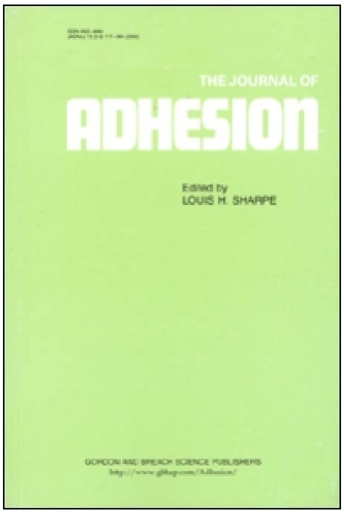

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Smith, Tennyson(1982) 'Mechanisms of Bond Endurance after Surface Treatment of Aluminum for Bonding (STAB) in Nonchromate, Alkaline Solution', The Journal of Adhesion, 14: 2, 145 — 174

To link to this Article: DOI: 10.1080/00218468208074898

URL: http://dx.doi.org/10.1080/00218468208074898

J. Adhesion, 1982, Vol. 14, pp. 145–174
0021–8464/82/1402–0145 $06.50/0

Printed in Great Britain

Mechanisms of Bond Endurance after Surface Treatment of Aluminum for Bonding (STAB) in Nonchromate, Alkaline Solution

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A search for a simple, inexpensive, nonacid, nonchromate surface treatment for aluminum alloys that would produce strong, durable adhesive joints under hydrothermal-stress, evolved from a hot water soak (STAB(1)) to a commercial detergent soak (STAB(2)), to a highly concentrated NaOH room temperature soak (STAB(3)). The first two treatments proved successful on some occasions, but not consistently reproducible. STAB(3) proved to be reproducible and inexpensive; it consists of a room temperature dip in highly concentrated sodium hydroxide (caustic soda will do) followed by a rinse and dry. The mechanisms of endurance failure for some cases of STAB(1) and STAB(2) and the consistent high endurance of STAB(3) are revealed by investigation of surface properties.

INTRODUCTION

Considerable work on the preparation of aluminum and its alloys for adhesive bonding has been reported. The industry standard for many years has been the FPL (Forest Product Laboratories) etch, which involves a degrease, alkaline clean, followed by a rinse, and exposure to sodium dichromate-sulfuric acid solution at 66°C for 13 min. Bowen[1] comes to the conclusion that the oxide film on FPL-etched Al 2024-T3 is 400 Å or less and is the hydroxide, boehmite. Weber and Johnston[2] as well as McCarvill and Bell[3] consider the fresh FPL etch oxide film to be γ-Al_2O_3. The very thin films make it difficult to make conclusive statements as to the hydration state. However, it is generally concluded that aging of FPL-etched surfaces in humid atmospheres causes a growth and transformation of the FPL oxide to a hydroxide. For example, Pattnaik and Meaking,[4] by sputter-time measurements, came to the conclusion that oxide films on FPL-etched aluminum are between 100 Å and 200 Å (which is in agreement with our sputter time, ellipsometry and photo emission results). They conclude that a layer of amorphous Al_2O_3 and γ-Al_2O_3 is formed, but with a thin outer layer of bayerite or boehmite after tap water rinse. Apparently the type of hydroxide and its structural strength depends on its thickness and conditions of growth. McCarvill and Bell[3] and Bowen[1] observed that aging of FPL-etched Al 2024-T3, in humid atmosphere, transformed the thin boehmite film to a thicker weak bayerite film which they postulate causes bond degradation. Although Bowen,[1] Bethune,[5] and we report that for aged samples, failure is in the oxide, Weber and Johnston[2] establish with ESCA that unaged FPL aluminum surfaces failed in the primer at the primer-metal interface, leaving <30 Å of primer. It should be noted that our results revealed failure in the oxide for thicker oxides (~ 500 Å), but we have not established this for thinner oxides, even after degradation by aging. We conclude that although hydroxide transformations may occur, more subtle processes are also probably involved. Bijlmer[6] used transmission electron microscopy (TEM) to examine stripped oxide films, and suggested a correlation between the appearance of the oxide at high magnifications and adhesive bonding behavior. More recently, Venables *et al.*[7] have used scanning transmission electron microscope (STEM) to obtain much higher resolution of the FPL-etched aluminum surface. They conclude that the oxide consists of 400 Å high oxide spikes that are about 50 Å in diameter. These spikes or protrusions are formed in a hexagonal array on top of a 50 Å barrier layer. They conclude that the excellent durability of the FPL-etched aluminum-epoxy adhesive joints is due to mechanical interlocking between the adhesive and these oxide spikes.

We have concluded that the nonuniformity of surface properties causes nonuniformity in bond strength, and that this nonuniformity is related to metallurgical nonuniformity rather than surface preparation. This conclusion is reinforced by the work of Weber and Johnston[2] who discovered that the FPL etch-rate was dramatically different on one side of a sample from that on the other.

McCarvill and Bell[3] studied the effect of time and type of water pretreatment on the bond strength of epoxy-aluminum joints, and conclude that the bond strength of unetched aluminum-epoxy joints, induced by tap and distilled water pretreatment at 10°C, increased to a maximum and then decreased as a function of immersion time. In distilled water, the maximum bond strength occurs after an immersion time of about 1 hr, after which the bond strength decreases. In the case of tap-water pretreatment, the maximum bond strength occurs at about 12 hr of immersion time. The bond strengths at the maxima found for the tap-water pretreated samples were greater than those found at the maxima for the joints pretreated in distilled water. Growth of the hydrated oxide bayerite was proposed as the controlling factor; the bayerite grows more rapidly and less perfectly in distilled water than in tap water.

Although McCarvill and Bell consider thick bayerite films to be weak, they believe that thin bayerite films are strong and promote adhesion. The higher bond strength for tap-water pretreatment was found to be induced by soluble cations of less than 0.8 Å radius: larger cations had no effect. They postulate that small soluble cations occupy cationic vacancies in the defect spinel structures of γ-Al_2O_3 and reduce the negative charge on the surface of the aluminum joints. Joints pretreated in 60°C tap water exhibited higher bond strengths than those pretreated in 60°C distilled water, as the growth of a thick, weak layer of bayerite was inhibited by large anions present in the tap water. Bell and McCarvill[3] also conclude from infrared analysis that no primary chemical bonds are formed between etched or unetched aluminum and an amine-cured epoxy resin, and that roughness only slightly increases bond strength.

Vedder and Vermilyea[8] have made a comprehensive study of the reaction of aluminum (and anodized aluminum) with water and they conclude, as do Bernard *et al.*[9] and Hunter *et al.*,[10] that the reaction between water and aluminum and water and anodic films on aluminum is essentially the same. The anodic film studied by Vedder and Vermilyea[8] was formed in 1% W/W ammonium borate solution at room temperature at 175 V. According to a review article by Tajima,[11] the anodic films formed in ammonium borate are non-porous α-alumina. Vedder and Vermilyea[8] conclude that the amorphous natural oxide, or the α-alumina, after anodizing, dissolves in water followed by precipitation of porous aluminum hydroxide (pseudo-boehmite). Pseudo-boehmite is distinguished from crystalline boehmite by its rapid formation and the exhibition of some evidence of crystallinity but a small particle size and a slow rate of crystallization. Vermilyea and Vedder showed that the transformation of amorphous oxide or anodic oxide to pseudo-boehmite is greatly inhibited by phosphate, silicate, arsenate, periodate, and tungstate ions, whereas chloride, nitrate, sulfate, bicarbonate, and permanganate and acetate ions have little influence, and citrate ions accelerate the attack. It may have been this information that prompted Bethune[5] to try phosphoric acid anodizing, and it is probably the presence of the phosphate ion that protects the anodic film from transformation to a weak porous film of pseudo-boehmite or bayerite.

The phosphoric acid anodize surface treatment[5] for aluminum alloys was thoroughly tested in the United States Air Force PABST program,[12] and was found to provide excellent endurance for aluminum-epoxy joints under hydrothermal stress. Other papers concerning preparation of aluminum for adhesive bonding can be found in Refs. 13–22.

The phosphoric acid treatment calls for an FPL etch prior to the anodize. However, because of the carcinogenic nature of chromates, various companies and government agencies have been attempting to find new durable nonchromate-containing systems which can be used to treat aluminum prior to bonding. The objective of this study was to discover a nonacid (nonchromate) surface treatment for Al 2024-T3 that would be both strong and durable.

Initial studies[23] indicated that a simple degrease and water soak process (STAB(1)) would provide strong durable joints. However, further testing revealed that this process was hard to reproduce on a consistent basis. A second process (STAB(2)) was discovered that was equally as simple, but was also difficult to reproduce. A third, even more simple process (STAB(3)), was discovered which did prove reproducible. This process eliminates the degrease step and involves no energy input (room temperature dip in superconcentrated sodium hydroxide). There are only three steps involved: dip in sodium hydroxide solution, rinse, and dry. This paper presents experimental data from which we developed the mechanisms of failure, in the case of STAB(1) and (2), and the mechanism of endurance in the case of STAB(3). Details of the experimental procedures and endurance results can be found in References 24 and 25.

This paper is divided into three sections, for STAB(1), (2) and (3). In each section experimental procedure, surface characterization, bond endurance and prebonding and post fracture analysis is discussed.

EXPERIMENTAL RESULTS

STAB(1)

Experimental procedure

STAB(1) involves a degrease step followed by a rinse and then exposure to 80°C stirred water for 10 min. It was originally discovered[23] that tap water would suffice for the hot water exposure. After checking the effect of cations and anions, it was decided that carbonate ions accounted for the improvement of tap water over deionized (D.I.) water. A number of solvents were tried for the degrease step. Ultrasonic degreasing in 9 parts solvent (Shell Sol. 140EC) plus 1 part concentrate (trade name "Gunk") proved best. If D.I. water was used, K_2CO_3 was added until the pH was ~ 9.8 at room temperature.

Bond strengths were measured with the lap shear test (ASTM D-1002), and durability under hydrothermal stress (60°C, 100% RH) was measured with the wedge test (ASTM D3762-79). Adhesive joints were made between the aluminum alloy and 121°C-curing, modified-epoxy, film adhesives (*i.e.*, Hysol-EA9628H *and* American Cyanamid-FM73). After surface preparation, the samples were primed by dipping in BR127 (American Cyanamid) or EA9210H (Hysol). The primed samples were cured for 1 hr at 121°C prior to placing the joints to be bonded in a heated platen (121°C) press at 50 psi for 1 hr. These bonding and testing procedures were used for all surface preparations reported here.

Surface characterization

Figures 1 and 2 show Auger electron spectrograms (AES) for as-received, STAB(1), STAB(2) and STAB(3) treated surfaces of Al 2024-T3. Figures 3 and 4 show Ar^+ sputter profiles for each treatment.

The alloy elements Al, Mg and Cu as well as oxygen, of the oxide, and some surface contamination are observed. Figure 1a is for the as-received Al 2024-T3 after 4 min of sputter etch. The appearance of the 60 eV neutral Al peak at about 3.5 min (see Figures 1a and 3a) is probably due to penetration of the thin ~280 Å oxide film on the as-received sample, although it may be due to reduction of the oxide by the electron and Ar^+ beams.[26]. For the thicker hydroxides formed by STAB(1), (2) and (3), no 60 eV peak is observed.

Auger electron spectrograms (AES) of Al 2024-T3 samples after STAB(1), (see Figure 1b) using tap water, reveal the surface to consist primarily of aluminum oxide or hydroxide with Na, N, Cl impurities from the water and Mg, Cu, Si, and Fe alloy constituents. The major contaminant at the outer surface contains carbon. The Ar^+ sputter profile can be seen in Figure 3b. After STAB(1), but with K_2CO_3 in D.I. water, the carbon peak is much smaller at the surface but distributed at higher concentrations through the oxide and the impurities N, Na, Cl, and alloy constituents Si, Cu and Fe are not present. Magnesium is present but at very low concentration. There is no evidence of potassium.

The initial carbon peak is about twice as high for STAB(1) with tap water as for STAB(1) with CO_3^{2-} or as-received. In each case (except STAB(1) with CO_3^{2-}), the carbon is mostly removed within about 2 min. In the case of STAB(1) with CO_3^{2-}, the Auger peak-to-peak height (APPH) has only slightly decreased after 5 min sputter (see Figure 3b). This may indicate some carbonate incorporation within the hydroxide for STAB(1) with CO_3^{2-} in solution (this is also noted for STAB(3), Figure 4b, but not for STAB(2), Fig. 4a).

The surface properties measured by ellipsometry (Δ), photoelectron emission (PEE), surface potential difference (SPD), and water contact angle (θ_{H_2O}) are rather erratic for STAB(1). (These techniques have been described in a

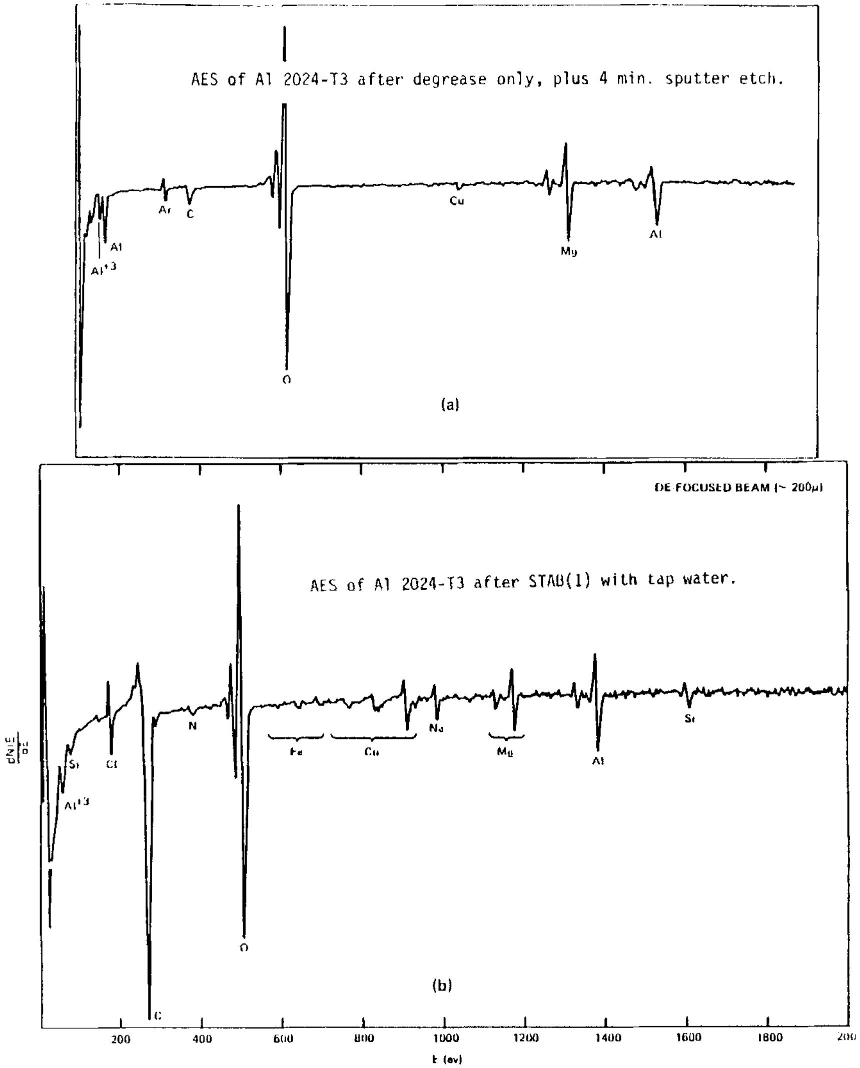

FIGURE 1 a) Auger electron spectrogram (AES) of Al 2024-T3 after degrease only, plus 4 min sputter etch with Ar^+; b) AES after STAB(1), with tap water.

previous paper.[27]) This indicates that the hot water reaction with aluminum is very sensitive to the surface condition of the aluminum, and is consistent with the poor reproducibility of bond strength and endurance.

In order to discover relationships between physical and chemical properties of surface films and their subsequent application for adhesive bonds of high strength and durability, a number of surface properties have been measured.

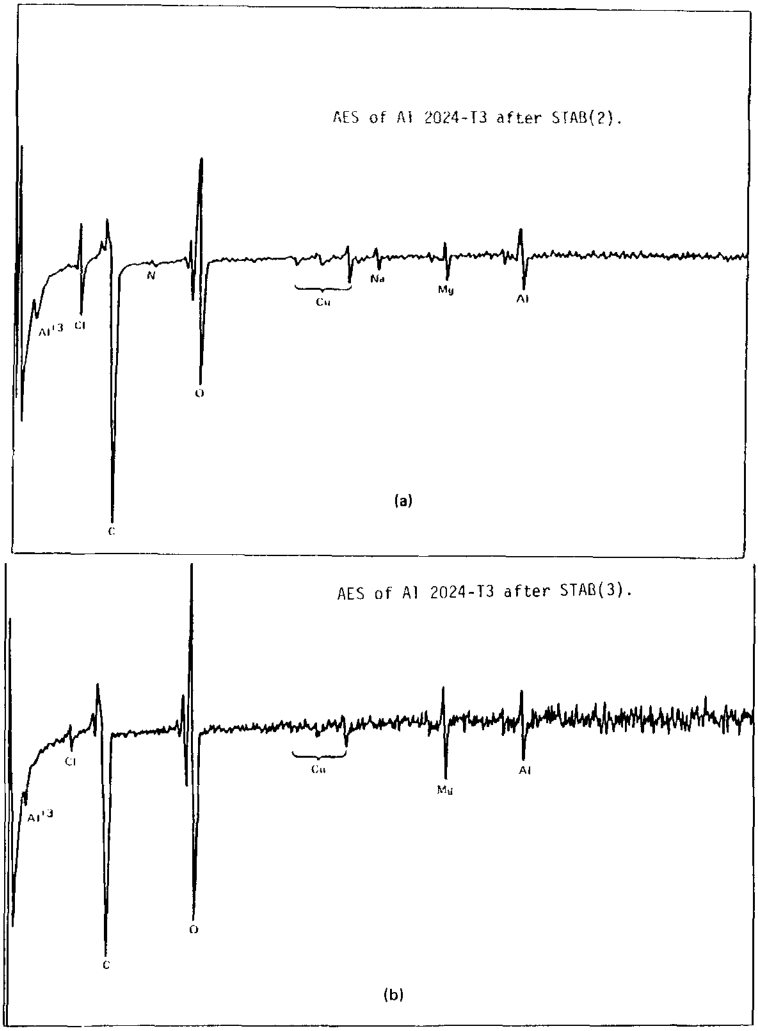

FIGURE 2 a) AES after STAB(2); b) AES after STAB(3).

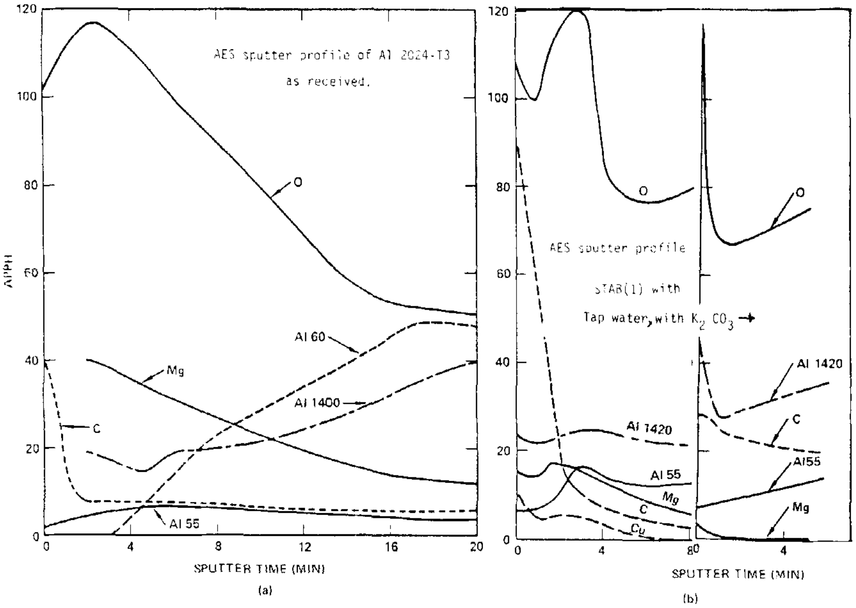

FIGURE 3 Sputter-etch profiles (Auger peak-to-peak height, APPH) after a) as-received, b) STAB(1) with tap water, and with K_2CO_3.

The process parameters are time in solution, temperature of solution, pH of solution, and ionic concentrations. The general strategy involved comparison of film properties that provide poor adhesive bond strength and endurance with those that provide good adhesive bond strength and endurance, in order to determine the optimum surface conditions for optimum joints. The following results indicate that the approach is fruitful.

SEM pictures (see Figure 5) of aluminum exposed to 96°C deionized water and 50°C deionized water indicate that long exposures provide thick enough films to produce a well developed morphology in each case. The 96°C water produces boehmite with the orthorhombic plate-like structure, whereas the 50°C water produces bayerite with the monoclinic cone-like structure. The interesting feature is that beneath the well-formed crystallites is a uniform layer of pseudo-boehmite[8] or bayerite that appears very porous or foamy. This is more evident with the 50°C (bayerite) than with the 96°C (boehmite) samples. To illustrate which of these crystalline structures is most advantageous for adhesive bonds, Figure 6 shows a sharp decrease in lap shear bond strength (σ) at the temperature transition from bayerite to boehmite. Values of $\sigma = 4500 \pm 500$ psi correspond to the cohesive strength of the adhesive used, and failure was observed to be cohesive in nature. Lower values of σ correlate with interfacial or partial-interfacial failure. All of the samples represented in Figure 6 were exposed for 10 min. The samples for Figure 7 were exposed for different lengths of time at 80°C, and the oxide film thickness was determined by ellipsometry after these exposure times. Figure 7 shows that below about 1000 Å, the film is stronger than the adhesive because these test specimens failed by cohesive failure. Beyond 1000 Å the bond strength decreases with film thickness.

Figure 8 compares the surface properties of films formed by different times of exposure in D.I. water and tap water. It was observed that additions of cations and anions to D.I. water had little effect on bond strength, except for those compounds that contained carbonate ions. Tap water (which contains CO_3^{2-}) and D.I. water with added carbonate ions inhibit the growth of the aluminum hydroxide (boehmite) film to about 1000 Å. The film formed in D.I. water is irridescent and transparent. About 500 Å of hydroxide forms in the first minute, with a corresponding sharp decrease in PEE, SPD, and water contact angle. According to Ref. 27, the decrease in PEE indicates the film is electron attenuating; the decrease in SPD indicates a change in outer dipole

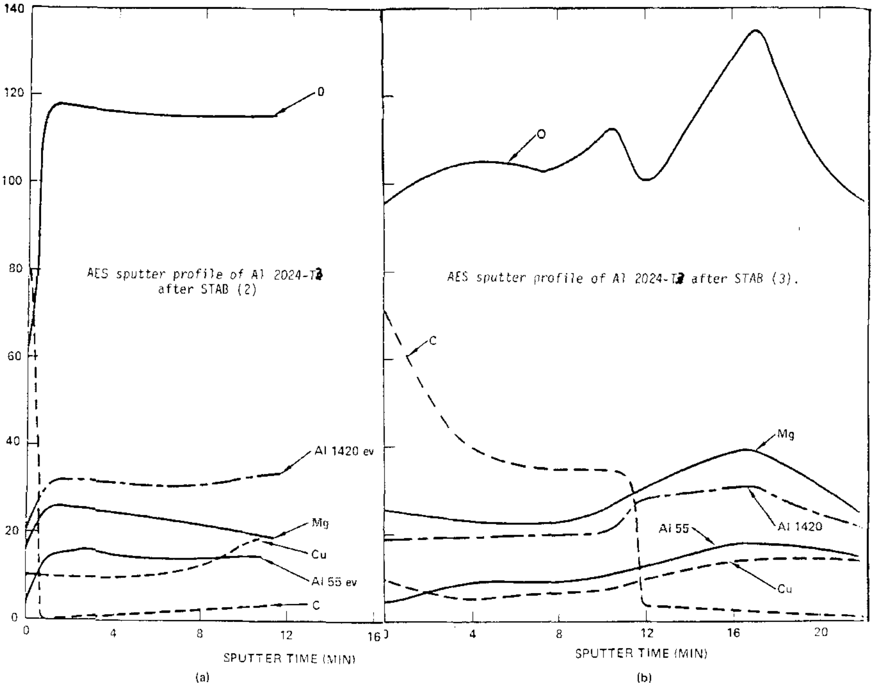

FIGURE 4 Sputter-etch profiles, a) after STAB(2), b) after STAB(3).

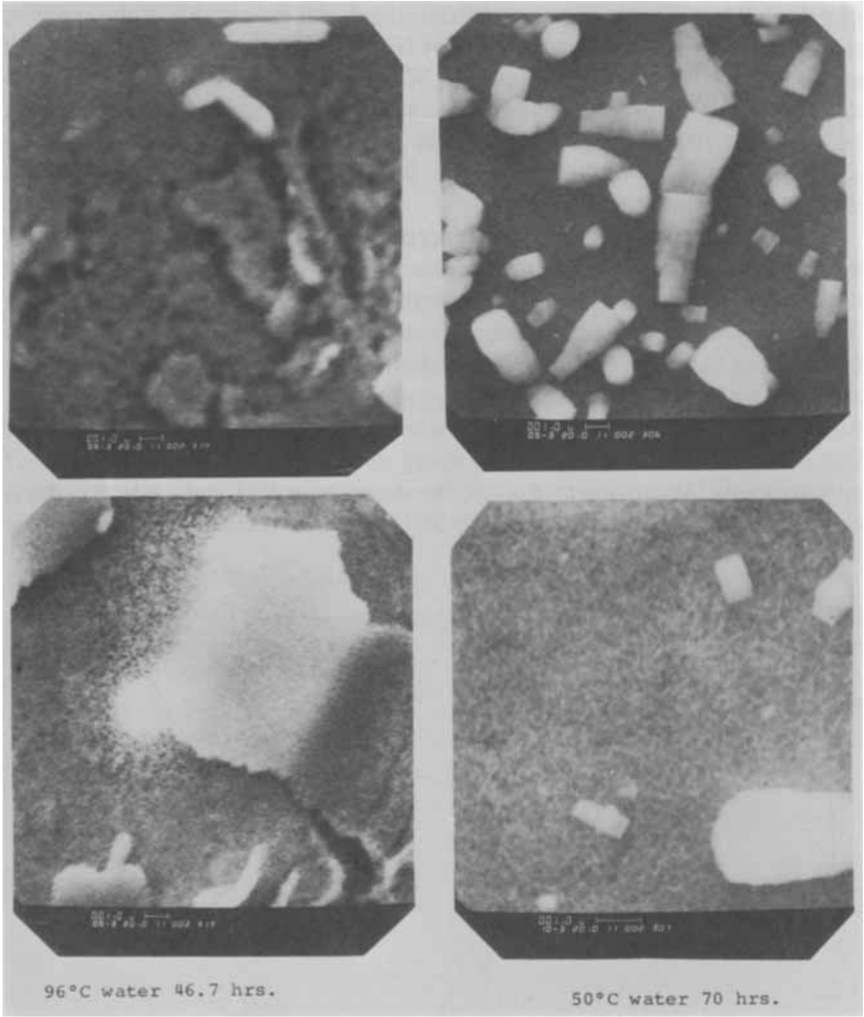

FIGURE 5 SEM pictures of aluminum after reaction with DI water at 90°C (left) and 50°C (right) for long periods.

nature (toward a surface with molecules having fewer positive ends pointing away from the surface). This is consistent with the lowering of θ_{H_2O} toward zero, which probably indicates removal of organic contamination. All of these properties are different for tap-water or carbonate solutions. The increase in PEE for a tap-water soak indicates the formation of less attenuating or an emitting film; the SPD and θ_{H_2O} decrease more gradually than for D.I. water.

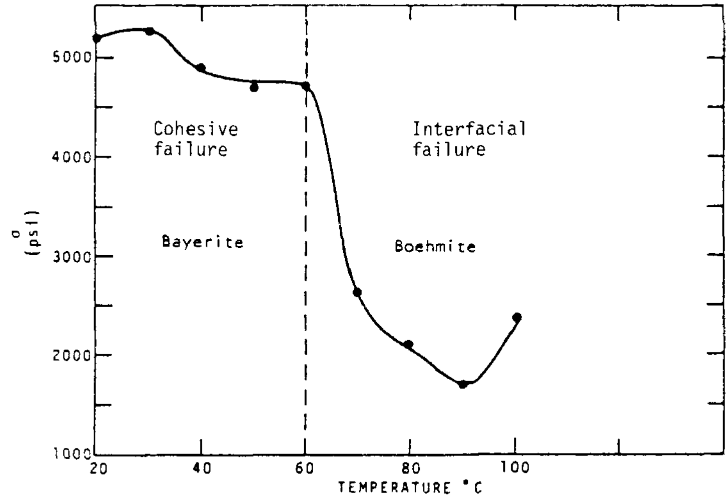

FIGURE 6 Lap shear strength as a function of the crystalline form of the aluminum oxide layer on the adherend before bonding.

Simple peel force tests (Scotch tape pulled in 180° peel) and contact angle measurements were performed to see how the results of these measurements were modified by the pH of the carbonate solution used for the soak. The aqueous carbonate solution (2.5×10^{-5} M K_2CO_3) had its pH adjusted with KOH and HCl. At low pH, θ_{H_2O} was high and the peel force was low. In the neutral and basic region (pH 5–10), θ_{H_2O} was low and the peel force was high. At high pH (>11), θ_{H_2O} increased and the peel force decreased. At this point it

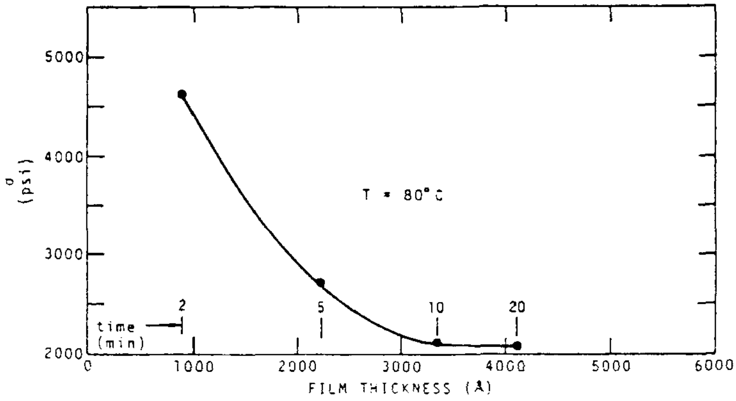

FIGURE 7 Lap shear strength of adhesive bonds formed on aluminum surfaces with oxide layers of various thicknesses.

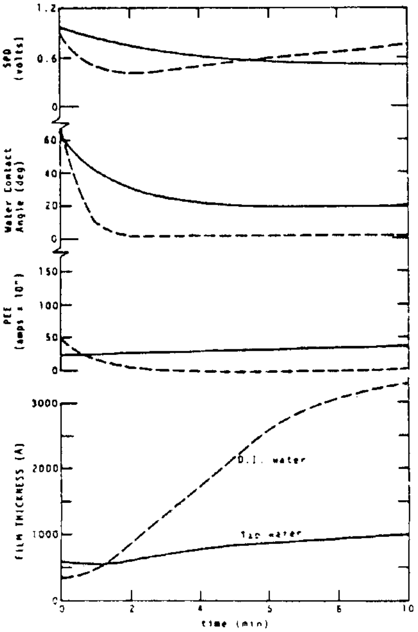

FIGURE 8 Variation of surface-layer-sensitive physical measurements as a function of time at which an aluminum surface is exposed to deionized water (D.I.) and ordinary tap water.

is not known if the contact angles are related to inherent properties of the hydroxide or to contamination of the hydroxide. This behavior may be an example of acid-base interactions as described by Bolger and Michaels.[28] They use the isoelectric points (IEPS, *i.e.*, the pH at zero point of charge reported by Parks[27]) of metal oxides and dissociation constants of organic acids and bases to predict the stability of the interaction between oxides or hydrous oxides with organic acids and bases. According to Ref. 28, the interaction of an organic acid with an oxide base should only be stable for $pK_{A(A)} < pH < IEPS$. Since the functional groups in the Scotch tape adhesive are the carboxyl groups of acrylic acid, $pK_{A(A)}$ should be close to that of acetic acid ($pK_{A(A)} \sim 5$, from Table IV, Ref. 28). If the IEPS of the aluminum hydroxide formed by STAB(1) is pH ~ 11, then the effect of pH on the peel test is predicted. Experiments to measure the IEPS after STAB(1), are needed to verify this concept.

Bond strength and endurance

For comparison with STAB, the FPL surface treatment gave crack growth of ~0.76 cm (~0.3 in)/24 hr, and phosphoric acid anodize (PAA) gave crack

TABLE I

Surface properties and resultant endurance for treated Al 2024-T3

Treatment	Film thickness (Å)	SPD (V)	PEE (nA)	θH_2O (deg)	Wedge test Crack growth cm/24 hr (60°C, 100% RH)
As received	280	0.7	0.15	60–90	9
STAB(1)	2000	0.1–0.4	0.02–0.7	5–60	0.25–9
STAB(2)	1600	−0.3	0.5	60	1–6
STAB(3)	4000	0.1	0.8	6	0.51
FPL-etch	200	0.45	10.0	2	0.76
PAA	5000	−0.2	0.08	2	0.25

growth of ~0.25 cm (~0.1 in)/24 hr, for the wedge test results, in our laboratory with Hysol EA9628 and Al 2024-T3 (see Table I). The original STAB(1) research[23] found that Al 2024-T3 and Al 7075-T6 gave strong lap shear strengths of ~34.4 MPa (~5 ksi) with cohesive failure and wedge durability tests of 0.25 cm (0.10 ± 0.05 in)/24 hr for EC2214 adhesive (3M Co.). These results looked excellent, but further work revealed the process to be nonreproducible, because acceptable results would be obtained on some occasions but not on others, for no apparent reason.

Prebonding and post fracture analysis

To examine the interface after the wedge test humidity exposure, the couples were split apart and about 0.5 cm of the 11.24 cm (6 in) specimen was cut out without disturbing the surface to be examined. The surface to be examined was the region of debond during crack growth in the humidity chamber. The cut-out piece was next bent until it failed, then mounted and gold deposited for SEM. Four surfaces were examined with SEM: the metal (with its hydroxide) that had debonded during the wedge test, the metal that did not debond during the wedge test but did debond on bending of the cut-out piece, and the mating adhesive to these surfaces. Figure 9 is an SEM picture of a STAB(1) surface prior to bonding, and Figure 10 is an SEM picture of the metal debond region of a wedge test that was good (~0.76 cm (0.3 in)/24 hr) after STAB(1). Figure 9 reveals the cellular porous structure of the hydroxide, and in Figure 10, failure appears to be in the primer-hydroxide interface. Figure 11 shows the metal surface that did not debond during the wedge test but fractured during metal bending. Again the failure is at the hydroxide-primer interface; failure had occurred in the primer, leaving primer embedded within the hydroxide.

Figure 12 is of the debond region of a joint after STAB(1) which was fair with regard to the wedge test (1.8 cm (0.7 in)/24 hr). The low magnification shows

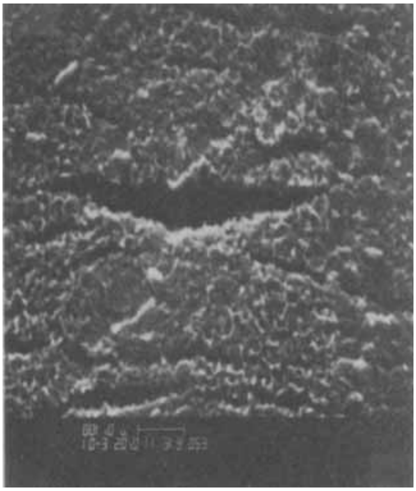

FIGURE 9 SEM micrograph of Al 2024-T3 after STAB(1).

FIGURE 10 SEM picture of the debond region of a good wedge test joint (STAB(1)).

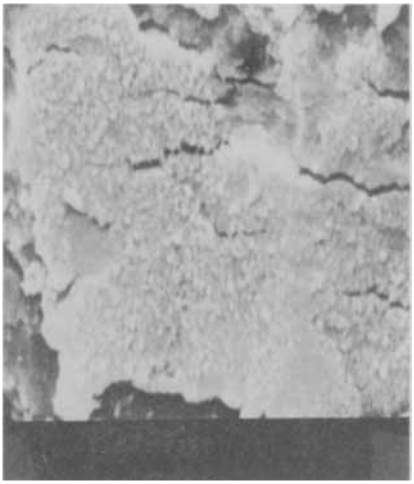

FIGURE 11 SEM picture of fracture during metal bending of a good wedge test joint (STAB(1)).

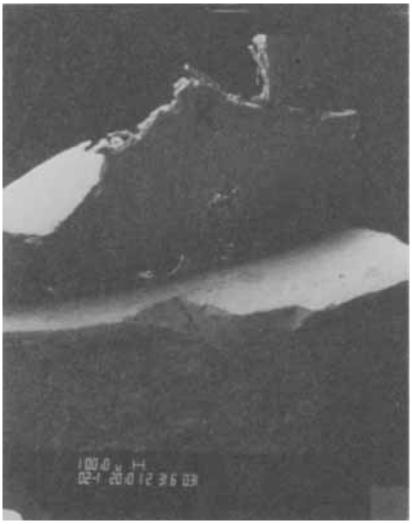

FIGURE 12 SEM picture of debond region of a medium wedge test joint (STAB(1)).

the adhesive peeled away from the metal during metal bending. The holes in the adhesive layer were caused by gas bubbles that are found in nearly every hexagonal cell outlined by the nylon scrim. If the bubbles are excessively large, the thin adhesive (or primer) layer tears away from the adhesive layer and remains on the adherend, and a hole is left in the adhesive film. Figure 13 reveals the mating adhesive surface, in the region marked by an × in Figure 12. The adhesive appears rather smooth and untorn, but a thin (2000–3000 Å) layer of hydroxide has been transferred from the metal. For example, Figure 14 shows the mating metal surface. The main feature is the layered hydroxide along with large particles of adhesive (upper left hand corner). Failure appears to be primarily in the hydroxide lamellae.

Figures 15 and 16 are for a wedge test that was bad (~3.0 cm (1.2 in)/24 hr). In Figure 15, large pieces of primer remain on the surface in the debond region. They seem too big to be formed by bubbles, but are probably due to poor contact between the primer and adhesive. Figure 17 is a larger magnification of the region 55 in Figure 16. The peeled back piece of primer (region 59) in Figure 16 and the enlargement of this region in Figure 18 reveals failure between lamellae in the hydroxide film; a layer of hydroxide has been transferred to the primer.

Apparently STAB(1) forms a layered structure of hydroxide with a porous outer layer in which the primer becomes mechanically attached. In some cases, separation between these layers causes crack growth under hydrothermal stress, making STAB(1) unreliable.

STAB(2)

During the study of the effect of various degreasing steps for STAB(1), it was discovered that a commercial cleaner MICRO† appeared to give considerable improvement in bond durability. Because of the simplicity of this treatment, an effort was expended to explore it in more detail.

Experimental

STAB(2) involves a degrease followed by room temperature soak in a solution of 60 ml of MICRO in 1 liter of water. This solution has a pH of about 9.8, as for STAB(1).

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† MICRO is a trade name for a detergent cleaning solution containing ammonium hydroxide. International Products Corp., P.O. Box 118, Trenton, NJ.

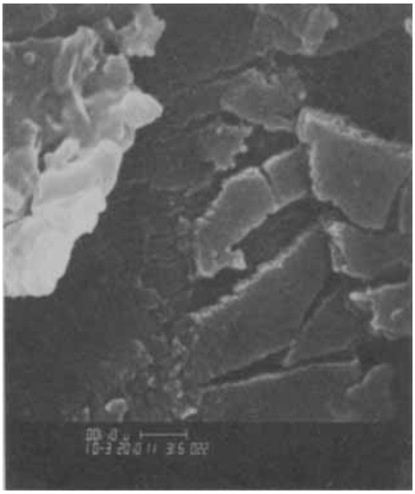

FIGURE 13 SEM picture of debond region (× in Figure 12) of a medium wedge test joint (STAB(1)).

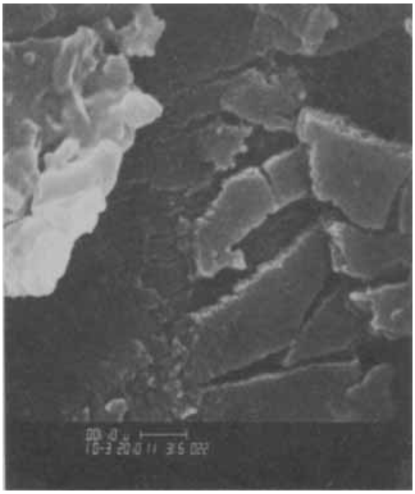

FIGURE 14 SEM picture of debond region (metal) of a medium wedge test joint (STAB(1)).

FIGURE 15 SEM picture for debond region (metal) in a bad wedge test joint (STAB(1)).

FIGURE 16 SEM picture for debond region (metal-adhesive) in a bad wedge test joint (STAB(1)).

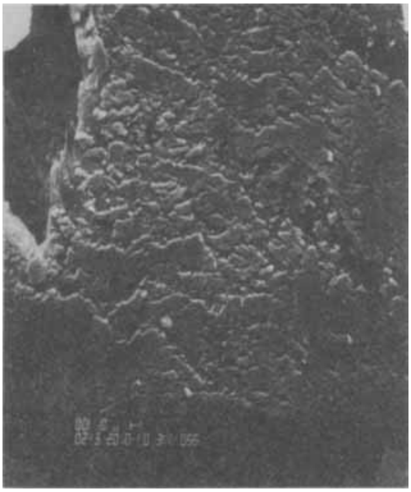

FIGURE 17 SEM picture for debond region (metal, position 55 in Figure 16) in a bad wedge test joint (STAB(1)).

FIGURE 18 SEM picture for debond region (adhesive, position 59 Figure 16) in a bad wedge test joint (STAB(1)).

Surface characterization

As for STAB(1), the film is stable in the electron beam. No Al 60 eV appears (see Figures 1c and 2c). The initial carbon peak is large, but is removed in less than a minute of Ar^+ sputtering. The oxygen peak increases as the carbon is removed, because the oxide is covered by the organic contamination.

Bond strength endurance

Ten minutes in MICRO solution gives much reduced crack growth over that for untreated samples [~3.05 cm (1.2 in)/24 hr *vs* ~ 8.89 (3.5 in)/24 hr with FM73] but is unacceptable for Hysol-EA9628H. A 20 min STAB(2) soak greatly reduced crack growth, in spite of high contact angles and low peel forces, and a 30 min STAB(2) reduced crack growth even more.

Prebonding and post fracture analysis

SEM pictures of Al 2024-T3 after STAB(2) but prior to bonding revealed a hydroxide film a few thousand angstroms thick, but the outer surface did not have the porous open structure as for STAB(1). The hydroxide layer on the metal that debonded from the adhesive during the wedge test revealed stringers stretching between fractured hydroxide, indicating that for a good bond, adhesive has penetrated into the hydroxide and failure is in the primer near the oxide-primer interface. Poor bonds fail by interlaminar separation in the oxide, as for STAB(1).

STAB(3)

Problems in reproducibly producing good wedge test joints by STAB(1) and STAB(2) prompted an investigation of the effect of NaOH concentration on bond endurance. This led to the surface treatment referred to as STAB(3), which appears to be very successful. STAB(3) has the advantage of being very simple and inexpensive.

Experimental procedure

Al 2024-T3 is dipped in a super-concentrated solution of NaOH (568 g/l D.I. water) at room temperature for 3 to 10 min, rinsed in D.I. water, and dried in flowing nitrogen. It is crucial that the rinse be hard sprayed to remove all excess NaOH. Simple dipping in rinse water does not remove the NaOH quickly enough. A simple test can be made by pressing pink litmus paper against the wet surface. If the paper remains pink, the NaOH has been removed. Drip drying in air is just as effective as N_2 blow-drying. In most cases, no degrease step is needed. The NaOH solution can be contained in glass or plastic, but we have used stainless steel tanks without noticeable attack over a 2 yr period.

Surface characterization

AES for Al 2024-T3 after STAB(3) (Figure 1c) reveals that the oxide contains the Mg and Cu alloy constituents, and some C and Cl surface contamination. The sputter profile (Figure 2c) shows that the film is stable to the electron beam (no 60 eV Al, no decrease in O) and has a peculiar C profile. The C remains high for 10 min and is removed sharply between 10 and 12 min. The significance of this is not understood; normal organic contamination is usually removed in 2 or 3 min or less. The surface carbon may be a stable carbonate compound, rather than surface contamination, since the surface does not yield large water contact angles as for normal hydrocarbon contamination. For example, as-received samples have values of $\theta_{H_2O} \sim 30-60°$, degreased samples have $\theta_{H_2O} \sim 60°$ and STAB(3) samples have values of $\theta_{H_2O} \sim 15$–$20°$.

Figures 19 and 20 show surface properties as a function of dip time in NaOH

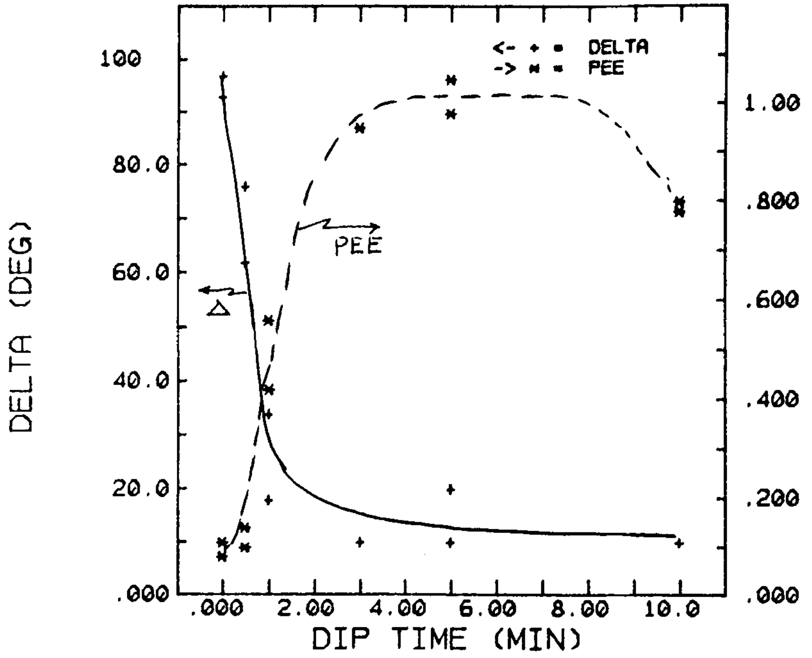

FIGURE 19 Delta and PEE *vs* dip time in NaOH for STAB(3).

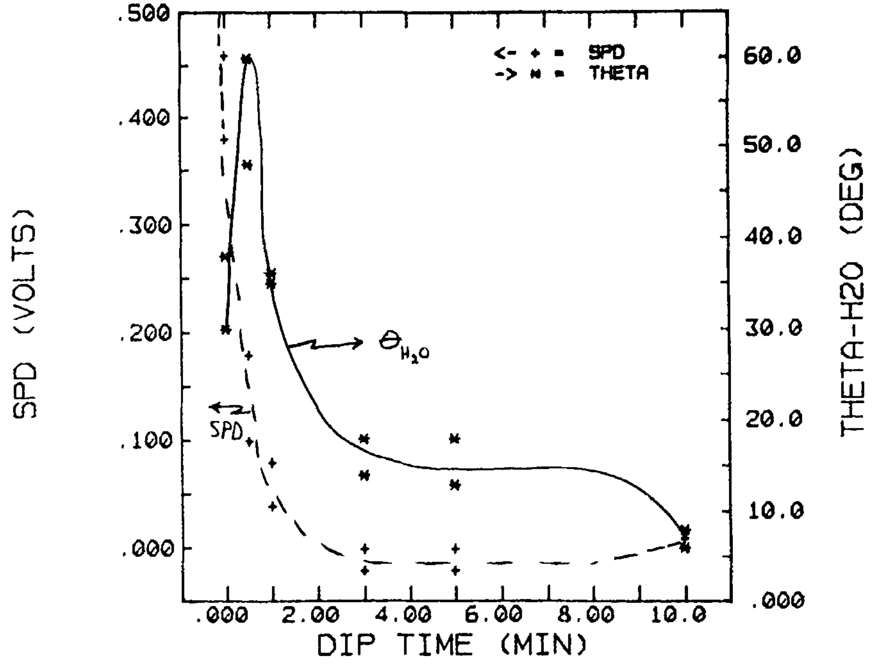

FIGURE 20 SPD and theta-H_2O *vs* dip time in NaOH for STAB(3).

solution. The results are consistent with the wedge tests, which indicate good durability for etching between 3 and 10 min. Figure 19 shows that the surface properties change dramatically during the first 2 or 3 min, but then remain essentially constant between 3 and 10 min. The drop in the ellipsometric phase shift Δ corresponds to film thickening, whereas the corresponding increase in PEE might be thought to indicate film thinning since the hydroxide is not emitting and the metal is. Both measurements are consistent if it is assumed that a thick porous layer is formed but that a barrier (electron-attenuating) layer is formed that does decrease with time in NaOH. Another possibility is that the thin outer carbonate layer is photo-emitting. Figure 20 shows that the SPD and water contact angle, θ_{H_2O}, also decrease and level off at about 3 min. The as-received samples are rather hydrophilic, as indicated by the low contact angles, but first increase then decrease with dip time.

The large initial value of SPD ($\sim$0.6 V) is consistent with hydrocarbon contamination with the hydrocarbon tail (positive end of the dipole) pointing away from the surface. The dramatic decrease in SPD ($\sim$0.0 V) with exposure to NaOH solution reveals the removal of the contamination and the formation of a basic (oxygen-rich) surface with O^{2-} or OH^- (negative ends of the dipole) pointing away from the surface. It is this basicity that could account for the stable interaction with acid functional groups (—OH), in modified epoxy (in acid-base theory[28]). In contrast, the acid FPL etch has high SPD ~ 0.5 V, even though AES reveals very little organic contamination. The high SPD value is due to the acid nature of the aluminum oxide with the $-O^{-}-H^{+}$ dipole pointing away from the surface. These acid sites interact strongly with basic functional groups (C=O, amines) in the modified epoxy adhesive, and account for the chemical stability of joints with this surface treatment.

The fact that all measurements remain fairly constant beyond 3 min indicates that the film that is formed is independent of the dip time beyond 3 min. That is, after 3 min in NaOH solution, the surface is about the same and forms the same type of film upon rinsing and drying.

Figures 19 and 20 indicate that all of the surface tools can be used for quality assurance, and that STAB(3) has been properly performed.

Figures 21a–d show the surface property changes as the STAB(3) samples are given the thermal-humidity history of a normal adhesive joint during preparation but without the adhesive. A duplicate set of samples was used to check reproducibility. The trends are reproducible and reveal definite

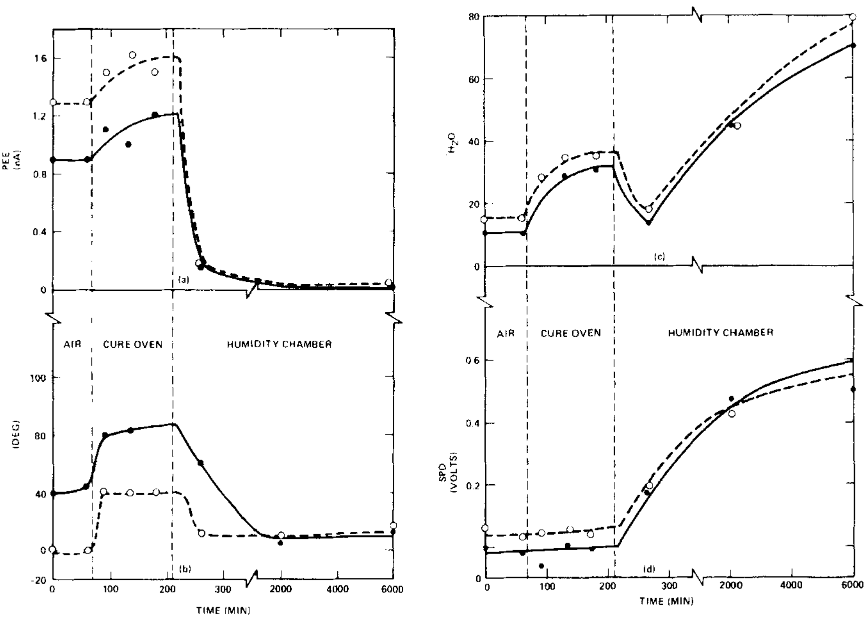

FIGURE 21 Surface properties of Al 2024-T3 (STAB(3)) during bonding and wedge test, process history, but without adhesive.

structural changes. During the first 30 min of air exposure after STAB(3), no changes occur. Exposure to the cure oven increases Δ, PEE, and θ_{H_2O}. The increase in Δ is interpreted as a decrease in film thickness and/or density. Surprisingly, SPD does not change during the oven exposure. This, plus the small change in θ_{H_2O} may indicate (as did the C sputter profile) that the carbonate is stable for STAB(3). Exposure to the humidity chamber decreases Δ and PEE, but increases θ_{H_2O} and SPD. This is interpreted as due to organic contamination, but AES or ESCA results are needed to confirm this.

There is always the concern that a surface treatment removes so much metal that it significantly thins or weakens the metal sheet. To check this for STAB(3), samples were etched for various lengths of time (0–10 min), rinsed, dried, and weighed. The weight loss proved linear with time, with a 1 min initiation period. The depth of metal removed was reproducible and can be expressed by the equation

$$d \simeq (5 \times 10^{-5}\ \text{cm/min})t,$$

where t is time in minutes after the first minute. It follows that the normal 3 min dip of STAB(3) only removes 10^{-4} cm (0.04 mil), considerably less than the FPL etch, but sufficient to remove the roll-damaged layer of aluminum that probably contributes to the instability of the as-received and degreased-only joints under hydrothermal stress. It is thought that the damaged layer may be removed in some cases with STAB(1) and (2), but not in others, resulting in the layered hydroxide (Figure 14) and subsequent degradation.

Bond strength and endurance

Effect of glue line thickness (GLT) The normal GLT averages about 4 mil. To check the effect of larger values, 5 and 10 mil copper wire shims were placed between adherends. The 5 mil shims produced actual GLT values between 4.1 and 4.6 mil and gave normal results, *i.e.*, ~34.4 MPa (5 ksi) lap shear strength and ~0.305 cm (0.12 in)/24 hr for the wedge test. The 10 mil shims produced GLT values between 7 and 9.3 mil. The actual GLT was less than 10 mil because the copper wires were pressed into the aluminum. The initial crack length was large [~5.24 cm (2.11 in)] for GLT of ~0.02 cm (9 mil), indicating weakened peel strength (fracture toughness), and the crack growth was low, probably due to the low stress intensity at the crack tip.

Effect of degrease A great advantage of STAB(3) is the elimination of a degrease step. However, some aluminum may be so contaminated that a degrease step will be necessary. To see if a degrease step would be detrimental to STAB(3), a set of control specimens was compared with a set processed in the same way except that the samples were degreased in MEK prior to STAB(3). The degrease step was not deleterious.

Effect of primer The length of time the primers had been in use had little if any effect on bond durability. The usual primer treatment involves warm up to room temperature, shake to mix solids, dip sample, and leave in air for 0.5 h followed by oven cure at 121°C (250°F) for 1 hr. Some primed samples were left overnight without oven cure. In this experiment, not curing the primer weakened the peel strength, as indicated by the average initial crack length of 4.83 cm (1.9 in) compared to a normal value of ~3.56 cm (1.4 in) to 3.51 cm (1.5 in). Although the crack growth in 24 hr was acceptably low, other experiments indicate that leaving the primer uncured causes degradation, with failure occurring at the primer-adhesive interface or in the primer.

The bond endurance and mode of failure is rather sensitive to the primer thickness. To estimate the primer thickness, as-received primer was brushed onto carefully weighed pieces of aluminum foil, cured, and reweighed. The primer thickness was estimated to be 1.5 μm (0.06 mil) by the weighing technique, compared to 5 μm (0.2 mil) with calipers, for normal application. The reason for the discrepancy is not known, unless the solids cause the calipers to read high.

Dipping the sample into (well mixed) primer, then allowing it to drip drain produces a layer too thin at the top and too thick at the bottom. This was evidenced further in the scale-up study.

Effect of primer cure time A 10 min cure produces initial cracks about 1.3 cm (0.5 in) longer than the normal 1 hr cure, indicating reduced peel strength. The average crack growth is about the same as for the normal cure, but the stress has been lowered at the crack tip due to the longer initial crack.

Effect of contamination After STAB(3), the samples were dipped in Three-in-One oil, hydraulic fluid, smeared with vacuum grease, fingerprints, and mold release agent to discover the tolerance of the STAB(3) treatment to contamination. It had been observed in our laboratory[30] that the phosphoric acid anodize surface treatment was extremely tolerant of organic contamination. This was shown to be due primarily to the absorption of the contaminant into the primer and adhesive, but also due to the ability of the 5000 Å porous oxide to absorb the remainder and still mechanically interlock with the primer. The FPL etched specimens were much more sensitive to contamination, and this was thought to be due to the lack of contamination absorption in the very thin (~400 Å) oxide film. Except for the samples sprayed with release agent, the average crack extension at 24 hr (60°C, 100% RH) was 0.9 cm (0.38 in). Apparently, STAB(3) can accommodate contamination that is not absorbed into the adhesive, as was found for PAA treated aluminum in a previous report.[30] The release agent caused complete debonding in 24 hr. It is thought that the release agent prevents wetting sufficient to stop entrance of the primer into the hydroxide pores, whereas the other contaminants do not.

Prebonding and post fracture analysis

Figure 22 shows that the hydroxide layer formed with STAB(3) is quite different from that for STAB(1) or (2). STAB(3) forms a single layer of hydroxide with an open structure that appears ideal for wetting and mechanical interlocking with the adhesive. Figure 23 shows an SEM picture of the debond region of a STAB(3) joint after the wedge test, and reveals that failure is near the hydroxide-primer interface but cohesive in the primer.

SUMMARY OF RESULTS AND CONCLUSIONS

The object of this program was to find a nonacid surface treatment (no carcinogenic chromates) for Al, 2024-T3 that was inexpensive but would produce strong, durable adhesive joints with Hysol EA9628H adhesive and Hysol EA9210H or BR 127 primer. The object of this paper is to describe mechanisms of failure and endurance for the STAB treatments.

Initial studies[23] indicated that a simple degrease and hot water soak (STAB(1)) would produce strong durable joints. Further investigation revealed great difficulty in reproducing this result, although occasional good results could be obtained. Investigation of surface properties revealed that Al 2024-T3 has a surface layer of metal that differs from the bulk. This layer is entirely removed in the standard FPL etch, but is only partially reacted during STAB(1). If the Al 2024-T3 is FPL-etched then given STAB(1), good bond endurance results, as measured by the wedge test. It is concluded that in some instances STAB(1) reacts with the entire outer layer of metal, yielding hydroxide that is stable to moisture (hydrothermal stress). In other instances, this layer is only partially reacted, leaving an unstable multilayered structure that can corrode or fracture between layers under hydrothermal stress.

In the course of studying STAB(1), a simple degrease and water soak (room temperature) in a water solution containing a commercial cleaning agent (MICRO) gave good bond endurance results. This was labeled STAB(2). Further investigation revealed that this treatment suffered from the same reproducibility problems as STAB(1).

In the process of studying STAB(1) and (2), the effect of sodium hydroxide concentration was investigated. It was found that a 36 w/o solution of NaOH in D.I. water (STAB(3)) gave excellent bond endurance by the wedge test. Of

FIGURE 22 SEM picture of Al 2024-T3 after STAB(3).

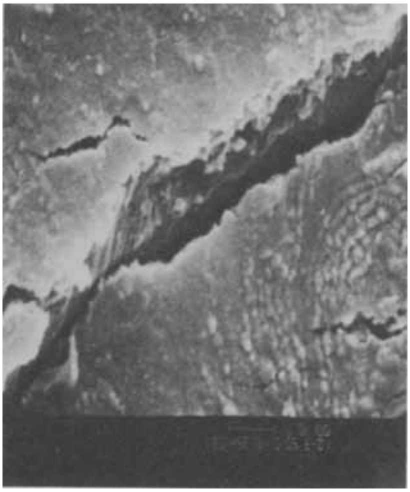

FIGURE 23 SEM picture of debond (metal) region of a good wedge test joint (STAB(3)).

322 wedge test specimens, the average crack growth in the first hour was ~0.10 cm (0.04 in) and after the first 24 hr, ~0.51 cm (0.2 in). Failure during the wedge test was primarily cohesive in adhesive or primer. The results for STAB(3) are comparable with the Boeing PAA and the standard FPL etch treatments as tested in our laboratory. The lap shear strength averages above 5.5 ksi, with cohesive failure, and is also comparable with the PAA or FPL results.

Investigation of the surface properties of STAB(3) revealed that the outer unstable layer of metal is removed in 3 min (*i.e.*, ~1 μm removal). After rinsing and drying, a very porous hydroxide single layer is formed. These properties are similar to that for PAA, in that primer is thought to become embedded within the hydroxide layer and the hydroxide and underlying metal is stable to corrosion under hydrothermal stress.

Auger electron spectroscopy with Ar^+ sputter etching reveals the chemical constitution of the outer atomic layers for films after the various treatments. As-received and degreased-only and STAB(3) Al 2024-T3 have aluminum oxide layers rich in Mg, whereas FPL etched and PAA do not. The as-received and degreased-only Al 2024-T3 have much thinner oxide films than STAB or PAA treatments (see Table I). STAB(3) forms a film with a much more stable carbonate compound than results from normal organic contamination. The source of the carbonate in the STAB(1) (with K_2CO_3) is obvious; the source for STAB(3) is expected to be from the interaction of the D.I. rinse water with CO_2 in the air. It is well known that neutral water will become slightly acidic because of the formation of carbonic acid (H_2CO_3) by reaction with CO_2. Figure 21 reveals the stability of the carbonate-rich aluminum oxide (hydroxide) film in high temperature humid environment. It is believed that this chemical stability, plus the mechanical interlocking due to the porous oxide, accounts for the hydrothermal stress durability of STAB(3). The other surface properties (ellipsometric parameters, Δ, Ψ, SPD, PEE and θ_{H_2O}, Table I) are fairly reproducible for FPL, PAA, and STAB(3) and can be used for quality assurance. These properties are very irreproducible for STAB(1) and (2), consistent with the irreproducible bond properties.

A number of process variables were investigated to delineate the range for good bonds and the boundaries beyond which poor bonds result for STAB(3). Table II lists the parameters, range, and remarks.

Although STAB(3) has been optimized for Al 2024-T3 and Hysol EA9628H adhesive and primer, it has been found to be as good for other 121°C (250°F) curing adhesives, *e.g.*, FM 73/BR 127 (American Cyanamid), AF 163/XB 3944 (3M Co.). The STAB(3) parameters that give good results for Al 2024-T3 have not been found optimum for other alloys such as Al 7075-T6 or Al 6061-T6. However, good endurance is obtained by changing the time or temperature of the bath, as indicated in Ref. 25.

TABLE II

Process parameter boundaries for STAB(3)

Parameter	Range of good bonds	Remarks
Glue line thickness	3–7 mil	Normal ~ 4 mil
Primer thickness	0.4–1.4 μ (wt chg.) 0.06–0.2 mil (calipers)	
Primer cure	1 hr normal 121°C (250°F)	10 min gave poor peel strength Left overnight before cure gave bad bonds
Degrease	Not needed in most instances	But does not degrade STAB(3)
NaOH conc.	> 140 g/l at RT, can be lowered at higher temperatures	Best results ~600 g/l at RT, caustic soda works well
Time of NaOH dip	> 3 min	Best results ~3–10 min
Delay between NaOH dip and rinse	10 min OK	Probably longer OK
Rinse	Spray rinse with D.I. water (must remove all NaOH) up to 20 min OK	Insufficient rinse leaves surface alkaline giving poor durability
Dry	N_2 blow, air blow, drip dry	
Contamination	Like PAA, very tolerant	
Delay before primer	> 24 hr, OK	
Delay between primer and cure	1/2 hr, OK, 24 hr, BAD	

Acknowledgement

This project was partially supported by Department of the Army, U.S. Army Armament R&D Command, Dover, New Jersey (Contract DAAK10-78-C-0274). Mr Raymond Wegman was program monitor.

It is a pleasure to acknowledge the help of G. W. Lindberg, L. R. Bivins, R. P. Haak and D. Collins.

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