ANALYSIS OF THE INTERPHASE OF A POLYIMIDE BONDED TO CHROMIC ACID ANODIZED TI-6AL-4V

R. K. Giunta* and R. G. Kander
Center for Adhesive and Sealant Science
Virginia Polytechnic Institute & State University
Blacksburg, VA 24061

INTRODUCTION

Structural adhesive joints, when tested as made, typically fail cohesively through the centerline of the adhesive. [1, 2] However, in any study of adhesive joint durability, failure near the adhesive/substrate interface becomes an important consideration. [2] In the current study, an interfacially debonding adhesive test, the notched coating adhesion (NCA) test, was applied to LaRC™ PETI-5 adhesive bonded to chromic acid anodized (CAA) Ti-6Al-4V. Post-failure analysis of the interphase region included X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), field emission scanning electron microscopy (FE-SEM), and atomic force microscopy (AFM).

Mechanical interlocking between an adhesive and a substrate occurs when the liquid adhesive flows into interstices of the substrate, solidifies, and becomes locked in place. Mechanical interlocking is believed to significantly contribute to the adhesion of substrates that exhibit microroughness, such as metal surfaces treated with chromic acid anodization or sodium hydroxide anodization. Filbey and Wightman [3] found that an epoxy penetrated the pores of CAA Ti-6Al-4V, one of the limited number of pore penetration studies that have been reported. [3, 4] In the current study, the penetration of PETI-5 into the pores of CAA Ti-6Al-4V is investigated through analysis of adhesive/substrate failure surfaces.

EXPERIMENTAL

Adhesive Specimens

LaRC™ PETI-5, a phenylethynyl-terminated polyimide adhesive, was bonded to Ti-6Al-4V. The adhesive was received from Imitec,™ Schenectady, NY, as an amic acid solution in NMP. The molecular weight of the PETI-5 precursor, which undergoes chain extension and crosslinking of the phenylethynyl endgroups during cure, is 5,000 g/mol. The substrate was pretreated by CAA prior to bonding. Preparation and testing of the NCA specimens have been discussed elsewhere. [5-7]

Surface Analysis

Auger Electron Spectroscopy. Depth profiling was performed on a Perkin-Elmer model 610 scanning Auger system using a single pass cylindrical mirror analyzer with electron excitation from a coaxial electron gun. The minimum electron beam diameter is less than 100 nm. The sputter rate was calibrated using a tantalum standard.

Field Emission Scanning Electron Microscopy. FE-SEM was performed on a LEO model 1550 Field Emission Scanning Electron Microscope at 0.25 to 2.0 kV. Samples were not sputter-coated, and no significant charging was observed.

Atomic Force Microscopy. A Digital Instruments Dimension 3000 Atomic Force Microscope using the Nanoscope IIIa controller was used in tapping mode to obtain height and phase AFM images.

RESULTS AND DISCUSSION

Mechanical Interlocking

Although failure between the adhesive and substrate appeared to be interfacial by visual inspection, polyimide adhesive and titanium dioxide were consistently detected by XPS on both sides of the failed adhesive bonds. [5, 7] Thus, it was suspected that polymer had become mechanically interlocked within the pores of the CAA substrate surface and that failure was occurring through a region containing both polymer and metal oxide.

For mechanical interlocking to occur in the current system, PETI-5 polymer molecules must penetrate the porous oxide layer of CAA titanium. FE-SEM images of CAA Ti-6Al-4V are shown in Figure 1. The dark circular regions are pores in the CAA oxide layer, approximately 30 nm in diameter. When PETI-5 is applied to the anodized substrate surface, it is a primer in the form of a 16% solids amic acid solution in N-methyl pyrrolidinone (NMP). Using gel permeation chromatography, the number average radius of gyration of the PETI-5 amic acid solution was found to be 3.6 nm, with weight average and z-average radii of gyration of 4.8 and 5.7 nm, respectively. The diameter of the coiled polymer chain conformation, therefore, is less than the diameter of the substrate pores. Thus, it is reasonable to assume that PETI-5 amic acid can penetrate the pores of the CAA substrate.

* Current address: Sandia National Laboratories, MS 0958, Albuquerque, NM 87185-0958

DISCLAIMER

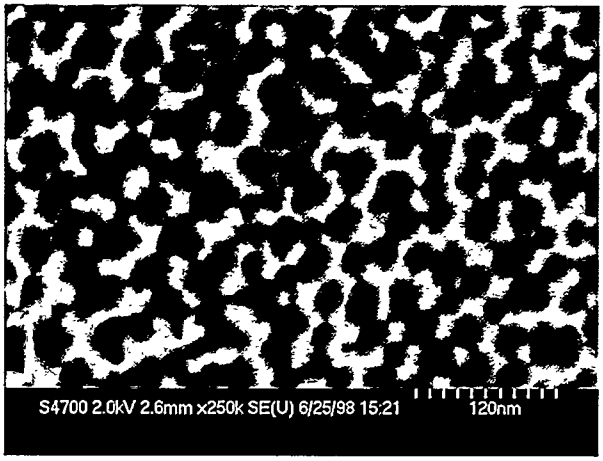

Figure 1: Field emission scanning electron micrograph of a chromic acid anodized Ti-6Al-4V substrate surface.

AUGER ELECTRON SPECTROSCOPY

From Auger depth profiling of a PETI-5 metal failure surface, carbon and titanium coexist in the top 70 to 100 nm of the failure surface. While this does imply the presence of polyimide at this depth, Auger data alone cannot be interpreted as confirmation of mechanically interlocked polymer. Auger spectroscopy cannot distinguish carbon as polyimide from carbon that may be present as a contaminant. However, if we tentatively assume that the presence of carbon represents polymer, we can construct a simple model of the interfacial region. Beyond the depth at which carbon is detected, titanium, aluminum, and oxygen (indicative of metal oxide) are present through an additional 50 nm. Deeper than this, only titanium and aluminum are detected. Thus, the polymer does not appear to penetrate the entire thickness of the titanium oxide layer. The validity of this interpretation of the Auger data can now be examined using additional surface analysis techniques. The model interphase is illustrated in Figure 2. The region in which adhesive and metal oxide are assumed to be present will be referred to as oxide A, and the area in which there is only metal oxide is referenced as oxide B.

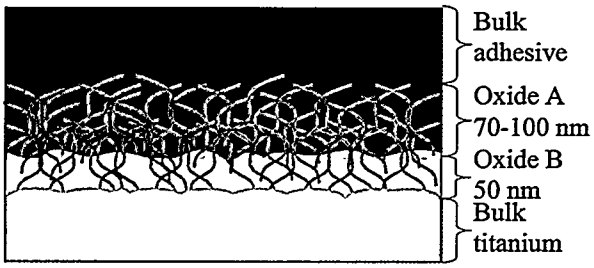

Figure 2: Schematic model of the PETI-5/CAA Ti-6Al-4V interphase based on Auger depth profiling data. Oxide A consists of the porous oxide layer embedded with adhesive. Oxide B is the porous oxide layer that contains no adhesive.

SCANNING ELECTRON MICROSCOPY

Field emission SEM was performed on the adhesive and metal failure surfaces of PETI-5 NCA specimens. In Figure 3, a FE-SEM of a metal failure surface, three distinct failure zones are observed. Region ① is the CAA substrate surface. The pores in the anodized oxide layer, which are believed to be infiltrated with polyimide adhesive, are clearly visible in this region. The failure here occurred between the bulk adhesive and the upper surface of oxide A. The porous structure of region ② is also apparent. Failure here occurred within the porous oxide layer. In region ③, however, the porosity is not well defined. Here, it appears that the failure occurred at the interface of oxide B and the bulk titanium substrate.

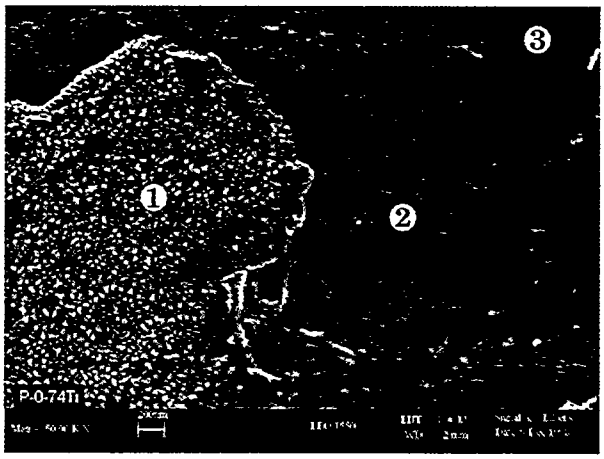

Figure 3: Field emission SEM of the metal failure surface of a PETI-5 NCA specimen. ①, ②, and ③ correspond to the three failure regions observed.

Additional features are observed in FE-SEMs of adhesive failure surfaces, Figure 4. The numbered failure regions correspond to those of the metal failure surface in Figure 3. In region ①, the layer of porous metal oxide was pulled away from the adhesive, leaving evidence of drawing and ductility in the adhesive. In region ②, features of two sizes are observed on the porous oxide surface. The larger features are approximately 150 to 400 nm in diameter, while the smaller features are less than 50 nm. The size, shape, and spatial distribution of the smaller features are consistent with the pores on the anodized titanium surface in Figure 1. The larger features could be the result of the failure propagating through the walls of several pores in close proximity. The features, small and large, in Figure 4 appear to be raised. This

was confirmed using atomic force microscopy. Referencing the model proposed in Figure 2, the failure within the oxide layer (region ② in Figure 3 and Figure 4) appears to be occurring at the interface of oxide A and oxide B. The raised features on the adhesive failure surface are attributed to polymer embedded in the oxide. Had the failure occurred through porous oxide that did not contain adhesive, these features would have appeared indented on both failure surfaces.

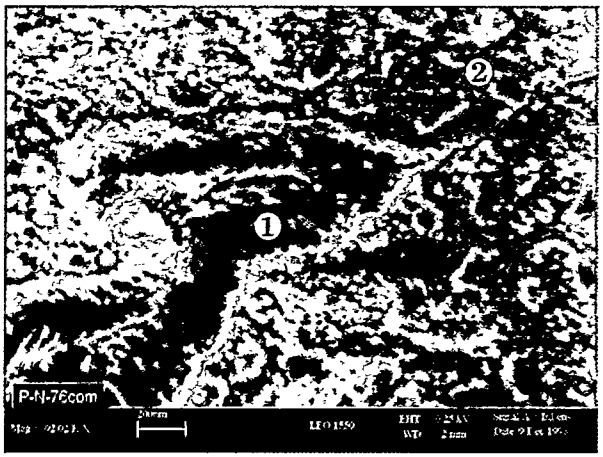

Figure 4: Field emission SEM of the adhesive failure surface of a PETI-5 NCA specimen.

ATOMIC FORCE MICROSCOPY

Additional information is obtained from AFM images of the metal failure surface, Figure 5. In the height image on the left, lighter colors indicate higher features. On the right, darker regions of the phase image indicate a higher phase lag that, in general, means dark areas are softer than light areas. Region ① of Figure 5, a metal failure surface, is both higher and softer than the surrounding area. This also corresponds to region ① of Figure 3 and Figure 4. To be softer than the surrounding metal and metal oxide, the higher region on the failure surface must contain embedded polymer. This again confirms that the substrate pores contain polyimide. All surface analysis data appears to validate the model in Figure 2. Thus, it is concluded that PETI-5 is penetrating the pores of the CAA substrate and becoming mechanically interlocked.

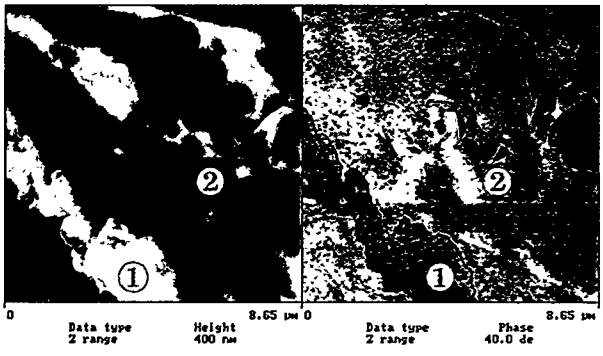

Figure 5: Height (left) and phase (right) atomic force microscopy images of the metal failure surface of a PETI-5 NCA specimen

CONCLUSIONS

The interface of PETI-5/CAA Ti-6Al-4V bonds was studied using several surface analysis techniques. From Auger spectroscopy, field emission SEM, and AFM studies, polymer is believed to be penetrating the pores of the anodized substrate to a depth of approximately 100 nm. These analyses indicate that the polymer is becoming mechanically interlocked within the substrate surface and remains embedded in the pores throughout the adhesive/substrate failure.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Center for Adhesive and Sealant Science at Virginia Tech and the Adhesive and Sealant Council Education Foundation for financial support. We would also like to thank the Composites and Polymers Branch, NASA Langley Research Center, for providing materials and research facilities, and Steve McCartney of the National Science Foundation Science and Technology Center at Virginia Tech for assistance with FE-SEM and AFM analysis.

In addition, we are grateful to Sandia National Laboratories for providing funding to attend the 23rd Annual Meeting of the Adhesion Society. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the Untied States Department of Energy under Contract DE-AC04-94AL85000.

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