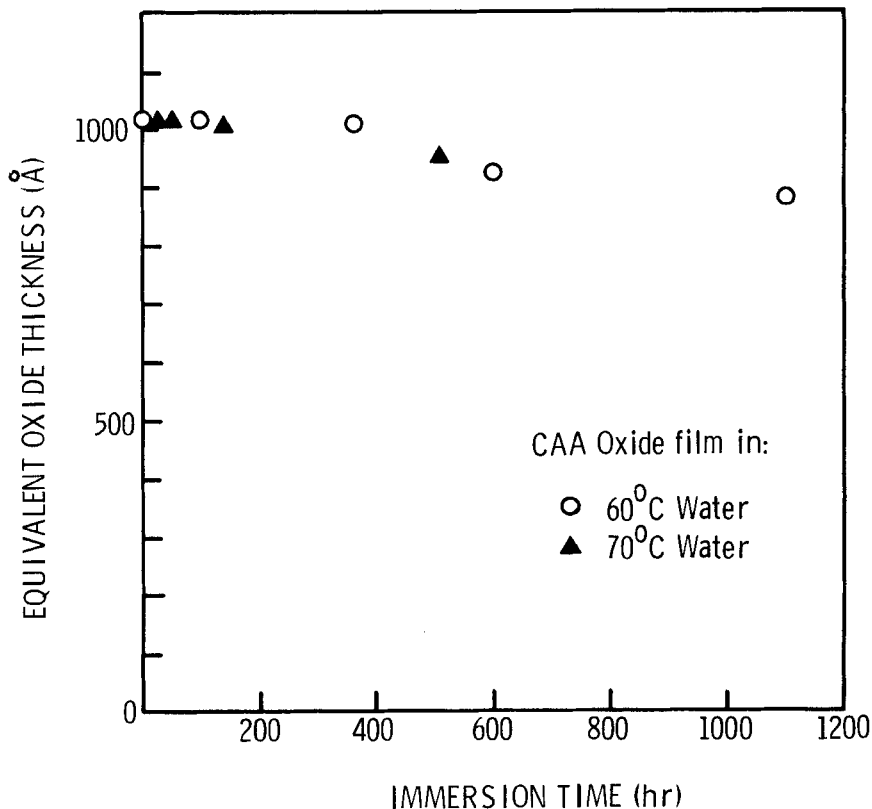


FIGURE 3 Equivalent oxide thicknesses (mass/unit area) of CAA oxides immersed in water at 60 and 70°C.

SAD pattern, Figure 5b, indicated faint traces of TiO, while the morphology remained identical to that of the original surface. At 70°C and 500 hours, the surface lost some of its well-defined cells, Figure 5c, and some areas appeared covered with a newly formed material that probably precipitated from the water and which again showed a TiO pattern in SAD, Figure 5d. At 85°C and 72 hours, the surface was covered with many elongated, evenly distributed crystallites, Figure 5e, which were identified by SAD as anatase, Figure 5f. The overall process of TiO and anatase formation on immersed surfaces was strongly temperature dependent, as illustrated by the fact that the incubation time was much shorter at 85°C (about 20 hours for some coupons) than at 60°C (about 1100 hours). The elongated shape of the crystallites suggests that they grew by precipitating from the solution, which had become super-



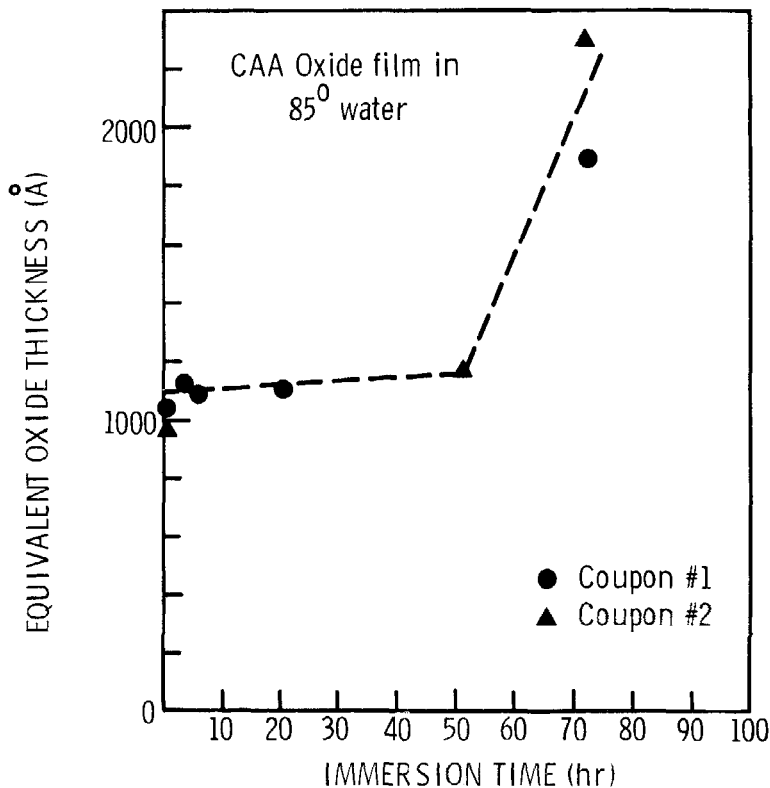


FIGURE 4 Equivalent oxide thicknesses (mass/unit area) of CAA oxides immersed in water at 85°C.

saturated with Ti ions or complexes in a region very close to the sample surface. The experimental evidence indicates that the dissolved ions arise from corrosion of the substrate and/or dissolution of the amorphous layer. Corrosion that could lead to formation of additional oxide is indicated by the increased mass in AES profiling (Figure 4) and dissolution of the amorphous cells can be deduced from the absence of cells, in the 72-hour, 85°C TEM specimen (Figure 5f). Although it has been shown previously<sup>9</sup> that Ti corrodes in pure water in the region 100–200°C, this study indicates that corrosion may occur even below 100°C and within a relatively short time.

### B. Vacuum-heated oxides

Titanium adherend oxides encounter high temperatures at various stages of the bonding process as well as in service. For example, the cure temperature for

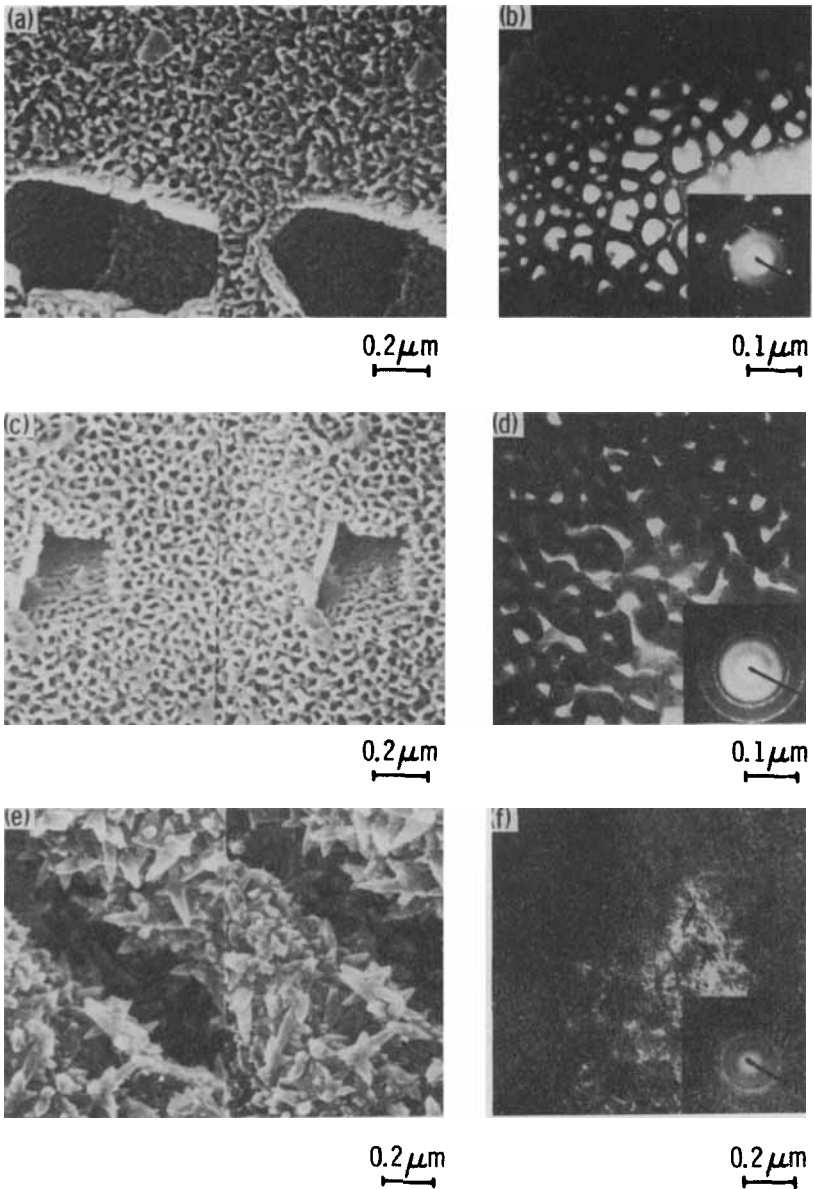


FIGURE 5 SEM stereo pairs and TEM/SAD views of immersed oxides after 1100 hours at 60°C (a, b), 500 hours at 70°C (c, d), and 72 hours at 85°C (e, f).

epoxy adhesives can be quite high (*e.g.*, 350°F or 176°C) and would be much higher for polyimides. Therefore, an effort was made to separate thermally induced changes in the oxides (*e.g.*, porosity decrease, crystallization) from processes requiring the presence of humidity. Vacuum heating to temperatures and times similar to curing conditions were considered relevant. The conditions chosen were 100, 150, and 250°C for 1 hour and 100°C for 24 hours. After heating, the oxides were depth profiled with AES. As seen in Figure 6, the

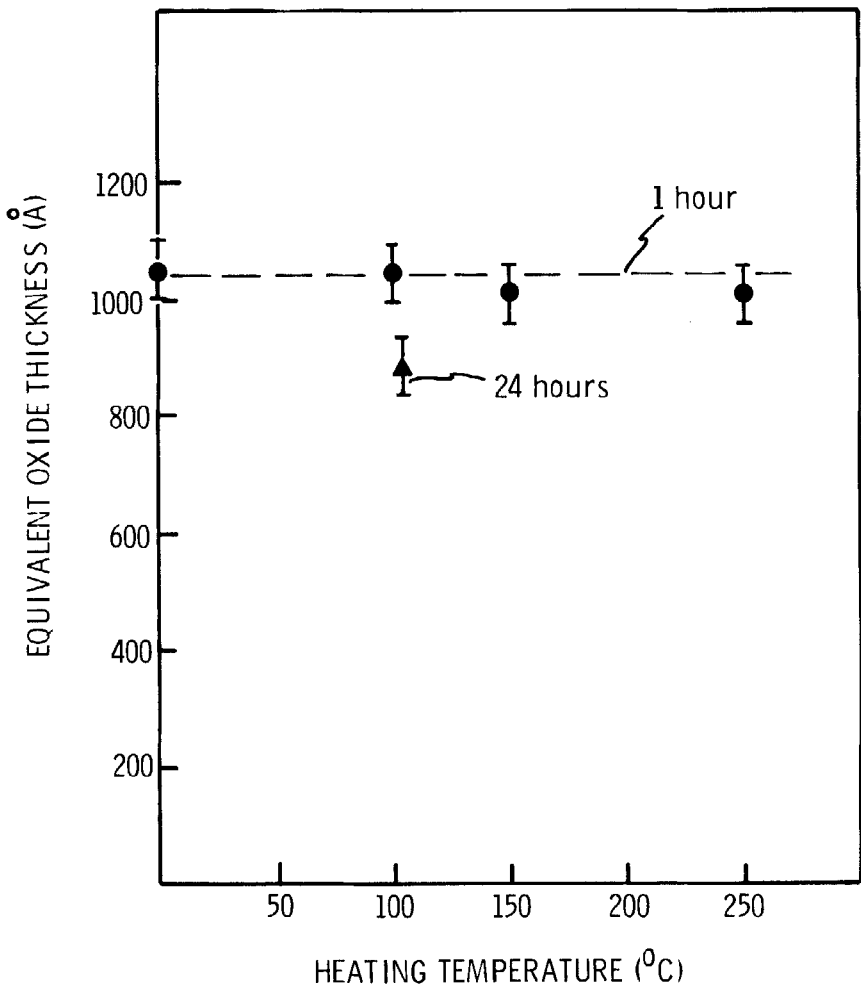


FIGURE 6 Equivalent oxide thicknesses (mass/unit area) of CAA oxides heated in vacuum.

oxide mass after the 1-hour runs remained unchanged at all temperatures, but seemed to decrease slightly after the 24-hour run. No chemical changes that could arise from diffusion of substrate elements into the oxide were detected, except for a possible slight increase in Al concentration in the long (24-hour) exposure at 100°C. Scanning electron microscopy stereo views taken after each run showed that oxide morphology remained unchanged; typical cells and fingers were seen on all surfaces.

Thin foils for TEM were prepared from the 1-hour, 150°C- and 250°C-, and the 24-hour, 100°C-heated oxides. The SAD patterns from all three were practically indistinguishable from that of the original oxide, thus proving that the amorphous structure remained unchanged after these treatments. These results indicate that the most extreme curing conditions presently used in bonding processes, *e.g.*, 1 hour at 176°C for the FM300K adhesive, will not cause oxide crystallization. This point was also proven by examining the oxide on a CAA lap-shear specimen adjacent to the bonded area. This area of oxide, which, together with the entire specimen was passed through the 176°C, 1-hour curing cycle, remained totally amorphous.<sup>10</sup>

In summary, the changes observed in the water-immersed amorphous oxides can be attributed to such processes as dissolution/precipitation and substrate corrosion, which cannot occur in the absence of humidity.

## CONCLUSIONS

1) It was found that TiO<sub>2</sub> films formed by anodization in a chromic acid bath at 10 V are totally amorphous.

2) Upon heating in a dry environment, the films remain amorphous after exposures of 1 hour at 250°C and 24 hours at 100°C.

3) In the presence of water, the substrate and film undergo changes at temperatures as low as 85°C. These changes appear to involve dissolution of the amorphous film, reprecipitation of both crystalline TiO and TiO<sub>2</sub> (anatase) and corrosion of the Ti substrate. Below 85°C, changes may occur, but at a very slow rate.

4) Consequently, the durability of titanium adhesive bonds in a humid environment may decrease as a result of oxide instability, especially above c.85°C.

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