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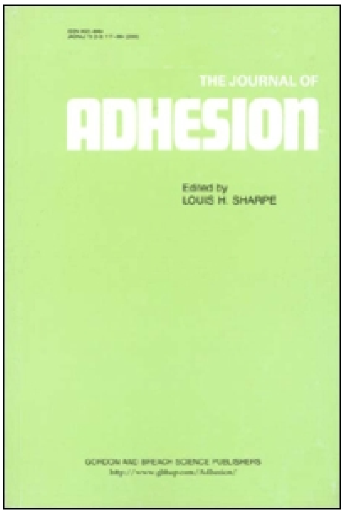

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A Surface Treatment for Ti–6Al–4V

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A simple nonchromate surface treatment that was developed for aluminum alloys (STAB (3)) has been found to provide Ti–6Al–4V, bonded with epoxy adhesives, with good hydrothermal endurance. The simplest form of the treatment is to degrease, dip in caustic soda, hard (*i.e.*, forceful) spray-rinse and dry. Although STAB (3) for aluminum was satisfactory with a room temperature dip in caustic soda, the solution temperature should be greater than 40°C for Ti–6Al–4V. A steel wool scrub prior to the NaOH dip enhances durability. Surface property measurements following the surface treatment indicate that a porous oxide layer is formed on top of a 300Å barrier layer. The durability of this treatment is attributed to mechanical interlocking between the adhesive and the porous oxide (hydroxide) and to the chemical stability of the oxide (hydroxide) under hydrothermal stress.

INTRODUCTION

Surface characterization, bond strength and endurance of Ti–6Al–4V have been reported[1–16] for many surface treatments. A recent surface treatment for aluminum bonding (STAB (3))[17] has been developed at the Rockwell International Science Center. This simple, inexpensive, nonchromate, room temperature treatment involves a 3–10 min dip in caustic soda, rinse and dry. The success of the treatment for Al was attributed to the formation of a porous hydroxide layer that is stable to hydrothermal stress and provides mechanical interlocking with the adhesive. The same treatment has proved successful with Ti–6Al–4V, with some modifications, and is reported here.

EXPERIMENTAL

Process parameters

Samples of Ti–6Al–4V (1 × 4 × 0.050 in) were scrubbed with steel wool in TMC (trichlorotrifluorethane/methylene chloride) solvent, ultrasonically degreased in TMC solvent, dipped in NaOH solution (deionized water), rinsed and dried. The samples were then dipped in a corrosion inhibiting primer from American Cyanamid, Stamford, CT, U.S.A. (BR127 primer), dried for 0.5 h and cured in an oven at 121°C for 1 h. For some samples, the steel wool scrub was omitted and, for some, the primer was omitted.

Bonding was performed with Hysol EA9628H, a 121°C curing epoxy (Hysol, Industry, CA 91749, U.S.A.). Wedge specimens (ASTM D3762-79) were prepared by forcing a 1 × 1 × 1/8 in aluminum wedge 1 in into the joint, measuring the initial crack length a_0 and placing in a humidity chamber at 60°C, 100% relative humidity (RH). The crack extension was then monitored as a function of time.

ENDURANCE RESULTS

Without steel wool scrub

Figure 1 shows plots of initial crack a_0 and a_0 + crack extension (Δa) in the humidity chamber for 1 h (□) and for 24 h (○) *vs.* NaOH concentration. Figure 1a is for 10 min dips at 60°C, after degreasing in TMC but not scrubbing with steel wool. Without the NaOH treatment (zero NaOH conc.), the initial crack a_0 is about 3 in. At 60°C and NaOH > 200 g/l, a_0 reduces to about 1 in and failure is cohesive at the bond line center. At 60°C, the crack extension, Δa, decreases to about 0.5 in for NaOH > 400 g/l. Most of the extension occurs in the first hour, as noted by the small increase of the 24 h (○) data points beyond the 1 h (□) data points. At 80°C, in Figure 1b, a_0 is slightly lower ($a_0 \sim 0.9$ in) and constant for NaOH > 100 g/l. The crack extension is also less, $\Delta a \sim 0.2$ in in 1 h and about 0.3 in in 24 h for NaOH > 200 g/l.

Figure 2 shows the effect of dip time in 600 g NaOH/l, at 60°C (Figure 2a) and 80°C (Figure 2b). At the highest NaOH concentration (600 g/l), the initial crack is about 1 in at 60°C and about 0.8 in at 80°C dip temperature. In either case, 10 min is adequate to obtain <0.5 in extension in 24 h. The results in Figure 2a and the data at 30 min dip time in Figure 2b, were obtained without the BR127 primer. All the rest of the experiments were performed with the primer. Although the amount of data for the effect of primer is meager, the results indicate that for Ti–6Al–4V after the STAB (3) treatment, the durability does not rely on the presence of the primer. This is contrary to the result for aluminum.[17]

With steel wool scrub

Figure 3 shows a plot of the initial crack length a_0 plus the crack extension after 24 h in the humidity chamber, as a function of the NaOH concentration with prior steel wool scrubbing. Splitting the wedge bonds prior to placing in

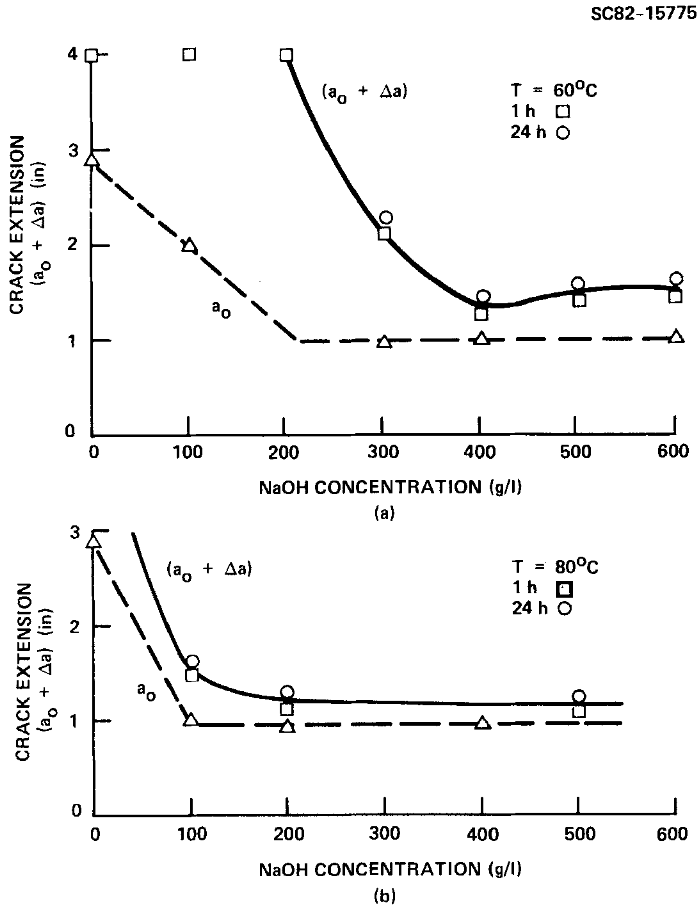

FIGURE 1 Crack extension *vs.* NaOH concentration for Ti–6Al–4V at 60°C (a) and 80°C (b) (no steel wool scrub).

the humidity chamber caused a 0.96 ± 0.08 in crack, a_0, to form, with center-of-bond cohesive failure. Without the NaOH surface treatment (steel wool scrub and degrease only), the crack growth in 24 h is about 1.4 in whereas, after a 10 min dip in 100–200 g NaOH/l at 80°C, the crack growth is only 0.14 in in 24 h. Figure 4 is a plot of crack extension at 1 h and 24 h as a function of NaOH solution temperature, for a 10 min dip in 200 g NaOH/l. Figure 4 indicates that bond durability is satisfactory for $T > 40°C$, for the 10 min dip and 200 g/l concentration.

A number of wedge test samples were tested at 60°C, 100% RH for 275 days.

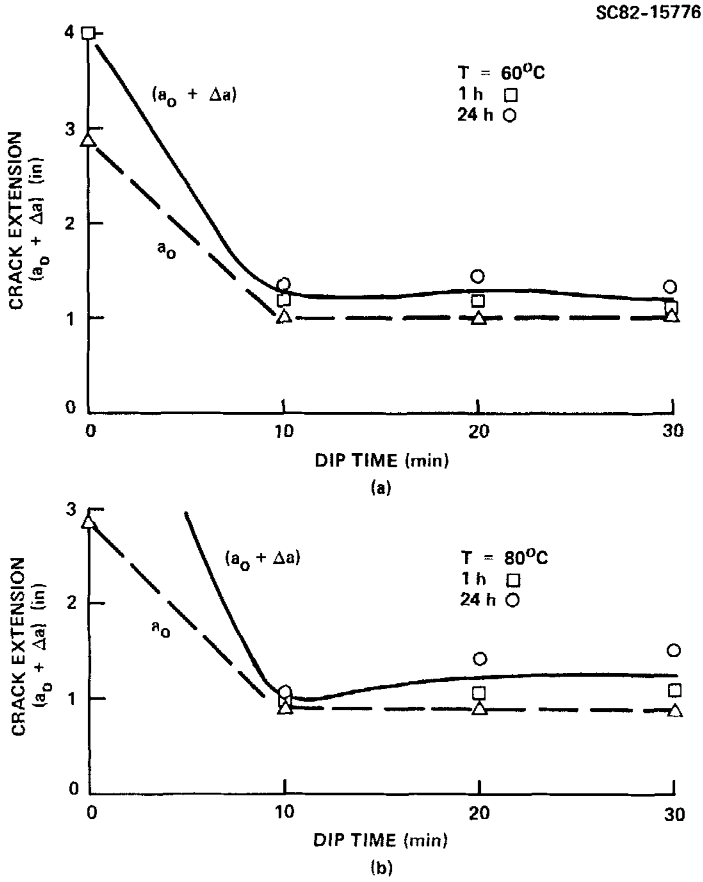

FIGURE 2 Crack extension *vs.* dip time for Ti–6Al–4V at 60°C (a) and 80°C (b) (no steel wool scrub).

The average of the data at each time interval are presented as solid points in Figure 5. The standard deviation from the mean at each interval is ±0.1 in. After 275 days, the crack has extended about 0.7 in, which is considered excellent endurance. These results are consistent with the results of Ditchek *et al.*,[8] who have divided the surface treatments of Ti–6Al–4V into three categories, depending on the ability of the interface to form a mechanical interlock with the primer or adhesive. In Figure 5, Group I is represented by the modified phosphate-fluoride (MPF) treatment which was shown[8] by scanning transmission electron microscopy (STEM) to produce no porous film. Endurance, or lack thereof, is governed by chemical stability. Group II is

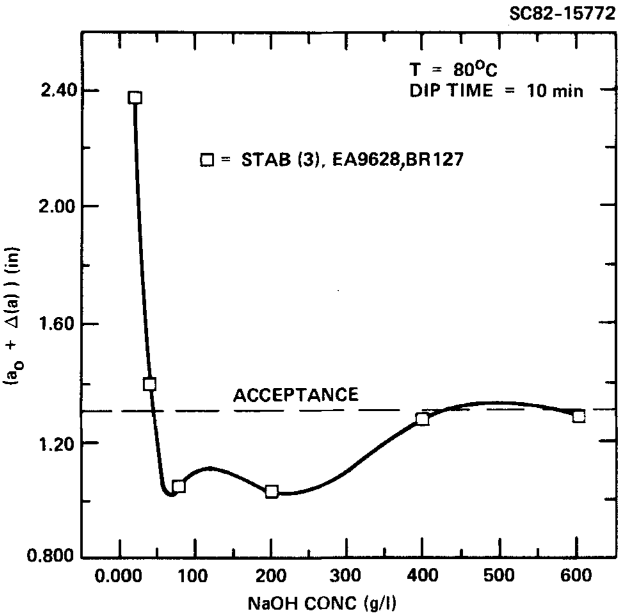

FIGURE 3 Crack extension *vs.* NaOH concentration for Ti–6Al–4V at 80°C (steel wool scrub).

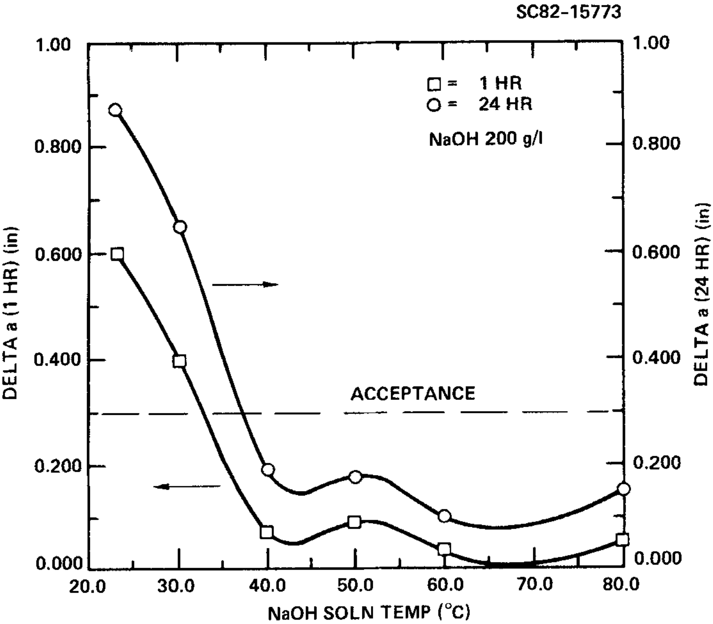

FIGURE 4 Crack extension *vs.* NaOH solution temperature.

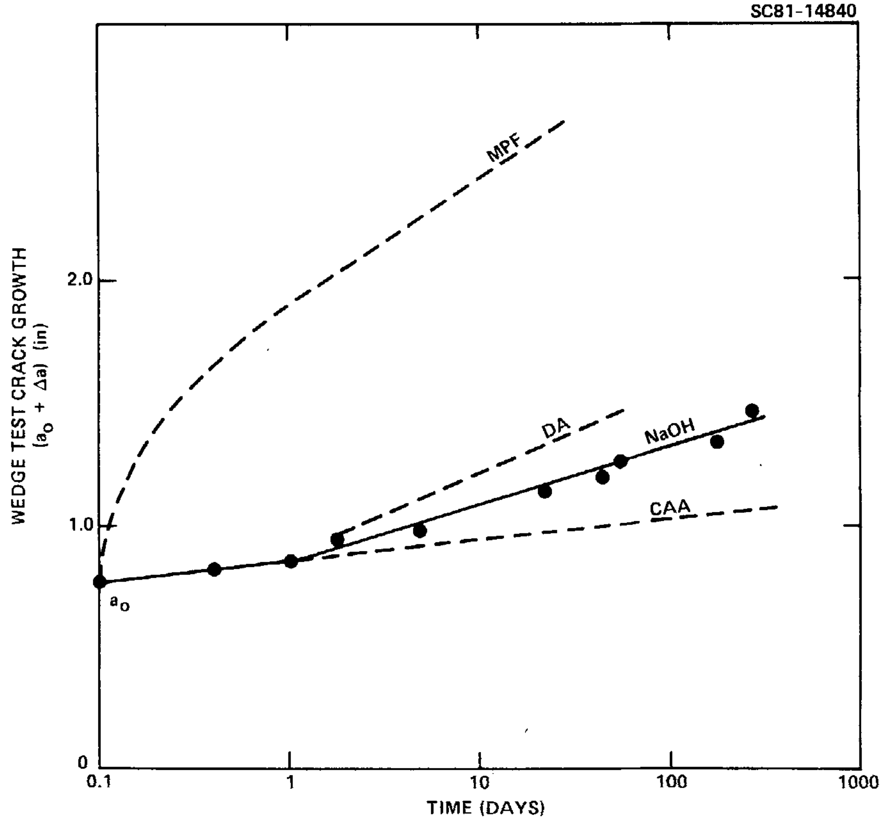

FIGURE 5 Long time crack extension and comparison to other treatments (dashed lines, from Ref. 8).

represented by Dapcotreat (DA) in Figure 5. This group showed macroroughness and some mechanical interlocking with metal protrusions. Group III is represented by the chromic acid anodize (CAA) which revealed microroughness. A similar microroughness was observed by Locke *et al.*[7] for the chromic acid-fluoride anodize, which appears similar to the film in Figure 6 for the NaOH treatment.

Other adhesives

Although most of the tests were performed with the 121°C curing EA9628H adhesive, some experiments were performed with another 121°C curing adhesive (*i.e.*, FM73, American Cyanamid) and a 177°C curing adhesive

TABLE I

Boundaries of process parameters that yield acceptable wedge test endurance

Parameters	Range	Remarks
Dip time at 80°C	> 10 min	
Soln temp. (at 200 g/l)	> 40°C	
NaOH conc. (at 80°C)	> 100 g/l	Caustic soda OK
Delay prior to rinse	8 min OK	Maybe longer
Dry step		N_2 or drip dry OK
Other adhesives		PL 729-3 and FM73 OK

(PL729-3, B. F. Goodrich, Akron, OH 44115, U.S.A.). For FM73, the initial crack length was the same as for EA 9628H (*i.e.* $a_0 \approx 1$ in), the crack growth in 1 h at 60°C, 100% RH, was 0.1 in and after 24 h, 0.2 in. For the higher temperature adhesive (PL729-3), the initial crack was 1.5 ± 0.1 in, due to the lower fracture toughness. The crack growth in 1 h was 0.05 in and in 24 h, 0.13 in. These results indicate the STAB(3) treatment modified for Ti–6Al–4V is satisfactory for adhesives other than EH9628H. Table I gives the process parameter boundaries that yield acceptable wedge test endurance. These boundaries are acceptable for normal factory processing.

SURFACE PROPERTIES

Figure 6 plots the time (in NaOH to yield the film thickness of the abscissa), the film refractive index, the photoelectron emission (PEE) and the surface potential difference (SPD). The instruments employed and the interpretation of their parameters are described in Ref. 18. In the first two or three minutes, the film grew from the initial 280 Å to about 700 Å, then grew approximately linearly with time to 2500 Å. Each set of experimental points is for a different Ti–6Al–4V sample. The dashed line in Figure 6 indicates the temperature (right ordinate) required to grow the oxide to the thickness (as indicated by the abscissa) by a 10 min dip in 200 g/l.

The surface potential difference decreased by about 0.3 V (*i.e.*, the Ti–6Al–4V work function increased by 0.3 V) upon the first few minutes of exposure to NaOH solution, then remained constant to 2500 Å. Although it is not shown in Figure 6, the contact angle for water was measured on each sample. The contact angle prior to the NaOH dip was 62° ; after each dip, rinse and dry, the contact angle was zero. Since the SPD and contact angle are specific to the outer atomic layer, the decrease in SPD is interpreted as due to the removal of

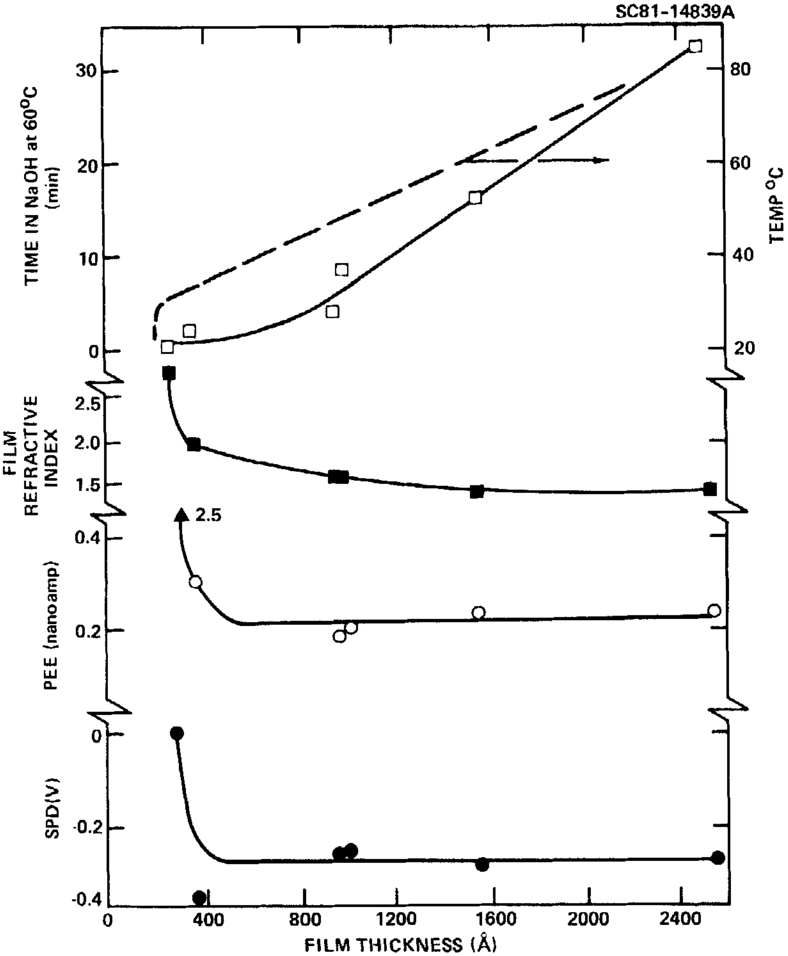

FIGURE 6 Surface properties *vs.* oxide film thickness for Ti–6Al–4V treated in 200 g/l NaOH solution.

organic contamination with positive end of the dipoles (hydrocarbon tails) pointing away from the surface.

The PEE also decreases dramatically (2.5 to 0.2 nanoamps) in the first few minutes and then remains constant at 0.2 namps as the film grows. The initial film growth attenuates the PEE but does not attenuate further as the growth becomes linear with time. This indicates the formation of an initial attenuation oxide barrier layer, followed by a porous nonattenuating oxide layer. This interpretation is supported by the change in refractive index from that for bulk

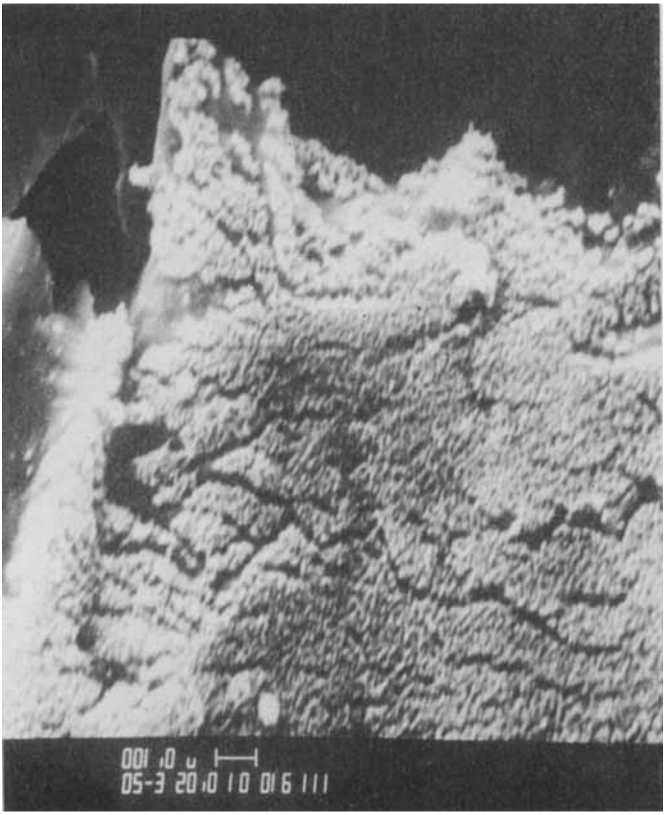

FIGURE 7 SEM picture of bent Ti–6Al–4V after the NaOH treatment.

TiO_2 of 2.7 to a low value (~1.4) that corresponds to a low density (porous) oxide. Further support is given by the SEM picture in Figure 7, for which the sample had been bent to fracture the oxide layer in order to estimate its thickness from a side view of layer particles. After a 30 min dip in 200 g/l NaOH at 60°C, a porous film is observed. The thickness of this film is estimated, from Figure 7, to be 2500 Å, in good agreement with the ellipsometer.

Hydrothermal stability

To check the chemical stability of the surface-treated Ti–6Al–4V, samples were exposed to the same process history for making adhesive bonds, but without the adhesive. Figure 8 is a plot of oxide film thickness, SPD, PEE and θ_{H_2O} as a function of process history. The solid points are for the sample that was given the 10 min dip in 600 g NaOH/l at 80°C, which yields very durable bonds, and the open circles are for a sample that was only steel wool-scrubbed in solvent, which yields very nondurable bonds.

The dramatic difference in film thickness after the NaOH dip, as compared to the degrease-only, is believed to account for the greatly increased bond durability for the NaOH treatment. The initial (as-received) film thickness is about 120 Å, which increases to about 210 Å after steel wool scrub in solvent. This 90 Å increase results from the exposure of fresh oxide-free metal by the abrasion. Exposure of the degrease-only sample to lab air for 30 min, 120°C oven for 60 min, and the humidity chamber for 2800 min increases the film thickness by only about 30 Å. The refractive index of the oxide film is normal for TiO_2 ($n_f \sim 2.7$), whereas the absorption index is very high ($\kappa_f \sim 0.5$) as compared to that for transparent oxide ($\kappa_f \sim 0$) [results not shown]. The large effective value of κ_f is due to the rough abraded metal and it remains constant. However, the NaOH-treated sample produces an 800 Å film with an $n_f \sim 1.4$ and $\kappa_f \sim 0$. The low effective value of n_f results from the porous nature of the film (see Figure 7), with index between 2.7 for dense TiO_2 and unity for air. The low value of κ_f indicates that the formation of the oxide film has smoothed the abraded metal surface. Exposure of the NaOH-treated sample to the oven at 121°C destroyed the porous structure, reducing the film thickness to about 200 Å, which remained constant with exposure to the humidity chamber, for some samples but not for others. The index of refraction of the oxide film changes from 1.4 to 2.7 (for dense oxide) and the absorption index remains low ($\kappa_f \sim 0.1$) due to the smoothed metal for those samples for which the humidity destroyed the porous film, but only to about 1.7 for those samples the porous film was not destroyed.

The abrasion-roughening increased the PEE from 0.2 nA to 1.6 nA for the degrease-only sample, which dropped to 1 nA during exposure to air for 30 min, then remained constant in the oven and humidity chamber. The large increase in PEE is due to the exposure of fresh metal, since the metal is photoemitting at the energy of the UV light ($\sim$5 eV), but the oxide is not. The oxide attenuates electron emission, causing the PEE current to decrease on exposure to air. Since the average oxide thickness only increases from 210 to 225 Å on exposure to air, the large increase and decrease in PEE must be due to a relatively small percentage of the surface that has enhanced emission (*e.g.*, sharp edges and points produced during abrasion). The sample treated in NaOH decreases PEE to about 0.2 nA, having removed sharp edges and points. The fact that the PEE is independent of the thick (800 Å) layer is consistent with the interpretation that the film is very porous. The base of the pores form a barrier layer, whereas the pores are transparent to electron

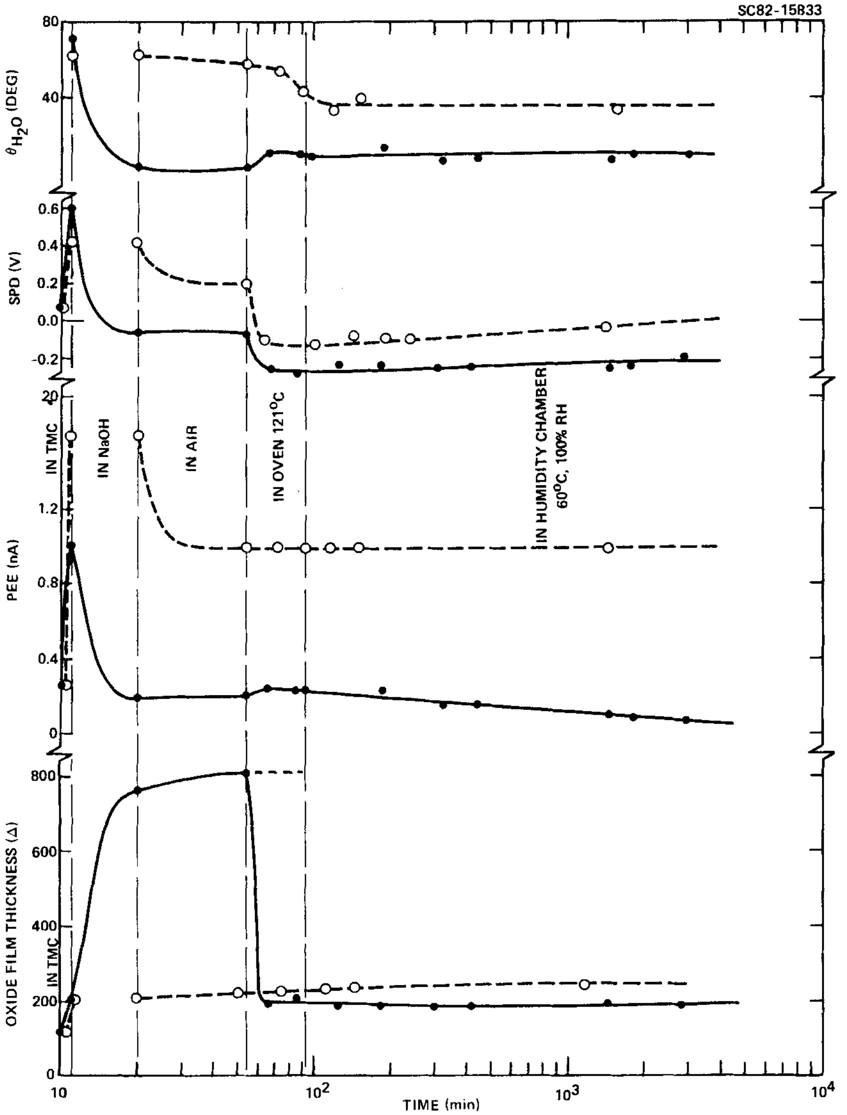

FIGURE 8 Change of surface properties as Ti–6Al–4V passes through the bonding and humidity process (but without adhesive present).

emission. Although the ellipsometric thickness of the oxide remains constant in the oven and humidity chamber, the PEE slowly decreases as the film restructures, becoming slightly thinner but more dense, thus increasing the attenuation index. The much higher constant value of PEE for the degrease-only sample, as compared to the NaOH-treated sample, is due to its much rougher surface.

Surface potential difference (SPD) can be theoretically expressed in its simplest form by the Helmholtz equation

$$\mathrm{SPD} = \pm 4\pi\mu\Gamma$$

where Γ is the surface concentration of dipoles and μ is the component of the dipole moment perpendicular to the surface. SPD is positive if the positive end of the dipole points away from the surface. Consequently, clean oxide usually has a more negative SPD than a contaminated oxide, since the oxygen is more electronegative than hydrocarbons. Abrasion of Ti–6Al–4V in solvent leaves a monolayer of solvent, increasing SPD, which is removed by the NaOH treatment and the oven heat treatment. Exposure to the humidity chamber only slightly recontaminates the surface, causing a small increase in SPD. The contamination-decontamination process is also reflected in the response of the water contact angle. The NaOH treatment reduces θ_{H_2O} from $\sim 70^\circ$ to $\sim 3^\circ$ and the oven heat treatment reduces the θ_{H_2O} from $\sim 60^\circ$ to $\sim 38^\circ$.

The conclusion from this surface analysis is that the oxide film on Ti–6Al–4V is rather stable in the humidity chamber for degreased-only or NaOH treated samples, *i.e.*, there is very little oxide growth or contamination. Although the porous oxide formed by the NaOH treatment is sometimes destroyed in the oven without adhesive coverage (the reason for this is not known), this is probably not the case with adhesive coverage, if the adhesive has filled in the pores. It is believed that the endurance of the NaOH treated samples is due to the acid-base interaction between functional groups in the adhesive and the Ti–6Al–4V surface, the stability of the oxide under hydrothermal stress and the mechanical interlocking of adhesive in the porous oxide.

SUMMARY AND CONCLUSIONS

Titanium alloy (Ti–6Al–4V) samples have been surface treated by a method which was previously used to give aluminum alloys excellent endurance under hydrothermal stress, but modified to optimize Ti–6Al–4V bonding. The treatment has the advantage of simplicity and does not involve carcinogenic chromates. For aluminum, the treatment involves a 3–10 min dip in room temperature caustic soda (or other NaOH concentrations), followed by a strong DI water spray-rinse and dry. For Ti–6Al–4V, the temperature and time must be increased, as per Table I, and it is advantageous to scrub the metal with steel wool prior to the NaOH solution dip. The surface properties (see Figures 6 and 7) indicate that the initial oxide film is about 280 Å thick and nonporous. Growth of another 400 Å or more of porous oxide provides a surface of sufficient chemical stability and mechanical interlocking to give good endurance for Ti–6Al–4V–Epoxy under hydrothermal stress.

It is concluded that the NaOH treatment reported here falls into Group III (Figure 5) and that the mechanism of endurance involves primarily mechanical interlocking between the porous oxide and the primer or adhesive, and the ability of this oxide to resist attack by humid environments.

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