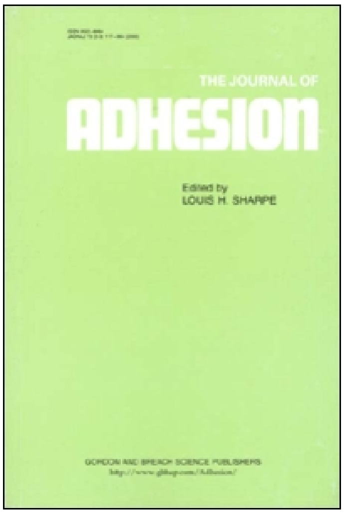

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NOTE

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KEY WORDS Bonding with epoxy adhesive; durability; sodium hydroxide anodization; surface characterization by SEM/XPS/AES; Ti-6Al-4V alloy; wedge test.

INTRODUCTION

The durability of adhesively bonded titanium structures is a topic of concern in a variety of fields today. There appears to be a definite connection between durability and surface pretreatment of the adherend. A variety of pretreatments are reported for Ti-6-4[1–3]. For example, the chromic acid anodization (CAA) pretreatment has received a lot of attention in creating surfaces resulting in improved durability of adhesive bonds.

Another pretreatment, sodium hydroxide anodization (SHA) has not received as much study. Kennedy, *et al.*[4] claim SHA provides a more durable bond than CAA. The SHA surface was evaluated using scanning electron microscopy (SEM) and bonding using either a 120°C or 175°C curing epoxy adhesive in both lap shear and wedge configurations.

This paper describes further surface characterization in addition to SEM, including x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) of the SHA surface accompanied by supporting adhesive bonding data using the wedge configuration.

EXPERIMENTAL

Materials

A Ti-6-4 alloy was used as the adherend for the entire study. Samples for surface analysis originally measured 2.54 × 12.7 × 0.13 cm (1 × 5 × 0.05 in). The wedge samples measured 2.54 × 15.24 × 0.38 cm (1 × 6 × 0.15 in). A 175°C cure structural epoxy, FM-300 (American Cyanamid) was used for all adhesive bonding. Chemicals, unless otherwise noted, were obtained from Fisher Scientific Company.

Surface pretreatments

The "optimum" SHA pretreatment as reported by Kennedy, *et al.*[4] was used. Ti-6-4 lap shear coupons were sand blasted with an Econoline gritblaster at 100 psi held approximately 5 cm. from sample and solvent wiped with methanol, methylethyl ketone or acetone. The degrease step entailed immersion in a solution (30 g/l) of an alkaline cleaner, Super Terj (DuBois Chemical), at 80°C for 15 minutes, followed by a 5 minute rinse in tap water at 43.5°C. Some samples were then immersed in a pickling bath (15 ml conc. HNO_3, 3 ml 49% w/w HF, 82 ml H_2O) at room temperature for 5 minutes. These surfaces are designated as PSHA. The anodization was performed in 5.0 M NaOH solution at 20°C and 10 V for 30 minutes over an area of 19.3 to 50 sq. cm. (3–9 sq. in.). The anodized surfaces were then rinsed in running tap water for 20 minutes and dried in an oven at 60°C for 10 minutes. No attempt was made to control the current density during anodization.

Surface analysis

SEM photographs were taken on a JEOL JSM-35-C electron microscope. Pretreated samples were punched as 0.95 cm (0.38 in.)

disks and sputter coated with gold, resulting in a 20 nm coating. The sample was photographed at 0 and 30 degrees tilt. Stereophotomicrographs were also taken.

Scanning transmission electron microscopy (STEM) photomicrographs were taken with a Phillips EM-420T electron microscope. Ti-6-4 foil samples, as received, were pretreated with sodium hydroxide anodization (SHA) with and without the pickle step. No additional gold coating was used.

XPS analysis was obtained on both a Kratos XSAM 800 spectrometer and a Perkin Elmer PHI 5300 ESCA system, using a Mg anode. Samples were punched as 0.95 cm (0.38 in.) disks and scanned from 0 to 1200 ev. Narrow scans were routinely made on any significant peaks noted in the wide scan spectrum. AES was done exclusively on a Perkin–Elmer PHI 610 scanning Auger microprobe with an electron beam voltage of 3 to 5 kV and a beam current of 0.05 μa. Narrow scan surveys were run from 300 ev to 600 ev. Samples were depth profiled by argon ion sputtering with an ion beam voltage of 4 kV, an emission of 25 ma and an ion beam current of 0.2 μa.

Acidity/basicity

A series of indicator dyes was used on the pretreated surfaces.[5] Bromthymol blue solution (LaMotte Chemical Products) was used as received. 0.01 g of Orange 1, Thymol blue (both Pfaltz and Bauer, Inc.), and Bromphenol blue (Arthur H. Thomas Co.) were each dissolved in 25 ml. of deionized water. 0.1 g of Bromcresol purple (Chemical Dynamics Corporation) was dissolved in 9.25 ml of 0.02 N NaOH and diluted to 250 ml. The color of each dye after contact with the dry pretreated surface was observed. A list of the dyes with the pH values is given in Table II.

Adhesive bonding and testing

Wedge samples were pretreated and bonded with FM-300 (American Cyanamid). The bonding cycle included heating from room temperature to 175°C (350°F) using 1.72 MPa (250 psi) bonding pressure. The 175°C temperature was held for 1.5 hours before cooling to room temperature and removing from the press. Two layers of epoxy were used with teflon film as spacers, yielding a thickness of 0.038 cm (0.015 in.). After bonding, a wedge made of Ti-6-4 was driven into one end of the sample, causing an initial crack to propagate. The sample was then placed in a hydrothermal environment held at 80°C. Periodically, the position of the crack was measured manually with a ruler.

RESULTS AND DISCUSSION

Surface topography

Photomicrographs were taken of both the SHA (sandblasted) and the PSHA (sandblasted and pickled) oxide surfaces. The pictures at 30 degree tilt are similar to those taken at 0 degree tilt but are different from those shown by Kennedy, *et al.*[4] A SEM stereomicrograph of the SHA surface is shown in Figure 1. The oxides of the sandblasted surfaces examined by Kennedy, *et al.*[4] appear to be more densely packed with the "nodular" formations than that of the sandblasted surfaces shown in Figure 1. Also the "nodules" appear to be sharper and more pointed in photomicrographs taken by Kennedy, *et al.*[4] than those in the present work.

Differences were also noted between the SHA and PSHA surfaces. The pickled SHA surface shown in Figure 2 appears to be a patchy version of the sandblasted SHA surface. The underlayer of the PSHA surfaces appears similar to a CAA surface.[6]

FIGURE 1 SEM stereophotomicrograph of SHA surface at 7800 × magnification.

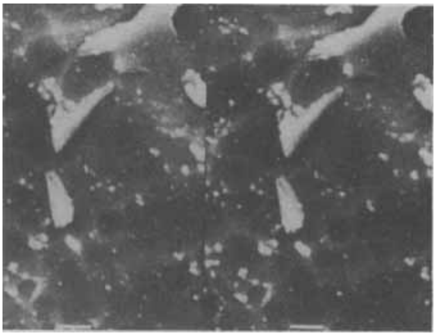

FIGURE 2 SEM stereophotomicrograph of PSHA surface at 7800 × magnification.

STEM photomicrographs, in Figures 3 and 4, clearly show the presence of macropores. The porosity of the PSHA surface appears to be more uniform than that of the SHA surface. The porosity present in the PSHA surface is quite similar to that of the CAA pretreatments as shown in Figure 5. The pore diameters are approximately 50 nm.[6]

The stated comparisons may be due to differences in the current density of each system, as the current density was not controlled during anodization. Initially the pickled surface will exhibit less resistance in the system because the barrier oxide layer has been etched away by the pickling process.

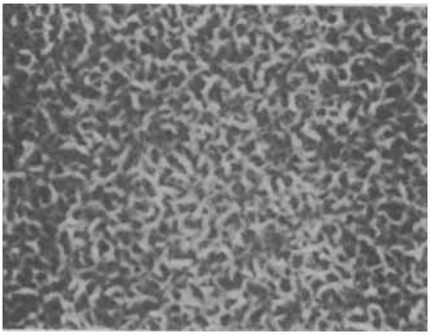

FIGURE 3 STEM photomicrograph of SHA surface at 100,000 × magnification.

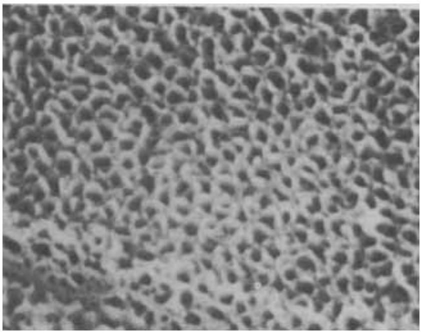

FIGURE 4 STEM photomicrograph of PSHA surface at 100,000 × magnification.

Surface composition

XPS and AES were used to determine the characteristic residuals left on the surface after treatment. Table I lists the XPS results from both electron spectrometers with the 0/Ti ratios reported using the curve fit portion of the oxygen peak corresponding to the 0-Ti bond. Note that in all cases the ratio is greater than 2. As expected, carbon, oxygen, and titanium were always found to be present with the titanium present in an oxidized form. Auger electron spectroscopy indicated phosphorous and calcium to be present on both surfaces with silicon present on only the SHA surface. X-ray photoelectron spectroscopy results from the KRATOS system showed the presence of phosphorous, calcium, fluorine and silicon.

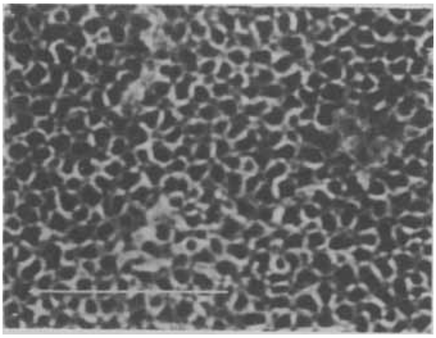

FIGURE 5 STEM photomicrograph of CAA surface at 100,000 × magnification.

TABLE I
XPS results from both electron spectrometers of SHA and PSHA pretreated Ti-6-4 surfaces

			SHA			
Photopeak	KRATOS B.E.	PHI B.E.	KRATOS A.P.	PHI A.P.	KRATOS O/Ti	PHI O/Ti
C 1s	285.0	285.0	31.1	23.5		
O 1s	529.9	530.0	46.4	67.4	2.7	4.6
Ti 2p	458.3	458.7	8.1	6.4		
F 1s	688.5 685.5	none	0.8	none		
Si 2p	102.8	102.9	8.5	1.1		
P 2p	133.2	none	1.4	none		
Ca 2p	347.1	347.3	3.8	1.7		

			PSHA			
Photopeak	KRATOS B.E.	PHI B.E.	KRATOS A.P.	PHI A.P.	KRATOS O/Ti	PHI O/Ti
C 1s	285.0	285.0	36.5	28.8		
O 1s	530.5	530.3	45.1	63.5	2.8	5.4
Ti 2p	458.8	458.7	10.9	6.0		
F 1s	689.1	none	1.4	none		
Si 2p	102.3	trace	1.4	trace		
P 2p	133.7	none	1.9	none		
Ca 2p	347.4	347.4	2.8	1.7		

The atomic fraction of silicon was smaller on the PSHA surface than on the SHA surface. The PHI XPS system showed a similar variation in the silicon atomic fraction. Phosphorous and fluorine were not detected with the PHI system, however, probably due to differences in the sensitivities of the two systems.

The silicon is believed to originate from the material used during the sandblasting step and is subsequently etched away in the pickling step. The presence of the other residuals can be explained by the tap water rinse. It is interesting to note that no sodium is detected by either XPS or AES.

Narrow scans, from 300 to 600 ev, were run to investigate that stoichiometry of the oxide surface. Solomon and Baun have shown that peaks between 400 and 420 ev are characteristic of Ti, TiO and TiO_2.[7] Both SHA and PSHA surfaces appear to match the spectra of TiO.

Oxide surfaces were depth profiled using AES. The time required to profile through the SHA oxide layer is significantly longer than that required to profile through the oxides created by CAA. Where CAA surface requires three minutes to reach the intersection of the O and Ti signal, the SHA surface requires 64 minutes. From the present understanding of titanium oxide thicknesses, an oxide approximately twenty times thicker than CAA oxide is not realistic. Therefore, it can be concluded that the sputter efficiency of the SHA oxide is much lower than CAA.[8]

Acidity/basicity

The results from the indicator dye tests are listed in Table II. The SHA surface is clearly basic with a surface pH greater than 8.0. The basic SHA surface strongly contrast the acidic surface left by a chromic acid anodization.[6]

TABLE II
Indicator dye results on SHA and CAA pretreated Ti-6-4 surfaces

	Bromphenol Blue	Bromcresol Purple	Bromthymol Blue	Orange 1	Thymol Blue
pH	3.4–4.6 Y>B	5.2–6.8 Y>B	6.0–7.5 Y>B	7.6–8.9 O>V	8.0–9.6 Y>B
SHA	blue	blue	blue	d. orange	d. green
CAA	yellow	yellow	orange	orange	orange

Y = yellow
B = blue
O = orange
V = violet

Wedge testing

The bonded SHA pretreated surface was exposed to 80°C, 95% rh and 80°C water immersion. In both cases, no crack propagation was observed in a 30 day period. The CAA pretreated surfaces exhibited the same behavior, while other pretreatments such as the phosphate fluoride acidic etch show complete failure within hours under the same conditions.[8]

CONCLUSIONS

The purpose of this paper is to expand the study of SHA pretreated surfaces with emphasis on surface analysis. The SHA pretreatment for Ti-6-4 appears to be a competitive pretreatment to CAA, as SHA produces a porous oxide of similar durability to the CAA porous oxide. In addition, no heavy metal or harmful acids such as HF, are used in the pretreatment. More work will be done to characterize the SHA oxide as well as its adhesive bonding performance.

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