SESSION 3B: Joining

SURFACE MODIFICATION OF TITANIUM BY ATMOSPHERIC PRESSURE PLASMA TREATMENT FOR ADHESIVE BONDING AND ITS APPLICATION TO AVIATION AND SPACE

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ABSTRACT

Titanium is one of the most effective materials for structural application of space craft and aviation. Titanium alloys are widely used in solid rocket booster cases, guidance control pressure vessel and other different applications demanding light weight and reliability. Aerospace industry is also a larger market for titanium products and adhesive bonding is advantageous in terms of its fabrication. However, surface treatment of titanium alloy is critical in improving the adhesive bond strength and long term durability of the adhesive joint. In this investigation surface treatment of titanium is carried out by plasma ion implantation in order to increase adhesive bond strength and durability. Optical microscopic and SEM analysis of untreated and atmospheric plasma treated specimens is carried out to examine the surface characteristics. A substantial improvement in the surface energy of Titanium is observed after the atmospheric plasma treatment. The Treated surface was basically characterized by contact angle analyzer for the activation property on the surface. The surface energy of titanium surface increases with increasing exposure time of atmospheric pressure plasma. The optimized time of plasma treatment suggested in this investigation results maximum adhesive bond strength with polyimide adhesive and consequently, this technology is highly acceptable for aviation and space applications.

Key Words: Titanium, Surface modification, Atmospheric pressure plasma and Surface Energy, Adhesive bonding

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1. INTRODUCTION:

Titanium used for structural elements of aerospace and spacecraft since early Mercury and Apollo operations. Aerospace industry is also a larger market for titanium products primarily due to exceptional strength to weight ratio, and high resistance to elevated temperatures and corrosion [1]. Often in fabrication processes titanium sheets are joined by using adhesive rather than welding or riveting. However, for improving the performance of adhesive bonding of titanium for aerospace and space climatic conditions, it is necessary to modify the surface of titanium[2]. The principle objective of this study is to improve the mechanical properties of titanium surface by increasing surface energy.

Traditional methods for surface treatment are mostly chemical. Materials are immersed in chemical baths which often exhibits hazardous and pollutant by-

products [3].In particular TiAl6v4 titanium alloy widely used in aeronautical industry often undergoes specific surface treatments for improving its adhesion properties. For this alloy typical treatment methods are mechanical and/or chemical or even electrochemical. To this day, the method more frequently used is chromic anodic oxidation. Plasma technology has emerged as an alternative solution to surface treatment, having the advantage of being environmentally friendly [4].
Plasma–chemical methods suitable for coating and surface treatment replace conventional galvanic methods since they are not as harmful for the environment as the classical ones. Many types of low pressure plasma chemical systems have been developed up to now, but most of them worked at low pressures in the range of several tens Torr or less. All these systems require high vacuum equipment whose cost is growing with dimensions of technological process. In this study, therefore, we report the investigations of surface modification phenomena of titanium by Plasma jet treated under the conditions of nearly atmospheric plasma jet.

2. EXPERIMENTAL DETAILS:

2.1 Materials Description

The material used in this study is the TiAl6V4 alloy. The samples are of industrial quality, typically used in aeronautical applications, implying that their surface presents morphological inhomogeneities and is polluted by oils/lubricants due to the manufacturing and cutting processes. Samples have the following dimensions: 100×25 mm (2.8 mm in thickness). The bulk composition of this alloy is given in Table 1, where it is shown that it mainly contains 6.75% of aluminum and 4.5% of vanadium as well as impurities in low concentrations.

Table 1.Chemical Composition of the TiAl6V4 Alloy

Element	Ti	Al	V	Fe	O	C	N	H
Weight (%)	88.105	6.75	4.50	0.30	0.20	0.08	0.05	0.015

Two test liquids, deionized water and form amide of known polar and dispersion components of surface energy were used to determine the polar and dispersion components of surface energies of substrate materials through measurement of contact angle by the sessile drop method. The known components of surface energy of liquids are shown in table 2.

Table 2.Polar, Dispersion and Total Surface energy of test liquids

Liquids	γ_{LV}^{P} (m N/m)	γ_{LV}^{D} (m N/m)	γ_{LV} (m N/m)
Deionized Water	50.2	22.0	72.2
Formamide	18.6	39.6	58.2

We investigated titanium samples which were categorized into following groups

1- As received titanium samples.
2- Grit blasted titanium samples using alumina 50 micron balls
3- Atmospheric pressure plasma treated samples

2.2 Surface Modification of Titanium

Before Titanium samples analysis, the substrates were sequentially cleaned in acetone, methyl alcohol and De ionized water by an ultrasonic cleaning method. Further, Titanium surface was modified by following methods:

Mechanical treatment was carried out using Alumina grit in a grit blasting chamber. The apparatus is rectangular cabinet and has a self-contained, recycling, sealed glove box design. A blasting angle of 90° was used. The grit blasting device was operated manually. To ensure repeatability and consistency in the grit blasting operation, the time spent blasting each substrate was limited to 120 sec. To remove any loose particles of alumina grit after grit blasting, the surface was cleaned with acetone and alcohol using ultrasonic cleaning method.

Five of above grit blasted samples were subjected to plasma treatment. Grit blasted and ultrasonically washed titanium samples were treated with atmospheric pressure plasma using TIGRES Plasma-Blaster MEF equipment. It operates at 230 V and 50/60 HZ frequency. For this particular study, the treatment distance of substrate from nozzle head of plasma equipment was 10 mm and the gas used for treatment was air with a total flow rate of 51 l/min at a pressure of 4.5 bars. Plasma surface treatment time was gradually increased from 5 minutes to 15 minutes and its effect on surface energy was observed.

2.3 Contact Angle Measurement and Surface Energy Estimation

Contact angles were measured by the sessile drop technique using the Modular "CAM 200– Optical contact angle and surface tension meter". The ultimate objective of measuring the contact angle was to estimate the surface energy of untreated and atmospheric plasma treated specimens. The surface energy and its polar and dispersion components for as received, mechanical treated and plasma treated samples were calculated using the following equation[5].

$$(1+\cos\theta)\gamma_{LV} = 2(\gamma_S^D \gamma_{LV}^D)^{1/2} + 2(\gamma_S^P \gamma_{LV}^P)^{1/2} \quad (1)$$

In equation (1), θ is measured contact angle of liquid with solid surface'γ_{LV}'is total surface tension of the liquid, γ_{LV}^D is the dispersion component of the liquid and 'γ_{LV}^P'is polar component of the liquid. Contact angles of both liquids on the solid surfaces were determined by sessile drop method and then unknown dispersion and polar components of the solid surface were determined. Finally, the total surface energy'γ_S' was estimated by adding γ_S^P and γ_S^D as given in Equation(2)

$$\gamma_S = \gamma_S^D + \gamma_S^P \quad (2)$$

2.4 Adhesive Joint Preparation and Tensile Lap Shear Testing

Rectangular specimens, having dimensions 110x25x3 mm^3, were used for tensile lap shear testing. The specimens were bonded for single tensile lap shear test by applying a high temperature resistant polyimide adhesive. Overlap joint have an adhesive thickness of about 0.20 mm. The adhesive thickness was controlled by adding 1 weight percent of glass beads in the adhesive and applying a uniform pressure. Pressure was applied to the lap joint during the curing cycle by two binder clips. The bonded specimens were cured at 175℃ for 1 hour with a subsequent post curing at 210°C for five hours. Lap shear testing was carried out using a computer-controlled Zwick 250kN Static test machine, and a load cell of 100kN. The specimens were loaded in tension at a test speed of 5 mm/min. five specimens were used for each treatment method.

2.5 Microscopic Studies of Substrate Surfaces

Scanning electron microscopy was used to study the surface roughness of the (i) as received Titanium samples (ii) mechanical treated titanium samples (iii) mechanically treated and atmospheric Plasma treated Titanium samples. Images were obtained using a "JOEL JSM-7500F" field emission scanning electron microscope (FE-SEM).

3. Results and Discussion

3.1 Contact Angle Measurements:

Contact angle measurement of as received titanium samples, grit blasted titanium sample and atmospheric pressure plasma treated samples are given in Table 3. The average contact angles of as received samples after washing with acetone were 98.28^o and 55.23^o with water and Form amide respectively. After grit blasting the contact angle reduced to 30.96^o and 14.31^o.These values decreased to lowest values of 8.13^o and 3.01^{o}after plasma treatment.

Table 3.Contact angle measurements of Titanium samples after treatments

Sr.No	Treatment	Liquid Phase	Contact Angle in degrees	SD
1	As Received	Water	98.281	0.438
2	Grit Blasted	Water	30.964	1.063
3	Grit Blast +Plasma Treated	Water	8.133	0.168
4	As Received	Form amide	55.232	0.142
5	Grit Blast	Form amide	14.318	0.010
6	Grit Blast+ Plasma Treated	Form amide	3.012	0.657

3.2 Surface Energy of As Received, Mechanical Treated and Plasma treated Titanium samples

The surface energy estimation of titanium surface as received titanium samples, grit blasted titanium samples and plasma treated titanium is given in table 4. As the surface of titanium was modified by grit blasting and atmospheric pressure plasma treatment a significant improvement in polar component of surface energy was observed as shown in Fig 1.

Table 4.Surface Energy Estimation of Titanium Surface after Treatments

Sr .No	Treatment	polar component γ_S^P	Dispersion component γ_S^D	Total surface Energy γ_S	SD
1	As Received	5.210$\pm$0.109	32,198$\pm$0.149	37.409	0.090
2	Grit blasted	40,962$\pm$1.136	22,017+0.578	62.980	0.558
3	GB+Plasma treated	55,928$\pm$0.611	16,712$\pm$0.198	72.640	0.424

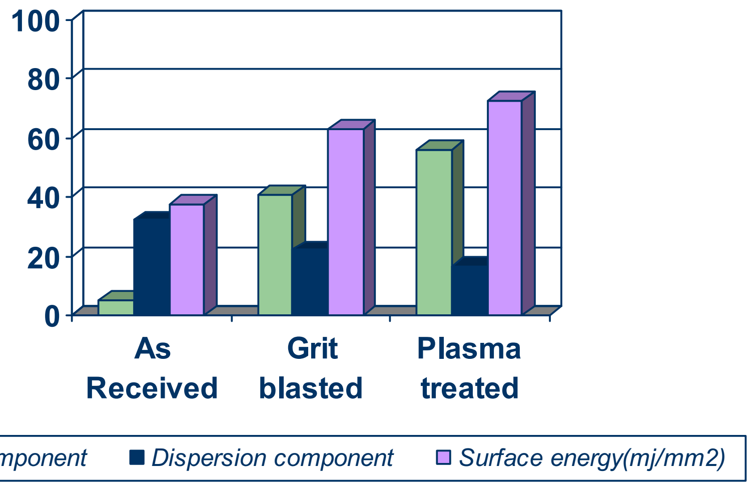

***Figure (1) Surface energy estimation of titanium after different treatments*.**

3.3 Scanning Electron Microscope Study:

A difference in surface roughness of as received Titanium samples and grit blasted samples can be observed in images of SEM in figure 2(a) and 2(b).There is remarkable increase in surface roughness after grit blasting of titanium sample surface. However comparison of fig 2(b) and 2(c) indicates that there is no distinct change in surface roughness of titanium samples after atmospheric plasma treatment.

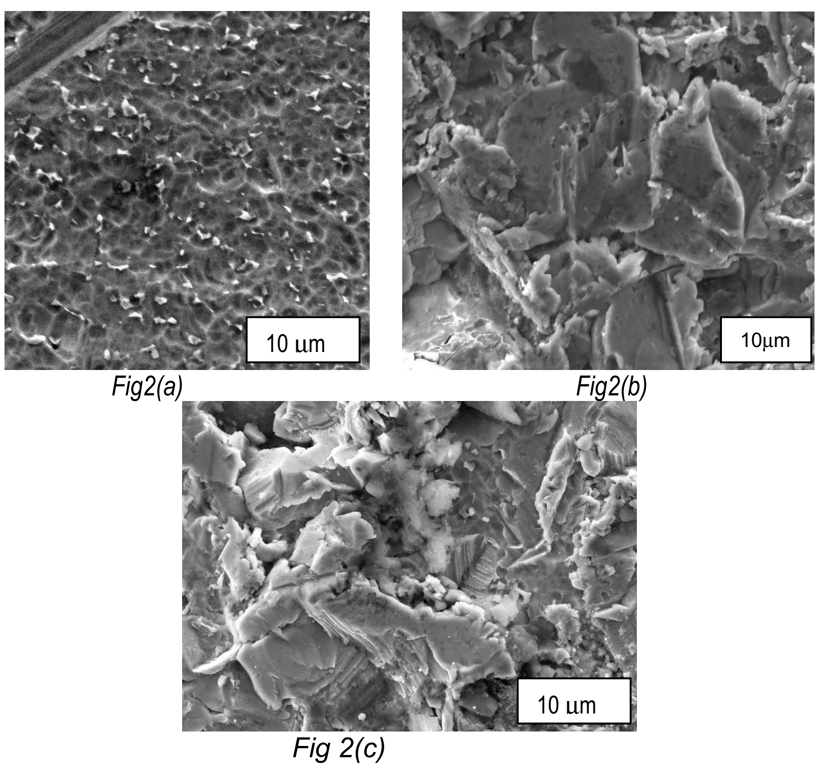

Fig 2(a) As Received Titanium alloy after ultrasonic cleaning with ethanol X1500 magnification, Fig2(b) Grit Blasted with alumina and ultrasonically cleaned with ethanol X1500 magnification, Fig 2(C) Grit Blasted ,Ultrasonically cleaned with Ethanol and plasma treated for 20 minutes X1500 magnification

3.4 Lap Shear Tensile properties of Adhesive Bonded joints

Table 5 reveals that the adhesive bond strength of titanium to titanium during lap shear tensile test of as received titanium samples bonded using high performance polyimide adhesive is 3.65 MPa. After Mechanical treatment, the bond strength raised to 7.75 MPa, and when mechanically treated surface further modified by atmospheric pressure plasma, we get a bond strength up to 10.01MPa. Adhesively bonded as received titanium samples failed at the interface of titanium substrate and the adhesive, but in other two cases failure mode is mixed and joint fail cohesively within the adhesive.

Table 5.Summery of test results of adhesive bonded joints

Substrate Material	Treatment	Joint configuration	Bonded Area (mm^2)	Failure Mode	Joint Strength (MPa)	SD (MPa)
Titanium	AS Received sample	Overlap joint	312.50	Interface failure	3,657	0.20
Titanium	Grit blasted Sample	Overlap joint	312.50	Mixed failure	7.759	0.54
Titanium	Atmospheric pressure Plasma Treated	Overlap joint	312.50	Adhesive failure	10.01	0.25

4. DISCUSSION

Surface treatment when applied to metallic alloys generally affects three distinct stages of physico-chemical conditions.The first stage is surface cleaning i.e. removal of oils on the surface of oils and other organic lubricants used during the samples' manufacturing and cutting process. Secondly, the superficial native oxidation layer has to be removed by etching.Finally, surface chemical conversion which is desired final state of the surface.
The aim of this work is to investigate, depending on experimental conditions, the efficiency of the “plasma jet” on achieving these distinct but closely related and overlapping stages of treatment. According to the initial nature of the metal (physical and chemical states) and the experimental parameters of the “plasma jet”, the aforementioned treatment phases (cleaning, etching and chemical conversion) could be necessary for industrial applications like painting and adhesion. SEM analysis of as received, grit blasted and plasma treated surface indicated that there is a remarkable increase in surface roughness of Titanium alloy after grit blasting. An increase in surface energy of Titanium after grit blasting could be attributed to increase in area available for adsorption of adhesive on metal surface. After plasma treatment increase in surface energy is due to some chemical reactions not simply due to increase in surface roughness. There is a weak boundary layer of organic contamination before plasma treatment on outer surface of titanium. The increase in wettability could also be an indication of removal of organic contamination leading to higher surface energy after cleaning. Before plasma treatment titanium percentage is lower in outer layer. After plasma treatment, percentage of titanium and oxygen increases where as that of carbon and silicon decreases. These results suggest cleaning and activation of surface by plasma treatment.

5. CONCLUSION

Grit blasting and atmospheric pressure plasma resulted an increase in macro roughness and removal of contamination, as well as weak boundary layer of titanium alloy. This phenomenon leads to an increase in adhesive bond strength of titanium with high performance polymers. Activated nitrogen and oxygen species could etch and oxidize the surface, resulting in increased surface energies. Plasma treatment resulted in increased Titanium oxide in upper layer of Titanium alloy. So it can be concluded that after plasma treatment increase in adhesive bond strength is due to more Titanium oxide available for Lewis acid/base interaction.

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