DURABILITY OF POLYIMDE TO TITANIUM BONDS

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Abstract
High temperature resistant adhesives are used in aviation, space, and automotive industries. Titanium and its alloys are usually bonded together using a high temperature polyimide or epoxy adhesives. Such adhesives can withstand temperatures from 200°C to300°C. Earlier research work indicates that Surface modification of titanium with mechanical treatment and atmospheric pressure plasma treatment techniques leads to improved adhesive bond strength of polyimide with titanium at room temperature. In this investigation, durability of these improved adhesive bond strength titanium samples is studied at elevated temperature and moisture level. Samples were exposed at 80°C and 60% Relative humidity conditions in moisture oven. Another set of samples was placed in heating oven at 80°C for dry aging of samples. After conditioning these samples were subjected to single lap shear tensile test. Combined effect of relatively high temperature and moisture on bond strength of titanium samples and only high temperature dry aged samples are studied. Single lap shear tensile test results indicate that conditioning at high temperature and moisture resulted in significant decrease of adhesive bond strength, where as dry aging at same temperature has no effect on adhesive bond strength. A complete comparison of the bond strength of these elevated condition samples and normal room condition samples will be presented in this paper.

1.Introduction

Titanium and its alloys are widely used in aviation and space applications because of many desirable high temperature properties, like excellent strength to weight ratio, and good corrosion resistance[1].Titanium alloys are extensively employed in solid rocket booster cases, guidance control pressure vessels and a wide variety of applications demanding light weight and reliability[2]. Titanium alloys are usually bonded together using high temperature Polyimide adhesive. Surface modification of titanium surface with atmospheric pressure plasma treatment and mechanical grit blasting lead to an improved adhesive bond strength at room temperature[2, 3].

Now a day adhesive bonding is the preferred joining technique for titanium structures, where as in the past focus was more on welding and riveting. There are numerous advantages for this technology, such as continuity of adhesive bond which allows more uniform distribution of stresses in the bonded area and the fact that most commonly used titanium alloys demonstrate poor weldability[4]. However, for the adhesive bonding the surface treatment appears to be the critical factor in order to generate a good bond strength and long term durability[5, 6].

The initial strength of these high performance adhesives is fairly high enough at room temperature. It is well established that long term durability of these adhesively bonded joints is influenced by presence of high humidity [7]. Earlier research work from authors showed that bonding of titanium sheet with polyimide adhesive can be improved by different surface modification techniques i.e. mechanical grit blasting and atmospheric pressure plasma surface medication [3, 8].

The properties of oxide films on metals are important in a number of surface phenomena, such as adsorption, localized corrosion and adhesion of organic coatings [9].The surface treatment leads to changes in the oxide chemistry resulting in a direct influence on the subsequent bonding behavior with organic functional groups [10].

Based on these considerations, this study investigates effect of moisture and dry aging on the adhesive bond strength of improved titanium samples bonded with polyimide adhesive after grit blasting and atmospheric pressure plasma samples.

2.Experimental

2.1 Materials

In this investigation, a titanium alloy Ti 6Al4V of AMS4911 Grade 5 supplied by AmEuro Metals BV Netherlands is used. The chemical composition of this titanium alloy according to chemical composition test result by manufacturer is given in Table 1.

Element	Ti	Al	V	Fe	O	C	N	H
Weight (%)	88.10	6.75	4.50	0.25	0.20	0.08	0.05	0.015

Table 1. *Chemical composition of the TiAl6V4 alloy*

High temperature resistant, thermally stable polyimide adhesive #124-41with Phenylenediamine as its main component is supplied by Creative materials Inc. USA and is used for adhesive bonding of Titanium alloy. The glass transition temperature of this polyimide adhesive is above 250^{0}C and the service temperature ranges from -55 ^{0}C to +250 ^{0}C.It is thermal stability at temperatures upto 325^{0}C.The listed tensile shear strength for this adhesive is 8.6 MPa.

2.2 Test sample preparation

Titanium alloy samples are made according ASTM standards D1002-05.i.e Standard test method for Apparent Shear strength of single lap joint adhesively bonded metal specimens by tension loading. Titanium samples are made of 100X25X3.2 mm dimensions. These samples are subjected to surface modification methods, i.e. grit blasting only and a combination of grit blasting and plasma surface modification. In this way three sets of titanium samples are made ready.

1. Untreated Titanium samples.
2. Grit blasted titanium samples
3. Grit blasted and plasma treated titanium samples

These samples are further divided into two categories

I- Dry aging at 80°C

II- Moisture conditioning at 60% RH and 80°C

Three sets of samples are joined using high performance Polyimide adhesive at room temperature with an overlap of 12.7± 0.25 as shown in figure 2.1 and subject to curing at 175 °C. Thickness of Adhesive film is controlled at 0.3mm using glass beads. These samples are now ready for moisture conditioning in moisture oven.

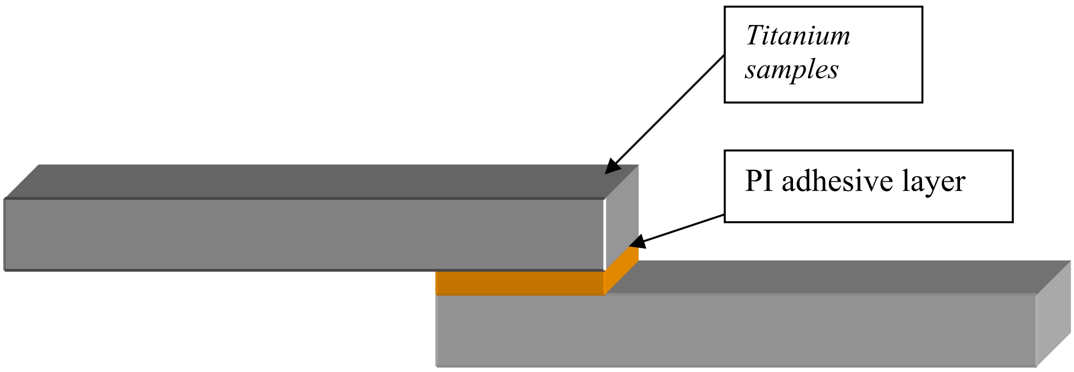

Fig 2.1.*single lap shear titanium samples for preconditioning in the moisture oven*

*2.3 Moisture conditioning in Q5000 moisture sorption analyzer***.**

In order to calculate the moisture saturation time for these samples in moisture oven, thin film of polyimide adhesive of dimension 12 X 8 X 0.3mm is prepared .Thin film of PI is exposed to 60%RH and 80°C in Q5000 moisture sorption analyzer as shown in figure 2.2.Moisture saturation level in thin film is determined by Fickan model fit[11]. Moisture saturation weight percentage Msat and Diffusion coefficient D is calculated at particular temperature using Fickian model fit . These values are used in Fickian equation 2.1in MATLAB simulations to determine moisture saturation level in thin film of Polyimide adhesive between two strips of Titanium, when placed in moisture conditioning oven.

$$M_t = M_\infty \left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\{-(2n+1)^2 \pi^2 Dt/h^2\} \right] \tag{2.1}$$

Adhesively bonded titanium samples are exposed to 60% RH and 80°C for 80 days as determined by equation 2.1 and moisture saturation level is achieved.

Fig 2.2. Q *5000 Moisture sorption analyzer*

2.4 Dry conditioning of samples.

An other set of surface modified and untreated samples bonded with Polyimide adhesive prepared under same conditions as mention above are placed in oven at 80°C for 80 days for comparison and study effect of moisture on adhesive bond strength.

2.5 Tensile Lap Shear Testing.

Lap Shear testing is carried out using a computer-controlled testing machine, Zwick 250KN static test machine, and a load cell of 100 KN. The specimens are loaded in tension at a test speed of 2 mm/min. five specimens were used for each material. All tests are performed at 80 ^{0}C [12].

3. Results and Discussion.

Moisture saturation level in thin adhesive layer between two titanium strips is determined by fickian equation and MATLAB simulations as presented in figure.3.1

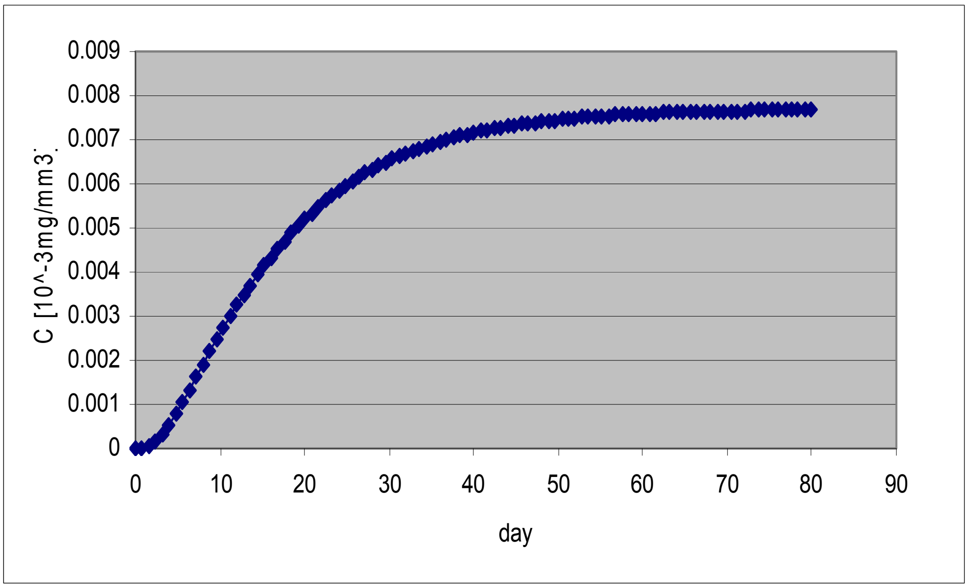

Fig.3.1. Moisture *saturation in PI adhesive layer at 60% RH and 80°C.*

From figure 3.1 it is clear that moisture saturation time is 80 days for thin layer of polyimide adhesive between titanium strips.

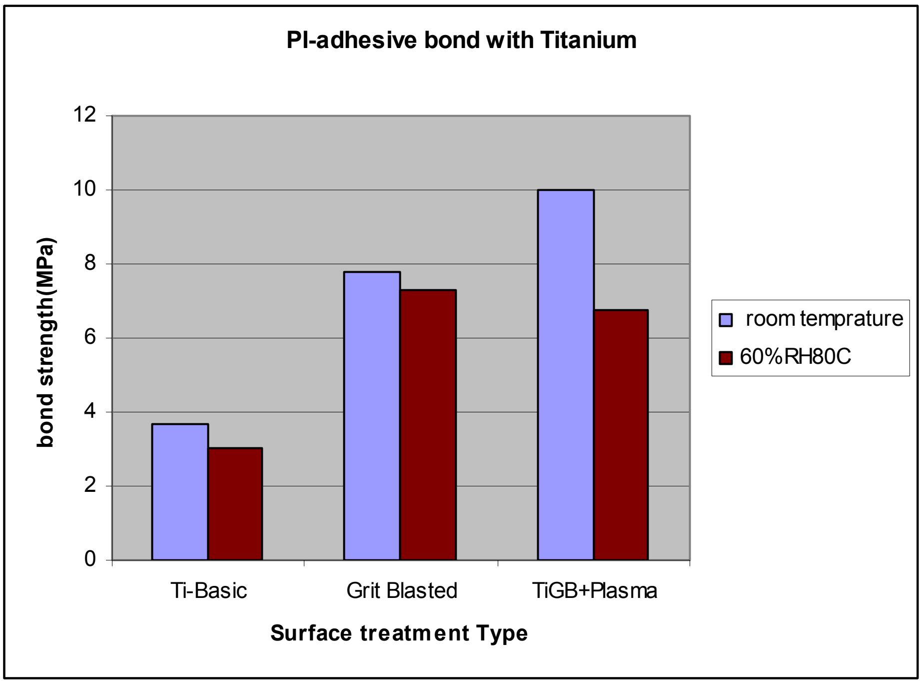

Fig.3.2. *Comparison of Polyimide adhesive bond strength with Titanium at room temperature and after precondition at 60%RH and 80°C*

A comparison of bond strength during single lap shear test of Polyimide with surface modified titanium at room temperature and preconditioned samples for 80 days at 60%RH and 80C is presented in Fig 3.2.Adesive bond strength improved at room temperature after surface modification at room temperature. After precondition there is significant decrease in bond strength of grit blasted followed by plasma treated titanium samples. However there is minor decrease in bond strength of untreated basic samples and Grit blasted samples.

Another comparison of lap shear test results of Polyimide with surface modified titanium after dry aging at 80°C and room temperature samples is presented in figure 3.3.

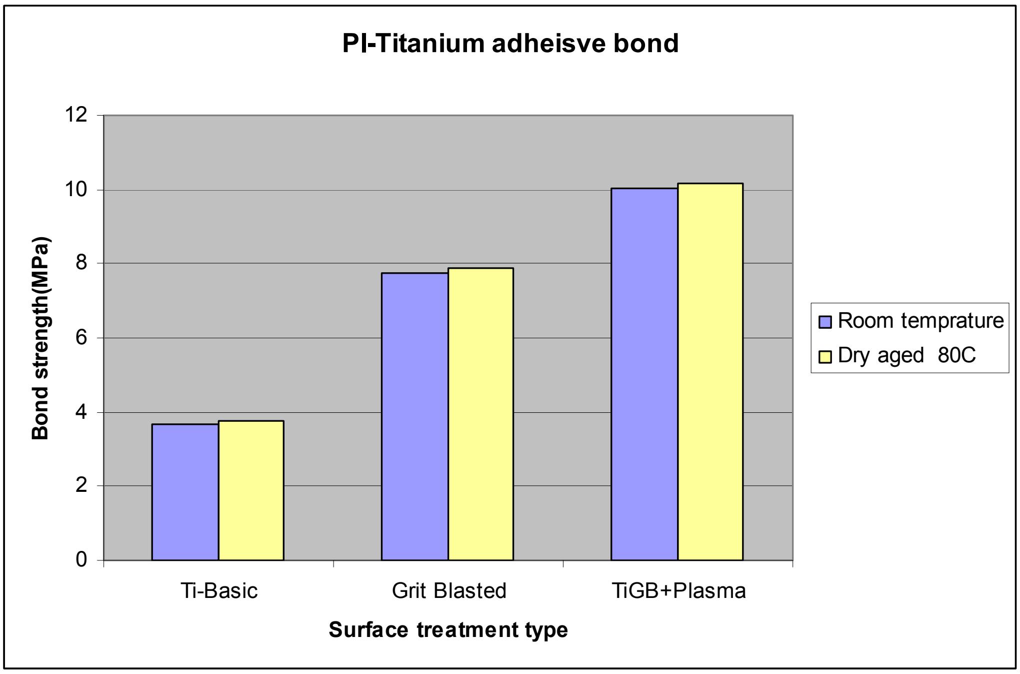

Fig.3.3. *Comparison of Polyimide adhesive bond strength with Titanium at room temperature and after precondition at 60%RH and 80°C*

There is no significant change in bond strength after dry aging at 80°C for 80 days in dry oven.

4.Discussion

Lap shear tensile tests of PI adhesive bonded titanium samples at room temperature shows an improvement in lap shear bond strength after surface treatment. After mechanical treatment bond strength improved from 3.66 MPa to 7.5MPa due to mechanical interlocking and more area available for bonding due to grit blasting. Atmospheric pressure plasma treatment of grit blasted samples results in a further improvement of bond strength from 7.5 to 10.1 MPa. The reason could be that oxide radical induced on titanium surface made it strongly acidic and react actively with amine anhydrate unsaturated group present in PI adhesive and lead to improvement in adhesive bond strength[3].

After preconditioning of PI adhesive bonded titanium samples at $80^{o}C$ and 60% Relative humidity in moisture oven, lap shear tensile tests are performed at $80^{o}C$.There is no change observed in bond strength of basic and grit blasted titanium samples as increase in bond strength is due to mechanical interlocking and not because of any chemical interaction . However titanium samples which are subjected to atmospheric pressure plasma treatment after grit blasting indicate a downward trend in bond strength after preconditioning. As increase in bond strength of after plasma treatment is due to bonding of oxide radical present on titanium surface with PI adhesive. During preconditioning these oxide radicals have attracted more polar water molecules and formed bonding with water molecules rather than PI adhesive groups. Because of this phenomenon, atmospheric pressure plasma treated samples indicates almost the same bond strength as Grit blasted titanium samples after pre-conditioning.Dry aging of atmospheric pressure plasma treated samples at $80^{0}C$ does not effect adhesive bond strength and it is comparable to adhesive bond strength of atmospheric pressure plasma modified titanium samples at room temperature. As there is no water molecule available for chemical interaction in case of dry aging.

5.Conclusion

Adhesive bond strength of titanium with polyimide can be improved by mechanical grit blasting and atmospheric pressure plasma treatment at room temperature. Mechanical Grit blasted samples adhesive bond strength can withstand both elevated temperature and high relative humidity (RH) conditions. However grit blasted followed by atmospheric pressure plasma treated samples can withstand its bond strength at high temperature in dry conditions only. Under high relative humidity and elevated temperature conditions, it lose its bond strength due to interaction of oxide radicals with polar water molecules, and bond strength becomes equal to mechanical treated samples bond strength.

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