

Final Technical Report
to
The U.S. Department of Energy
On a research project entitled:
*Oxide Film Microstructure: The Link between Surface Preparation Processes and
Strength/Durability of Adhesively Bonded Aluminum*
By

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Project Summary

Strength and durability of adhesive bonding of aluminum alloys structures are intrinsically determined by the surface microstructures and interfacial failure micromechanisms. The current project presents a multidisciplinary approach to addressing critical issues controlling the strength and durability of adhesive bonds of aluminum alloys. Three main thrust areas have been pursued: surface treatment technology development to achieve desirable surface microstructures; relationship between surface structure and properties of adhesive bonds; and failure mechanisms of adhesively bonded components.

Reproducible adhesive bonding of aluminum alloys requires that a surface oxide film be grown in a controllable manner. To study the growth of this oxide, its microstructure, including composition, pore-size distribution, and thickness, must all be well-characterized. A unique experimental apparatus, Cylindrically-Rotating, Axially-Translating Electrochemical Reactor, has been developed to study the dependence of oxide film microstructure on processing parameters. Relationship between microstructure and durability of adhesive bonds has been examined under various mechanical, microstructural, and environmental conditions. The durability of epoxy/Al bond was determined using the conventional trilayer double cantilever beam, asymmetrical trilayer double cantilever beam, and flexural peel interface fracture mechanics specimens. The failure mechanisms of adhesively bonded structures have also been studied. The emphasis was on interfacial fracture due to surface porosity-induced cavitation. A model has been developed to evaluate the interfacial fracture toughness as a function of initial cavity size, cavity spacing and material parameters.

I. Development of Surface Treatment Technology for Aluminum Alloys

Oxide film microstructure can depend on temperature, electrolyte composition, applied potential, and mass transfer rate. To facilitate the study of how microstructure depends on these processing parameters, we have developed a Cylindrically-Rotating, Axially-Translating Electrochemical Reactor (CRATER), which allows for temporal variation of one processing parameter (in our case, applied potential) to be mapped into a spatial variation of oxide microstructure along the length of a single (cylindrical) working electrode. This allows for the parametric dependence of oxide microstructure to be studied in a single experiment, with surface analysis (SEM, XPS, etc.) performed on a single specimen, thus greatly simplifying the study of the process and how microstructure depends on process variables.

The CRATER has been characterized as to mass transfer characteristics (purely azimuthal flow, stable Taylor vortices, and transition to wavy Taylor vortices), specimen translation uniformity, positioning and oxide formation reproducibility, and fluid level maintenance precision. Several presentations at national analytical chemistry and electrochemistry meetings have been made, some of which have also resulted in

Proceedings publications. A full paper on the apparatus and its use to characterize electro-oxidation of Al 6061 is nearing completion.

To study the effect of potential on oxide film microstructure, we have used Al 6061 annular stock as the translating working electrode, and a platinized Ti inner cylinder as the counter electrode. The variation of mean pore size in the oxide was studied as a function of applied potential, and the results obtained on the single working electrode were found to be in good agreement with previous results in which multiple specimens were each electro-oxidized at different potentials. We have shown that, over the range of mass transfer coefficients available in the CRATER, oxide growth on aluminum is kinetically limited. This means that electrical bias and time, not the rate of electrolyte transport to the metal or metal/oxide surface, controls the structure of the oxide.

We have also used the CRATER with a polysulfone annulus machined to accept planar coupons of aluminum sheet alloys suitable for adhesive bonding and mechanical testing. In the latter configuration, we have used a steady potential to develop a highly uniform oxide film that is most convenient for preparing Al 6111 specimens of a size suitable for adhesive performance testing. Such testing has recently commenced.

II. Structure-Property Relationship of Adhesive Bonds

Using conventional and asymmetric tri-layer double cantilever beam specimens, the relationship between surface microstructures and adhesive bond properties has been studied. Both the crack growth mechanism and resistance were found to depend strongly on the crack tip loading condition. Elastoplastic finite element analysis showed that such dependence was consistent with roles of the crack tip plasticity manifested under various mechanical conditions. Several model microstructures of the adhesive bond were developed by using self-assembled monolayers and by controlling electrochemical oxidative surface preparations. Self-assembled monolayers based on phosphonic acid and amine functional group were found to significantly enhance the durability of epoxy/Al bond in both air and aqueous environments. The surface preparation produced porous surfaces with pore dimensions ranging from ten nanometers to fractions of millimeter, resulting in significant differences in crack growth mechanism and durability of the adhesive bond. Experiments conducted in air and aqueous environments uncovered the first direct evidence of a stress corrosion-cracking plateau for the adhesive bond. Microscopic and spectroscopic analyses indicated that effects of the environment were related to the stability and morphology of the surface oxide in the test medium and to the ingress of the aggressive species along the interfacial crack.

2.1 Dependence on Crack Tip Mechanics

Crack path selection. The crack path selection in the trilayered double cantilever beam (DCB) specimens was examined under monotonic and cyclic loading conditions. Under both monotonic and cyclic loading, the crack propagation path zigzagged from one

interface to the other through the polymer interlayer, alternating frequently between the two interfaces. The development of this alternating crack path was found to result from simultaneous crack formation on both interfaces and the subsequent coalescence of these separate interface cracks through the polymer layer, rather than from continuous kinking of a single crack as previously suggested for a brittle adhesive. The simultaneous crack formation on both interfaces is shown to be consistent with the favorable stress condition along the other interface, set up by the crack along one interface in the layered DCB specimen.

Suppression of alternating crack path. Experiments were conducted to substantiate the finite element calculations that pointed to the unique crack tip stress distribution as the potential cause of the alternating crack path. For this purpose, two types of specimens were used: asymmetrical double cantilever beam (a-DCB) and flexural peel specimens. In the a-DCB specimen, the geometry and thus the mechanics condition of the DCB specimen was maintained, but the two interfaces were made uneven. The precrack was introduced on the weaker of the two interfaces. Under the same loading condition as used in the conventional DCB specimen, subsequent crack propagation was confined to the weaker interface. The second specimen, the flexural peel, was similar to the trilayer DCB specimen but only one beam was loaded while the other beam stood free with the end fixed. This asymmetric loading reduced the stress on the other interface ahead of an interfacial crack, resulting again in crack path along only one interface.

Dependence of interfacial crack resistance on crack path. The effect of crack path selection on the toughness and fatigue crack growth resistance in sandwich specimens was investigated experimentally. Under monotonic loading, the load-displacement response of the specimen was non-linear when the crack path alternated between the two interfaces in the conventional DCB specimen. By contrast, the load-displacement diagram was linear up to the point of fracture for the a-DCB specimen where the crack was confined only to one interface. Consequently, the apparent fracture toughness obtained from the conventional DCB specimen was more than fifty percent higher than the interface toughness measured from the a-DCB specimen. Similarly, crack growth rate in the conventional DCB specimen was several orders of magnitude faster and showed much larger scatter. When the crack resistance under different load mixities was compared using the data obtained from the conventional DCB specimen, the mode-I toughness was much higher than mixed Mode-I/II toughness. However, when the comparison was made with the data from the a-DCB specimen, the interface crack resistance increased steadily with the phase angle. The difference was explained in terms of the crack tip shielding by uncracked ligaments in the conventional DCB specimen.

Effect of bond thickness. The effect of adhesive layer thickness on fatigue crack growth along polymer/metal interface was examined by conducting fatigue experiments on the flexural peel specimens and by performing elastoplastic finite element analysis of the interfacial crack tip field. The crack growth rate along the polymer/metal interface was correlated with the total strain energy release rate, G , and obeyed the Paris law at the intermediate growth rates. The fatigue crack growth threshold was found to decrease gradually with increasing adhesive thickness for large thicknesses. However, below a

certain bond thickness, the fatigue threshold dropped suddenly. Elastoplastic analysis of crack tip field and microscopic examination of failure mechanism indicated that the thickness dependence of interfacial fatigue threshold could be explained by the variation in the crack tip loading condition and in fracture mechanism with adhesive thickness.

Temperature dependence. The dependence of the crack resistance on temperature was examined by using a layer-bonded bend specimen. The sandwich specimen was first cut to have an edge precrack along polymer/metal interface, and then loaded in three-point bending mode under impact. Finite element analysis was used to correlate the fracture energy with impact energy for this specimen. The experiments were conducted in the temperature range between -30° to 100°C to investigate impact sensitivity of the adhesive layer. Fracture energy of the adhesive bond was found to increase with temperature below a certain temperature, beyond which the opposite trend was observed. The peak toughness was obtained at a temperature close to the glass transition temperature as determined from the dynamic mechanical analyzer. The temperature dependence was explained in terms of the crack tip plasticity at different temperatures.

2.2 Microstructural Effects

Role of ordered monolayers. Fatigue crack growth study was performed in air and sodium chloride solution on the epoxy-aluminum interface prepared by the Forest Products Laboratory (FPL) procedure with and without modification by the self assembled monolayers of alkyl phosphonic acid. With surface modification by self assembled monolayer of α,ω metal bisphosphonate, the fatigue threshold was increased by 2~3 times; but the fracture resistance of the interface was weakened. Scanning electron microscopy and X-ray photoelectron spectrometer were used to characterize the morphology and chemistry of the crack surface. XPS results showed that bisphosphonic acid chemically reacted with aluminum surface and altered the crack path partly to aluminum oxide.

Effect of surface preparation. Fatigue crack growth experiments were conducted on the polymer-metal interfaces formed using three different surface preparations, acid etching, sulfuric acid anodizing and phosphorous acid anodizing. The fatigue threshold of the interface was found to differ significantly for three surface preparations. The acid etching resulted on the lowest fatigue threshold while phosphorous acid anodizing the highest threshold. The difference in the fatigue resistance was even more pronounced in water than air, and was attributed to the interfacial morphology.

2.3 Environmental Effects

Structural applications of adhesive bonding are largely limited by the durability of polymer-metal interface in aqueous environment. Fatigue crack growth and slow crack growth studies were performed in sodium chloride solution on the epoxy-aluminum interface prepared by the Forest Products Laboratory (FPL) procedure. Compared to the

interfacial fatigue behavior in the room air, the fatigue crack growth rates in the aqueous environments were increased by several orders of magnitude and the fatigue threshold decreased by a factor of 10. In the aqueous environments, fatigue crack curves exhibited distinct plateau, characteristic of stress corrosion cracking process. Atomic force microscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and scanning electron microscopy studies of crack surfaces were used to characterize the morphology and chemistry of the FPL treated fresh surface and crack surface. The results showed that the chemistry of the surface oxide was altered by hydration to produce a hydroxide with poor adhesion strength to the substrate metal. The loss of adhesion in aqueous environment was related to the stability of interfacial microstructure.

III. Interfacial Fracture Resistance

A new method utilizing fluid mechanics solutions is developed to study interfacial fracture resistance due to cavitation in a thin ductile layer. Solutions of fluid flow field are used to approximate the plastic deformation field in the corresponding solid body with a cavity. Equilibrium condition is satisfied by using the principle of virtual work. Stress-separation curves due to cavitation in the thin layer can thus be obtained. The method is validated by re-evaluating the 1-D problem of cavity growth in a sphere — a problem for which an exact, analytical solution exists. A 2-D, plane strain cavitation problem is analyzed using the new method. The stress-separation curves and the fracture resistance due to this mechanism are obtained. The results show that both the stress-separation curves and the fracture resistance are sensitive to the strain hardening exponent and the initial void size, but not to the yield strength of the material. The new method has clear advantages over numerical methods such as the finite element method when parametric studies are performed.

Furthermore, the model is extended to a 3-D problem — the growth of an initially spherical cavity in a cylindrical bar of finite length subject to uniform traction at its ends. The results show that the interfacial fracture resistance decreases monotonically with increasing initial cavity volume fraction, indicating that an interfacial microstructure with sparsely distributed cavity nucleation sites is preferable. On the other hand, surface preparation processes that give rise to a finer initial cavity size are desirable since a higher peak stress is needed to initiate cavitation instability. The method has clear advantages when dealing with large plastic deformation and post-instability behavior.

An experimental setup has been designed to measure the interfacial fracture resistance. Single crystalline sapphire is first used to study the intrinsic interface energy between an aluminum oxide and an adhesive. Aluminum alloy specimens with different surface microstructures will be used to study the effects of surface microstructures on interface fracture resistance.

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