

Chapter 3. Experimental Methods

3.1 Materials

The Ti-6Al-4V alloy plates for wedge tests were obtained from President Titanium Company, Hanson, Massachusetts. The elemental composition of the as received titanium alloy is given in Table 3.1. The yield point, tensile strength and elongation of Ti-6Al-4V alloy, as reported in the material safety data sheet, are 135.7 lbs/inch², 141.4 lbs/inch² and 11.6%, respectively. The wedge specimens have dimensions of 101.6 × 25.4 × 2.3 mm (ASTM B 265 GR5 standard). For the single lap shear (SLS) test, the Boeing Company provided the bonded joints of Ti-alloy plates in the SLS test configuration. The dimension of the specimens were 101.6 × 25.4 × 0.254 mm, with 25.4 × 12.7 mm being the bond area overlap.

The FM-5® adhesive, a woven glass-cloth supported polyimide (LaRC PETI-5 based) adhesive film was obtained from CYTEC Engineered Materials Inc., Havre de Grace, Maryland. The FM-5 adhesive film typically consists of 85% (maximum) by weight PETI-5 resin. FM-5 adhesive also contains other polyimides and has some added thermoplastic. The chemical composition of the FM-5 adhesive is given in Table 3.2. The molecular weight of the resin is about 5000 g/mol; the molecular structure of the PETI-5 adhesive resin is given in Figure 3.1.

The woven glass cloth (type-112, finish 538, from BGF Industries, Inc.) used as reinforcement material in the FM-5 adhesive film, consists mainly of the textile grade fibrous glass (99.5% maximum by weight). The glass fibers have an amino terminated silane coating (0.4% maximum by weight) and physically adsorbed glycerine (1.2% maximum by weight). The FM-5 adhesive film also contains 4% by weight N-methyl-2-pyrrolidone that has a boiling point of 81-82°C.

A thin sheet, 0.254 mm (10 mil) thick stainless steel shim was used to control the bond line thickness in the fabrication of bonded joints (for wedge test configuration).

Table 3.1. The elemental composition of as received titanium alloy, from President Titanium Company, as reported in the material safety data sheet.

Elements	Ti	Al	V	Fe	O	C	H	N
Weight (%)	89.93	5.82	3.92	0.18	0.13	0.01	0.0051	0.005
Atomic (%)	85.82	9.86	3.52	0.15	0.37	0.04	0.23	0.02

Table 3.2. The chemical composition (weight %) of as received FM-5 adhesive film from CYTEC, as reported in the material safety data sheet.

Fumed silica (amorphous)	4.0 maximum
N-methyl-2-pyrrolidone	4.0 maximum
Fiberglass	10 maximum
Polyimide resin	Balance

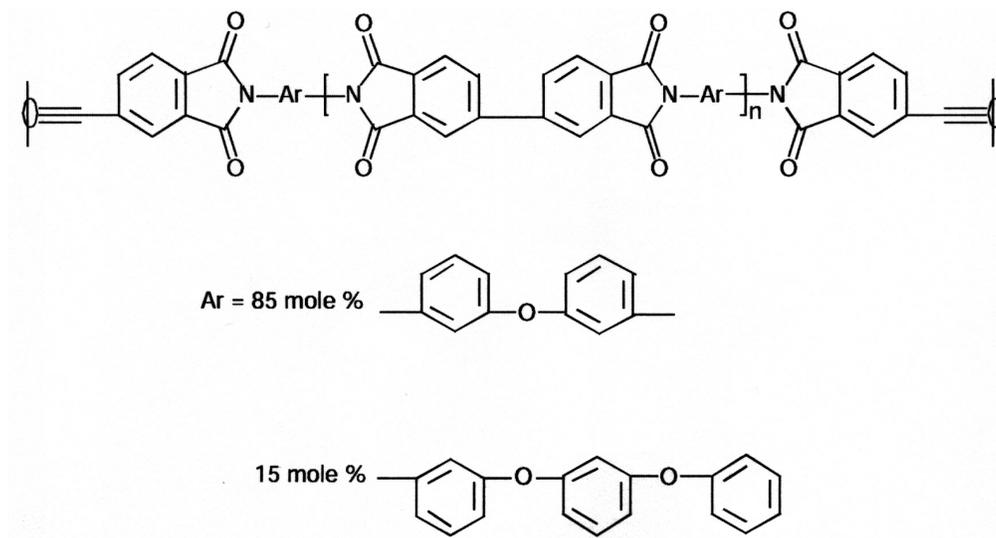


Figure 3.1. The molecular structure of LaRC PETI-5 adhesive resin ($\langle M_n \rangle = 5,000$ g/mol.).

Chromium(VI) trioxide (CrO_3) anhydrous crystals with 99.99% purity, were obtained from Fisher Scientific. Fuming nitric acid, 90% (w/v), reagent grade, was obtained from Fisher Scientific and was used as received. The hydrofluoric acid (47.0–52.0% (w/v), technical-grade) was obtained from J. T. Baker and was used as received. Isoprep 177 was obtained from MacDermid Inc., Waterbury, CT.

The standard reference materials of high purity (>99+%), used for obtaining baseline XPS data, were purchased from various sources. Titanium (IV) oxide powder of 99+% purity was obtained from Johnson Matthey. Aluminum oxide (gamma, Al_2O_3) powder of 99.99% purity was obtained from Johnson Matthey. Aluminum fluoride (AlF_3) powder, 99.9+% purity, was purchased from ACROS.

3.2 Surface Preparation

3.2.1 Chromic Acid Anodization (CAA)

Prior to bonding, the titanium substrate was chromic acid anodized. Both sides of the as received titanium alloy plate surface were scrubbed using a Scotch-Brite™ (3M company) scrubbing pad and acetone to remove the ink marks and organic surface contaminations. The plate was rinsed with acetone after removing the ink marks and deep scratches. The titanium plate was then scrubbed using a crocus cloth (emery paper, 800 grit finish) to obtain a shiny mirror-like finish. Only the surface to be bonded was polished to a mirror-like finish. The substrate was then rinsed with acetone and wiped (usually three times) with a white oil absorbing Kim-Wipe paper towel until no grease was detected on the paper towel. The plate was then rinsed with de-ionized water and was checked for a water break-free surface. If water did not wet the surface, the surface was scrubbed again and the above procedure was repeated until water spread on the surface. Next, the plate was soaked in Isoprep 177 solution (75g/L) for 10 minutes at room temperature with constant stirring. The plate was then soaked in boiling de-ionized water for 5 minutes with constant stirring. It was then rinsed three times in the de-ionized water. The plate was then

immersed in an acid solution (114 mL de-ionized water + 151 mL fuming nitric acid + 10.9 mL hydrofluoric acid, HF), at room temperature with constant stirring for 1 minute. The plate was then rinsed, three times, in de-ionized water and checked for a water break-free surface. If water did not wet the surface completely, the plate was again soaked in acid solution for a few additional minutes. Water must spread on the surface before proceeding to the next step.

The plate was then anodized using a chromic acid solution (45 g/L CrO₃, in water). 4.0 mL of hydrofluoric acid (52%) was added to about 4.0 L chromic acid solution to anodize 5 titanium plates (dimension 88.9 × 25.4 mm). The addition of HF to the anodizing bath permits attaining the desired current density of 13.45 amps/m² (1.25 amp/ft²). The plate was anodized in chromic acid bath with constant stirring at room temperature for 20 minutes at 5 Volts and at a constant current density of 13.45 amps/m². A Sorensen DC power supply (Model M50, DC R 150-6B), was used for maintaining a constant 5 volts during the anodization process. Following anodization, the anodized specimens were rinsed three times with de-ionized water and then dried in an oven at 50°C for one hour. The dried specimens were stored in a desiccator prior to bonding. The bonded joints were fabricated within 72 hours after anodization.

3.2.2 Priming

For Single Lap Shear (SLS) tests, the CAA titanium plates were prepared by Boeing scientists. The plates were primed prior to bonding. Three coatings of BR-X5 primer were applied to the CAA surface. The plate was allowed to dry in air at room temperature for about 30 minutes between the coatings. The exact method of primer application is not known, but the method used by Boeing to cure the primer is known. The primed surface was subjected to the heating cycle (curing) outlined below.

- Heat oven and sample to 100°C (212°F) at 2.22°C/min (4°F/min) and hold for 30 minutes.
- Heat oven and sample to 200°C (392°F) at 2.22°C/min (4°F/min), and hold for 30 minutes.
- Heat sample to 250°C (482°F) at 2.22°C/min (4°F/min), and hold for 60 minutes.
- Cool at a rate of 1.11°C/min (2°F/min).

3.3 Bond Fabrication

Chromic acid anodized titanium alloy plates were bonded in a wedge configuration using FM-5 adhesive film. A thin strip of adhesive film was cut and placed on top of the CAA surface of the Ti-alloy plate so that it covered all but 25.4 mm of the surface from one end. A stainless steel shim having a thickness of 0.254 mm (10 mil) was placed on the surface of the plate on either side of the adhesive film, before placing another piece of Ti-alloy plate on top. The stainless steel shim was used to control the bond line thickness. For bonding, at least ten assemblies were prepared and sandwiched between two large flat stainless steel plates, which were then placed inside the Smart press for bonding. The smart press was heated to 250°C at the rate of approximately 7°C/min, thereafter the temperature was held constant for 0.5 hour (B-staged). After the B-stage cycle was completed, specimens were heated to 350°C at the rate of 5°C/min under a pressure of 0.518 MPa (75 lbs/inch²). Subsequently, the temperature was held constant at 350°C and the adhesive was cured for 1 hour under a pressure at 0.518 MPa (75 lbs/inch²). Bonded specimens were then cooled to room temperature under 0.518 MPa pressure inside the smart press at a cooling rate of 5°C/min. A diagram of the adhesive bonding time-temperature curing profile is shown in Figure 3.2.

3.4 Thermal Treatment

A stainless steel sample rack was built to allow simultaneous thermal treatment of many samples. The wedge and lap specimens were thermally treated at various temperatures for selected times in air in a Thermolyne Model Number FA1730 furnace with a Furnatrol type-53600 controller. The furnace was preheated to the desired temperature prior to introducing the specimens into the furnace and the time of thermal treatment was measured. After the thermal treatment at a set

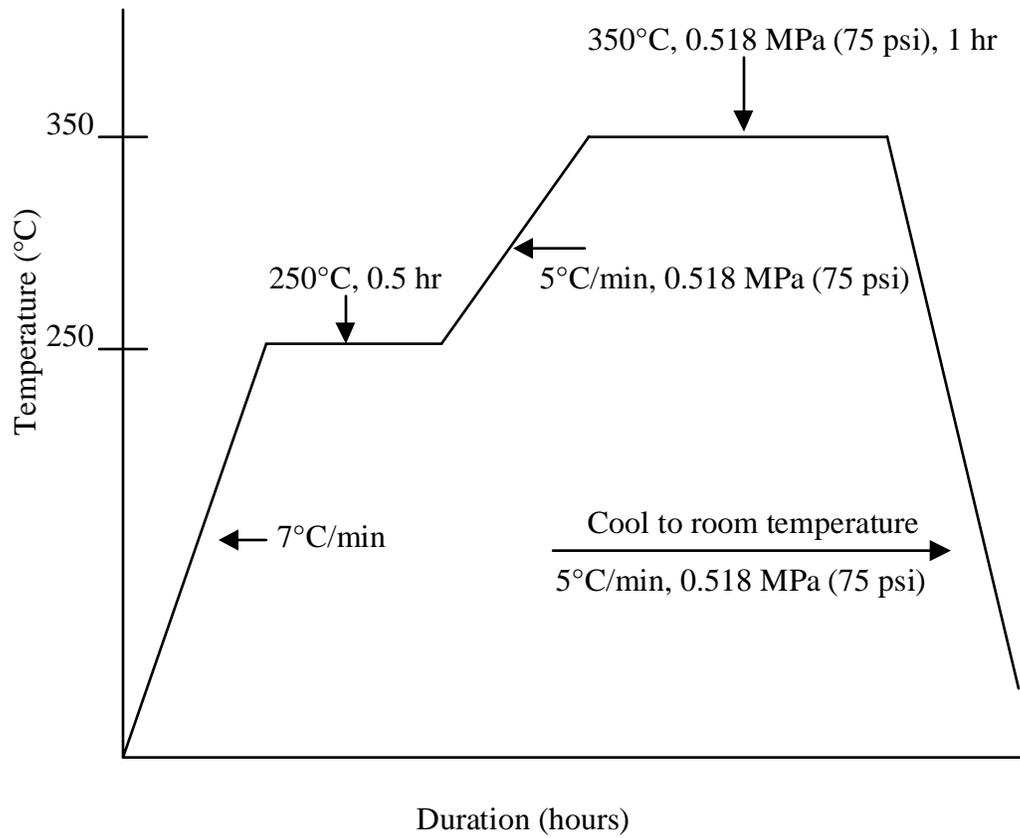


Figure 3.2. A schematic diagram showing the adhesive bonding time-temperature curing profile for FM-5/Ti-6Al-4V bonded joints.

temperature for a set duration of time, the test specimen was cooled inside the furnace to 200°C and subsequently air-cooled to room temperature outside the oven. The bonded lap specimens, thermally treated at 204°C and 177°C, were air-cooled to room temperature outside the oven immediately after the timed thermal treatment.

3.5 Material Characterization

3.5.1 FM-5 adhesive characterization

The surface and bulk chemical compositions of cured and uncured FM-5 adhesive were determined using XPS. XPS analysis of bulk adhesive was carried out primarily to simulate the failure surfaces of bonded joints which often revealed scrim cloth. XPS analysis of adhesive bulk (sub-surface region) was carried out by scraping off a small amount of adhesive from the surface of FM-5 adhesive film until scrim cloth could be seen underneath.

Thermo-oxidative stability of FM-5 adhesive was determined from thermogravimetric analysis of cured FM-5 adhesive. Dynamic TGA scans were obtained using a V5.1A DuPont 2100 thermogravimetric analyzer. The air flow rate to the sample chamber was adjusted to 60 mL/min. The sample was heated at the rate of 10°C/min in air and the weight loss of the polymer was monitored as a function of temperature. The glass transition temperature (T_g) of cured FM-5 adhesive was determined from DSC measurement. The T_g Measurements were conducted on a V4.0B DuPont 2100 Differential Scanning Calorimeter at a heating rate of 10°C/min. The glass transition temperature of cured FM-5 adhesive as a function of additional heating at 371°C and 399°C for various times was also determined.

3.5.2 Adherend characterization

As anodized (chromic acid anodized) Ti-6Al-4V alloy specimens, anodized and thermally treated Ti-6Al-4V alloy specimens, and anodized and boiling water exposed specimens were

characterized using XPS, AES, SEM and AFM techniques. Following boiling water exposure, the CAA Ti-6Al-4V specimens were dried in an oven at 50°C for 1.0 hour and then characterized using various techniques. The surface and bulk chemical compositions of the CAA Ti-6Al-4V alloy were determined using XPS sputter-depth profile analysis.

3.6 Test Methods

3.6.1 Wedge Test

The wedge test configuration was used to study the influence of thermal treatment history on the bond durability of adhesively bonded Ti-sample immersed in boiling water [161]. Chromic acid anodized titanium plates were either first thermally treated in an oven in air for different times and then bonded with FM-5 adhesive or were bonded with FM-5 adhesive first and then thermally treated in air for various times. Primer was not applied to the chromic acid anodized titanium substrates for the wedge tests. Thermal treatment was carried out at 371°C, in air, for 0.5 or 1.0 or for 3.0 hours. After the thermal treatment, a 2 mm thick stainless steel wedge (25.4 × 25.4 mm) was inserted at that end of the bonded specimen where a part of the adherend surface was not covered with the adhesive. The wedge was inserted at the rate of 25.4 mm/min, in the test specimen until the edge of the wedge was flush with the specimen end (25.4 mm). The initial crack length was measured immediately after wedge insertion and then the specimen was transferred to the glass vessel containing boiling water. The crack growth was monitored as a function of immersion time. The strain energy release rate (G) of adhesively bonded joints as a function of crack length was also calculated [160, 162]. The modulus of elasticity for Ti-6Al-4V alloy, used in the calculation of G, is $E = 1.60 \times 10^7$ psi (11.03×10^4 MPa). For each treatment condition at least five specimens were tested. A few non-thermally treated chromic acid anodized and bonded Ti-6Al-4V specimens in the wedge test configuration were also exposed to boiling water to serve as control samples. After about 144 hours of immersion in boiling water, a representative specimen from each treatment condition was removed from the test vessel and debonded. To understand the failure mechanism, the failure surfaces of debonded specimens

were characterized using x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), scanning electron microscopy (SEM), energy dispersive analysis of x-rays (EDAX) and Fourier transform infrared spectroscopy (FTIR).

To study the influence of temperature on the bond durability of non-thermally treated adhesively bonded Ti-6Al-4V alloy in air, the wedge specimens were prepared as described below. The titanium plates were first chromic acid anodized and then bonded, in a wedge test configuration with FM-5 adhesive film. No primer was applied to the chromic acid anodized titanium plates prior to adhesive bonding. Immediately after the wedge insertion, the initial crack length was measured before placing a specimen in a particular environmental condition (temperature). The crack growth was then monitored as a function of exposure time. The specimens were placed in one of the three environments: (i) cold temperature (-25°C), freezer (ii) room temperature (24°C), desiccator and (iii) high temperature (177°C), forced-air oven. The selection of above three test temperatures is justified since aircraft are expected to experience a very cold temperature ($< -50^{\circ}\text{C}$) during normal flight and a high temperature of about 177°C on the surface of the aircraft during supersonic flight due to friction in the air. Since the aircraft will be exposed to the ambient atmospheric environment for the most time when it is not flying, the selection of 24°C as one of the test temperature is obvious. At least five specimens were tested for each environmental exposure condition. Since the crack propagation was slow in each exposure condition, the specimens were allowed to remain in the test condition for well over 10,000 hours before removing a representative sample for failure analysis. To determine the failure mode, the failure surfaces were characterized using x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

3.6.2 Lap Shear Test

The bonded specimens in the lap shear configuration were fabricated by the Boeing Company and were provided for thermal aging and testing. The lap shear test configuration was used to study the influence of long-time air exposure at a relatively low temperature and short-time air

exposure at a relatively high temperature on the lap strength and failure mode(s). For studies involving long-time/low temperature thermal treatments, bonded specimens were thermally treated in air at 177°C for 4 weeks and 4 months and at 204°C for 1 week and 4 weeks. For studies involving short-time/high temperature thermal treatments, specimens were thermally treated at 350°C for 0.5 hr, 1.0 hr, 2.0 hrs, 3.0 hrs, 5.0 hrs, 11.0 hrs and 24.0 hrs, and at 371°C, 385°C and 399°C for 0.5 hr, 1.0 hr, 2.0 hrs and 3.0 hrs each.

Following thermal treatment, the specimen was debonded in air, at room temperature in an Instron Machine (Model 4505). The ASTM standard method for lap shear test (ASTM D1002 standard) was used, and the failure force (lap shear strength) was measured. The testing rate was set at 1.27 mm/min [183].

To establish the failure mode, a representative specimen from each treatment condition was selected for the post-failure analysis. These failure surfaces were characterized using x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), scanning electron microscopy (SEM), energy dispersive analysis of x-rays (EDAX) and Fourier transform infrared spectroscopy (FTIR).

3.7 Analytical Techniques

3.7.1 Fourier Transform Infrared Spectroscopy

The Nicolet 5DXB FTIR spectrometer, equipped with a DTGS KBr detector and external reflection accessories provided by Harrick Scientific Co., was used to obtain the diffuse reflectance spectra of samples. The diffuse reflectance method [165-168] was employed to obtain the reflectance spectra of the adhesive film, failure surfaces and pretreated bare alloys. The individual spectra were obtained at a 45° angle with respect to the incident beam direction. The sample chamber was purged with dry nitrogen for at least 30 minutes before a spectrum in the range 400 to 4000 cm⁻¹ was obtained. One thousand co-added interferograms were scanned

at 4 cm^{-1} resolution. The Kramers-Kronig transformation [169] was carried out only on those regions of the spectrum that showed derivative-shaped bands. The baseline correction was carried out, where necessary, to correct a sloping, curving or any undesirable baseline in the spectrum.

3.7.2 X-ray Photoelectron Spectroscopy (XPS)

The XPS [170] surface analyses were carried out on oxide coatings of an as anodized surface, anodized and thermally treated surfaces and on the wedge and the lap failure surfaces. XPS surface analyses were also carried out on each failure surface. XPS spectra were obtained on a PHI Perkin-Elmer Model 5400 photoelectron spectrometer. The excitation radiation was a Mg K α X-ray ($h\nu = 1253.6 \text{ eV}$). The X-ray generator was operated at 14 kV and 300 watts. A PHI 10-360 hemispherical energy analyzer was used which operated in the constant pass energy (E_0) mode, where $E_0 = 44.75 \text{ eV}$ for survey scans and $E_0 = 17.9 \text{ eV}$ for high-resolution narrow scans. The vacuum was maintained below 5×10^{-7} torr during analysis. The XPS spectra were obtained at take-off angle of 45° with respect to the surface of the sample unless otherwise noted. Initially a wide scan spectrum (survey scan) over a binding energy range of 1 to 1100 eV was obtained. All the elements were then identified from their binding energies, and then a narrow scan was carried out for each element identified in the survey scan. The 1s level spectra were obtained for carbon, oxygen, nitrogen and fluorine, and 2p level data were collected for silicon, aluminum, titanium and calcium. The peak positions were referenced to the background carbon 1s photopeak at 285.0 eV. The analysis area was $1 \text{ mm} \times 3 \text{ mm}$ unless otherwise noted. At least three spots were analyzed on a representative sample surface and the average atomic concentrations for different chemical species were obtained. For some elements, the spectra were curve fit. The curve-fitting procedure assumed peaks of Gaussian shape, and the background was assumed to be linear. During curve-fitting, three basic parameters; peak position, full width half maximum (FWHM) and peak height were input for each sub-photopeaks, and curve-fitting software (Standard PHI software) was allowed to refine the fit by adjusting each parameter within pre-defined limits. The parameter limits on peak position, FWHM and

peak area were set at ± 0.1 eV, ± 0.1 eV and $\pm 20\%$ abs., respectively, with respect to initial set values. The initial value of the XPS photopeak or sub-photopeak position and FWHM was chosen based on the prior knowledge of chemical nature of the sample material and from XPS data of standard reference materials.

The XPS sputter-depth profile was carried out on as anodized non-treated and thermally and water exposed CAA treated Ti-6Al-4V. The sputter rate was $5 \text{ \AA}/\text{min}$ ($0.5 \text{ nm}/\text{min}$), the sputter rate was calibrated using a standard tantalum material of known oxide (Ta_2O_5) thickness (1000 \AA).

3.7.3 Auger Electron Spectroscopy (AES)

The Scanning Auger Microprobe, PHI Perkin-Elmer Model 610 was used to obtain the AES spectra. The AES [170] spectra were obtained with electron beam voltage at either 3 kV or at 5 kV and the beam current at 0.05 \mu A . Depth profile was carried out using an energetic argon ion beam (Ar^+ ion at 4 kV, argon gas pressure $15 \times 10^{-3} \text{ Pa}$) with an ion beam current of 0.2 \mu A . The raster size was set at $1.7 \times 1.7 \text{ mm}$. The standard tantalum oxide (Ta_2O_5) film, of known thickness (1000 \AA), was used to calibrate the Ar^+ ion etching rate for thickness measurements. The etching rate was $5 \text{ nm}/\text{min}$ ($50 \text{ \AA}/\text{min}$) for $1.7 \times 1.7 \text{ mm}$ raster size (sputtered area). Initially a wide scan spectrum (survey spectra) was collected between 1 – 2000 eV, following which the depth profile was carried out.

3.7.4 Secondary Ion Mass Spectrometry (SIMS)

Dynamic SIMS [178] spectra were collected on a Perkin-Elmer PHI 610 scanning Auger microprobe with a model 3500 SIMS II attachment which incorporates a 90° spherical sector ion analyzer and a quadrupole mass analyzer. The sample surface was sputtered with an argon or xenon ion beam with the sample set at 45° with respect to the emitted ions. The ion beam voltage and beam current were set at 4.0 kV and 5.0 \mu A , respectively. The sputtering rate,

calibrated using a tantalum oxide standard, was 5 nm/min (50 Å/min) for 1.7 × 1.7 mm raster size (sputtered area). SIMS spectra were obtained for positive and negative ions having mass to charge ratio from 1 to 100 daltons. The chemical composition of the surface oxide on chromic acid anodized Ti-6Al-4V alloy was analyzed using Ar⁺ and Xe⁺ ions as probes. The dynamic SIMS technique was also used to examine the chemical composition of the oxide on the failure surfaces of lap shear specimens that were debonded following the thermal treatment at 399°C for 2 hours in air.

3.7.5 Scanning Electron Microscopy (SEM)

The scanning electron photomicrographs [176] were obtained with an International Scientific Instruments (Model SX-40) scanning electron microscope. All test samples were sputter coated with a 200Å thick layer of gold to avoid undesirable charging of the sample surface during the imaging process. An Edwards Sputter Coater Model S150B (Edwards High Vacuum, Manor Royal, Crawley, West Sussex, RH102LW, England) was used for sputter coating gold on the sample surfaces. The SEM photomicrographs of test samples were obtained at appropriate magnification to reveal the surface topography. The SEM photomicrographs were obtained mostly at 20, 200 and 1000 times magnification. EDX analysis were carried out on some failure surfaces for lap specimens to obtain a elemental mapping of certain features visible in the SEM photographs.

A Field Emission Scanning Electron Microscopy (FE-SEM) was used (LEO model 1550 Field Emission Scanning Electron Microscope) to characterize the oxide surfaces of non-treated (as-anodized), boiling water treated and thermally treated CAA Ti-6Al-4V alloy specimens. The FE-SEM was operated at 0.25 to 2.0 kV.

3.7.6 Atomic Force Microscopy (AFM)

A Digital Instruments Dimension 3000 with a Nano Scope 111a controller was used for obtaining AFM images of samples. The Tapping Etched Silicon Probe (TESP) with a mean spring constant of 35 N/m and a mean resonant frequency of 317 kHz was used to obtain tapping mode AFM images. First, a large surface area of the sample was scanned, a representative area was selected and an AFM image of that area was obtained. The roughness analysis was carried out on a $1\ \mu\text{m} \times 1\ \mu\text{m}$ or $5\ \mu\text{m} \times 5\ \mu\text{m}$ area of the surface image obtained for each sample. The surface oxide roughness parameters, the root mean square deviation of the roughness curve profile (RMS), mean value of the roughness curve relative to the center line (R_a) and the difference in height between the highest and lowest points on the cross-sectional profile relative to the center line over the length of the profile (R_{max}) were determined in addition to other surface roughness statistics.

AFM has a definite advantage over other imaging techniques such as, SEM and STEM in imaging nonconductive materials. Since AFM imaging does not require that the material surface be coated with a thin layer of metal to make the surface conducting, this technique is non-destructive.

3.7.7 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was used to determine the glass transition temperature (T_g) of the uncured and cured scrim cloth supported FM-5 polyimide adhesive. Measurements were conducted on a V4.0B DuPont 2100 Differential Scanning Calorimeter at a heating rate of $10^\circ\text{C}/\text{min}$ in air. The T_g values were taken as the midpoint of the change in slope of the baseline.

3.7.8 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed to evaluate the thermo-oxidative stability of the cured FM-5 adhesive. Dynamic TGA scans were obtained using a V5.1A DuPont 2100 thermogravimetric analyzer. The powdered sample was placed in the aluminum pan connected

to an electric microbalance. The air flow rate to the sample chamber was adjusted to 60 mL/min. The sample was heated at the rate of 10°C/min in air and the weight loss of the polymer was monitored as a function of temperature. The temperature corresponding to a 5% weight loss of the polymer material was reported.