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Investigation on nanoadhesive bonding of plasma modified titanium for aerospace application

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Abstract. Physico-chemical changes of the plasma modified titanium alloy [Ti-6Al-4V] surface were studied with respect to their crystallographic changes by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM).The plasma-treatmentof surface was carried out to enhance adhesion of high performance nano reinforced epoxy adhesive, a phenomenon that was manifested in subsequent experimental results. The enhancement of adhesion as a consequence of improved spreading and wetting on metal surface was studied by contact angle (sessile drop method) and surface energy determination, which shows a distinct increase in polar component of surface energy. The synergism in bond strength was established by analyzing the lap-shear strength of titanium laminate. The extent of enhancement in thermal stability of the dispersed nanosilica particles reinforced epoxy adhesive was studied by Thermo Gravimetric Analysis (TGA), which shows an increase in onset of degradation and high amount of residuals at the high temperature range under study. The fractured surfaces of the joint were examined by Scanning electron microscope (SEM).

Keywords: titanium; plasma; adhesion; XRD; contact angle; SEM

1. Introduction

Titanium alloys are widely used in aerospace industries demanding lightweight and reliability. It is used in aeroplanes, missiles and rockets where strength, low weight, resistance to high temperatures and corrosion resistance are of prime importance (Bhowmik *et al.* 2009). According to Baker (2010), the normal approach to modify the surface properties of titanium alloy such as tribological characteristics is to increase the wettability and hardness of its surface with respect to the native one while retaining the bulk properties of the alloy intact. Recently, the AIRBUS Company is giving special attention for surface modification of titanium, which could enhance the adhesive bond durability (Bhowmik *et al.*2006a).

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In this investigation, surface modification of titanium has been carried out by plasma nitriding process (Bhowmik *et al.* 2009) that makes use of a glow discharge to harden the surface and sub-surface of metals by introducing active nitrogen to their surface for subsequent diffusion into the bulk, up to a depth of some microns. The process had been traditionally used to improve wear, corrosion and fatigue resistance of various metals.

Adhesive bonding technique has shown itself to be capable of replacing conventional joining methods such as riveting (Bhowmik *et al.* 2008), welding (Shenton *et al.* 2001) and mechanical fastening in a variety of applications because of better fatigue performance and high strength to weight ratio (Dean *et al.* 2006). Adhesives contribute highly to structural integrity, ease of manufacturing, enhanced performance, improved safety, cost and time saving (Bhowmik *et al.* 2001). In general, riveting and welding result in high stress concentration, which is absolutely negligible in the case of adhesive bonding where any stress developed, gets distributed over the entire surface area (Custódio *et al.* 2009). Present trend of research on surface modification of metals including titanium reveals that diffusion of nitrogen atoms inside the crystal lattice of a metal surface, a phenomenon known as nitriding essentially improves corrosion resistance leading to better service performance of titanium under aerospace climatic conditions as revealed by Bhowmik and Chaki (2004). Plasma nitriding is a sub-atmospheric pressure process in which titanium sample is biased negative in a gas mixture, with nitrogen as the dominant gas.

It is to be noted that the main problem associated with the application of adhesive for supersonic and hypersonic aircraft is its exposure to high temperatures. The aerodynamic frictional heating of the structure causes this as it moves through the air (Bhowmik *et al.* 2006b). Conventional adhesives such as epoxy, polyurethane etc. could not be used due to low thermal and mechanical properties of adhesive. Therefore, use of high temperature resistant epoxy adhesive and appropriate dispersion of ceramic nano powders in desired weight ratio into the matrix adhesive in order to essentially improve its thermo-mechanical properties has been thought of (Ahmed *et al.* 2011).

Based on these considerations in our present work plasma nitriding treatment is employed to modify the metal surfaces. The surface energy of the titanium is estimated both for untreated and plasma treated specimens. Surface changes of the metal are analyzed by X-ray diffraction (XRD), Optical microscope and SEM. The improvement in adhesion properties of the material after plasma treatment is correlated in terms of lap shear strength of the basic as well as nano epoxy adhesive joints on both native and plasma treated titanium laminates. Finally, scanning electron microscope (SEM) is used to investigate the failure modes of the bonded joints.

2. Experimental

2.1 Materials

Metal titanium sheets of grade 5 (ASTM B 265) are used for this experiment. The high temperature resistant epoxy adhesive (DURALCO 4703) manufactured by Cotronics Corp. Brooklyn, NY, USA having the service temperature ranging from -250^{0}C to 350^{0}C is used to join the titanium sheets. The mixing ratio of resin to hardener, curing temperature and time for this adhesive being 1:0.22, 120^{0}C and 4h respectively. Unmodified silicate nano powder of 50 nm particle size, manufactured by Glassven, La Victoria, Aragua 2121 United States, is used as

Table 1 Polar, dispersion and total surface energy of test liquids

Liquids	Υ_{LV}^{P}	Υ_{LV}^{D}	Υ_{LV}
Deionized Water	50.2	22.0	72.2
Formamide	18.6	39.6	58.2

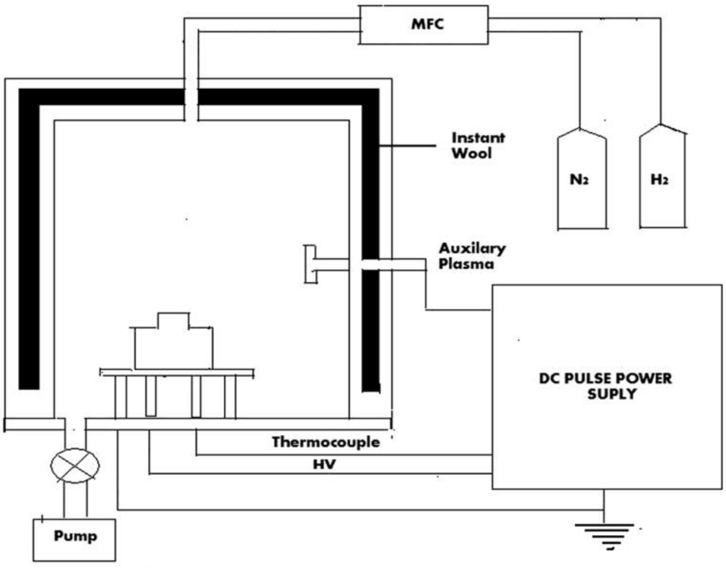
Table 2: Process parameter used of plasma nitriding process

Process parameters		
Base pressure (mbar)		0.08
Sputter cleaning		
Duration (h)		1
Voltage (V)		250-565
Current (Amp.)		0.1-0.3
Gas (SCCM)	Nitrogen	0
	Hydrogen	174
Temperature (^{0}C)		265
Time (h)		1
Pressure of the vessel (mbar)		1.1
Plasma Nitriding		
Pressure (mbar)		7.17
Voltage (V)		661
Current (Amp.)		1.2
Gas (SCCM)	Nitrogen	110
	Hydrogen	27
Temperature (^{0}C)		700
Time (h)		2.08

dispersing nano particles for reinforcement of adhesive. Two test liquids, deionized water and formamide of known polar and dispersion components of surface energy were used to determine the polar and dispersion components as well as 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 1.

2.2 Method: surface modification

Prior to lamination, the surface of the titanium sheet was mechanically polished, cleaned with acetone and then modified by plasma nitriding process. Plasma nitriding was carried out in a 500 mm diameter and 500 mm height bell shaped stainless steel vacuum chamber. The titanium sample was kept on a titanium based circular plate (sample holder), 5 cm in diameter. Initially the vacuum chamber was evacuated to a base pressure of 0.08 mbar by a rotary pump. The sample was first sputter cleaned using hydrogen gas. A pressure of 1 mbar controlled was maintained. Plasma was generated using a direct current (D.C.) power supply having a frequency of 10KHz. Sputter cleaning process was performed for 1 h at 265˚C to remove the native oxide layer on the surface of



MFC- Mass Flow Controller; HV- High Voltage
N_2-Nitrogen; H_2-hydrogen; DC-Direct Current

Fig. 1 Schematic diagram of plasma nitriding system

titanium so as to expose a fresh surface of the sample for plasma nitriding. After completion of the sputter cleaning process, the mixture of nitrogen and hydrogen gas was introduced in the reactor for plasma nitriding. Plasma nitriding was carried out using gas mixture of 80% nitrogen and 20% of hydrogen as decided by trial and error method (Singh *et al.* 2006) under a base pressure 7.17 mbar at 700˚C for 2 h, the discharge voltage for 80% nitrogen being 661 V. After 2 hours, these nitrided samples were cooled in vacuum chamber under the flow of gas mixture till the temperature decreased to 150 ˚C. This is mostly performed to eliminate the chance of formation of oxide layer on surface of the sample. Schematic diagram of plasma nitriding chamber is shown in Fig.1.Various parameters, which are used during plasma nitriding, are shown in Table 2.

2.3 Characterization

2.3.1 X-ray diffraction, scanning electron microscopic and optical microscopic study

X-ray diffraction (XRD) measurements, in θ-2θ geometry (Bragg-Brentano goniometer), were carried out in a Bruker AXS Diffractometer with monochromatic Cu K_α radiation.

The scanning electron microscopies (SEM) analysis of the titanium surface is carried out using JEOL JSM 7500F field emission scanning electron microscope.

The Optical Microscope study of titanium surface is carried out using Leitz make Optical Microscope.

2.3.2 Contact angle measurement and estimation of surface energy

The surface energy and its polar and dispersion components for titanium are calculated using contact angle measurement. Prior to contact angle measurement the titanium surface was cleaned by acetone. Contact angle was measured by sessile drop technique using water and formamide. The Modular "CAM 200– Optical contact angle and surface tension meter" from KSV's instruments (using deionized water and formamide) was used to perform contact angle measurements. The ultimate objective of measuring the contact angle was to estimate the surface energy of untreated and plasma treated specimens. The surface energy and its polar and dispersion components for titanium were calculated using the following equation.

$$(1+\cos\theta)\Upsilon_{LV} = (\Upsilon_S^{D}.\Upsilon_{LV}^{D})^{1/2} + (\Upsilon_S^{P}.\Upsilon_{LV}^{P})^{1/2} \quad (1)$$

Where Υ_{LV} is total surface tension of liquid and Υ_{LV}^{D} and Υ_{LV}^{P} are Dispersion and Polar component of liquids.

From the standard data as shown in Table 1 and with the help of the Eq. (1) we can easily calculate the dispersion and the polar component of solid surface using two liquid surface energy tools. Finally, the total surface energy 'Υ_S' was estimated by adding 'Υ_S^{P}' and 'Υ_S^{D}' as given in Eq. (2).

$$\Upsilon_S = \Upsilon_S^{P} + \Upsilon_S^{D} \quad (2)$$

Where Υ_S^{P} and Υ_S^{D} are the polar and dispersion component of solid surfaces and Υ_S total surface energy of solid surfaces.

2.3.3 Thermal characterization of adhesive

Thermal characteristics of the pure epoxy adhesive and nanosilicate reinforced epoxy adhesive were carried out by using PERKIN-ELMER STA-6000 module TGA instruments, under nitrogen atmosphere at a heating rate of 20˚C / min and scanned from 50˚C to 700˚C. The furnace was purged with nitrogen gas at a rate of 200 ml/min to prevent oxidation.

2.3.4 Mechanical characterization of adhesive

Mechanical characteristics of adhesive were analyzed by lap-shear tensile test. The tensile lap shear test is performed according to the American Society for Testing Material (ASTM D5656 - 10) under a load cell of 10 KN at a test speed of 5mm/min at room temperature.

The tensile lap-shear test samples are prepared using titanium sheets with dimension of 125×25×6 mm^3 by applying the high temperature resistant epoxy adhesive at an overlap length of 25mm. The following two types of the adhesive tensile lap- joints are tested:

(a) Lap joint of titanium to titanium was fabricated with the basic high temperature resistant epoxy adhesive, which was subsequently cured at 120˚, the cure time being 4hrs.

(b) Silicate nano powder to the extent of 5% by weight with respect to the pure adhesive (Resin 2.5 gm, Nanofiller 0.125 gm) was dispersed into the epoxy adhesive by mixing with the help of a mechanical stirrer and then the adhesive lap joints of titanium to titanium were fabricated with this reinforced adhesive and cured at 120˚C for 4 hr.

3. Results and discussion

3.1 X-ray diffraction (XRD) studies

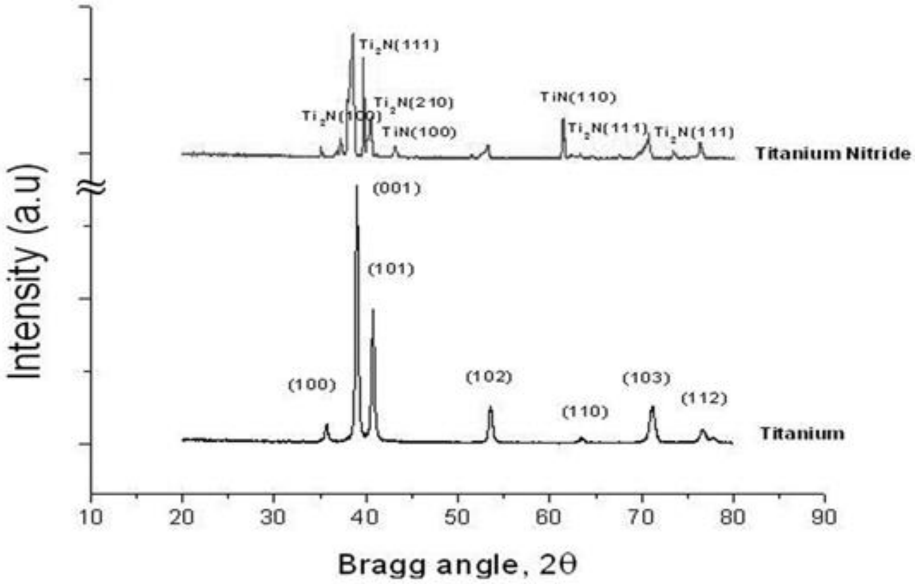
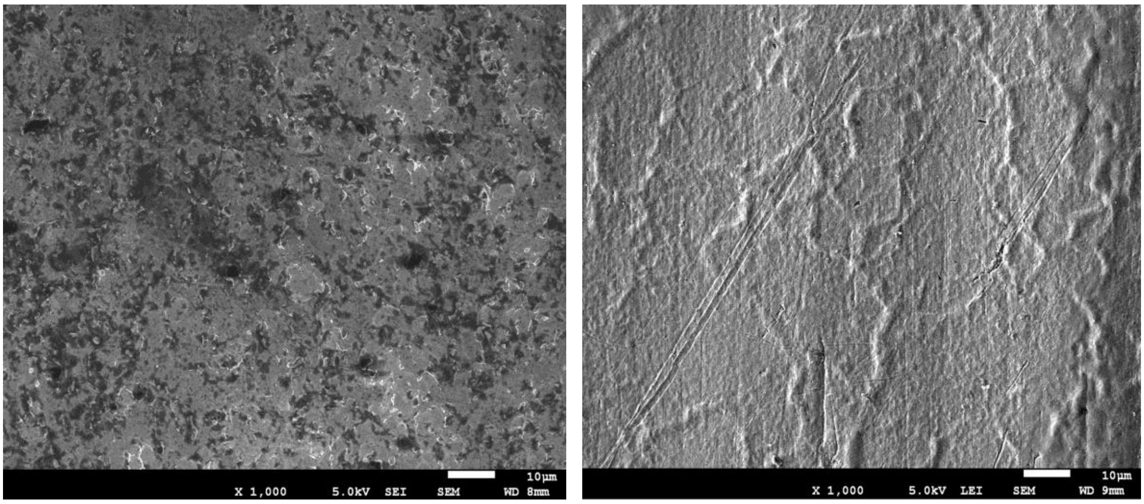


Fig. 2 XRD result of untreated and plasma treated titanium surfaces

The X-ray Diffraction spectrum of both untreated as well as plasma treated titanium surfaces are described in Fig. 2. The crystallographic planes characteristics of titanium metal include (100), (101), (110) and (102), (103), (112) as observed in XRD. Some of them like (110), (100) are still present in plasma nitrided titanium surface while the others are replaced by newly generated (111), (210) planes as manifested in the Fig. 2. This well describes the change in crystallography on the titanium surface due to plasma nitriding. As the XRD result of titanium nitrided surface shows the presence of (100), (110), (111) series of planes, it can be concluded that the nitrided titanium surface possesses cubic close packing (ccp) type lattice structure as indicated in the study described by LeClair (1998). After plasma nitriding at 700^0C newly generated planes (111) and (210) corresponding to Ti_2N (Tetragonal phase) appeared. This observation was corroborated from the findings of Avelar-batista *et al.* (2005), wherein it was confirmed that the appearance of nitrogen was attributed to the formation of Ti_2N phase. The plasma treated surface also showed the formation of TiN and there was confirmed by the presence of (100) and (110) planes. Although the (110) plane is also present in untreated titanium but its peak intensity is marginal. The existence of δ-TiN phase in the plasma nitride sample is confirmed. This finding was also found to be co-incident with those of Yilbas *et al.* (1996).

3.2 X-ray diffraction (XRD) studies

The SEM images of both unmodified titanium as well as plasma nitrided titanium are shown in Fig. 3(a)-(b). In order to correlate the topography of the unmodified, polished and cleaned surface of titanium and that on plasma nitrided titanium surface, we can see a drastic change in topography on nitriding. While the unmodified surface reveals a rough surface full of peaks and valleys with irregularly distributed crests, trough and craters, the nitrided surface shows a regular pattern of distribution of the peaks and valleys with somewhat oriented topography, possibly offering greater



(a) (b)

Fig. 3 Scanning electron microscopic images of titanium surface before and after plasma treatment

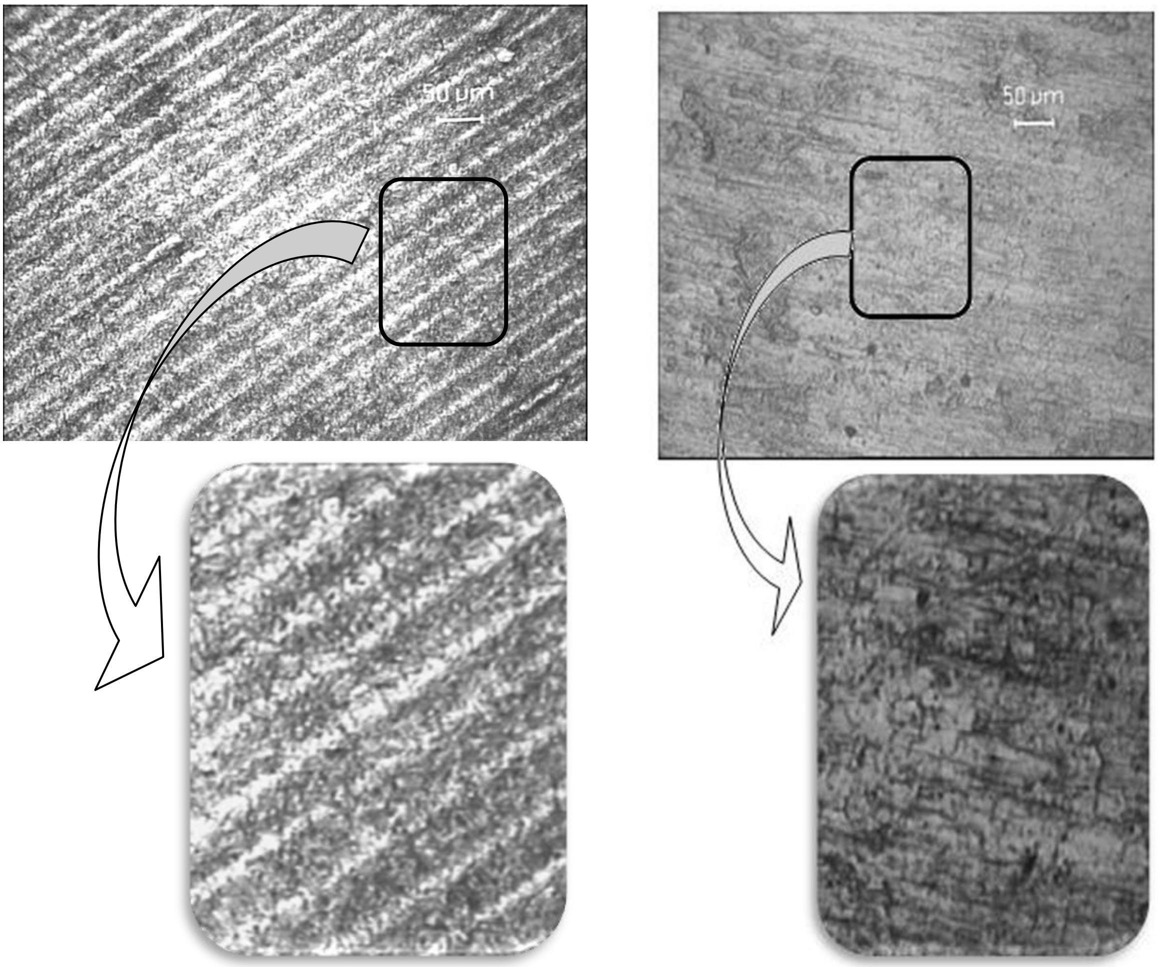
surface contact with the adhesive layer during lamination. Evidence of crystallographic modification on the surface of the plasma nitrided titanium surface is revealed from the appearance of thick sharp grain boundaries separating the individual crystallites or spherulites as indicated in the study described by Bhowmik and Chaki (2004). In the untreated sample no such boundary has been observed. This is well reflected by the S. Jha et.al experiment where they showed that, with increasing the proportion of titanium nitride the evenness of the rough surface that is more uniform distribution of the peaks and valleys occurs (Jha *et al.*2010). These findings are corroborated by the optical microscopic observations described in Fig. 4(a)-(b). In the plasma nitrided surface the manifestation of crystallographic changes in relation to the untreated one is quite apparent. The regular smooth cascading planes in unmodified titanium surface are replaced by well-defined grain boundaries in plasma treated surfaces.

3.3 Contact angle and surface energy measurement on titanium surfaces

It is observed that due to surface modification of titanium by plasma nitriding, there is a significant increase in surface energy when compared to the surface energy of untreated titanium surface. A comparison of surface energy; its polar and dispersion components for titanium before and after plasma treatment is shown in Fig. 5. The figure shows that due to plasma nitridinga significant increase in polar component of surface energy is observed though dispersion component of surface energy decreases a little due to exposure. The total surface energy of metal surface is thus increased. This increase in surface polarity augments in distribution of the adhesive (polar in nature) applied there in a uniform pattern. This in-turn helps in improved spreading and wetting of the adhesive on the titanium nitrided layer.

3.4 Thermal properties of high temperature adhesive and nano adhesive

Thermogravimetric analysis (TGA) was employed to determine the thermal stability of epoxy adhesive (DURALCO-4703), employed in the present study for laminating titanium to titanium. TGA results for pure epoxy adhesive and nanosilicate reinforced epoxy adhesive are shown in Fig. 6. A comparative analysis of the thermal stabilities of the filled and unfilled laminating epoxy adhesive systems reveals an increased stability of the filled system in the temperature range under investigation. It is well documented by literature review that thermal and mechanical properties of epoxy adhesive improve considerably due to incorporation of nanosilicate powder into the polymer matrix (Iqbal *et al.* 2010). The initial weight loss of the filled adhesive, which occurred at approximately 125^0C may be attributed to the loss of moisture, which may account nearly 2% of the initial weight. The subsequent loss or the second step of degradation occurred over a region of 125 ^{0}C to 350 ^{0}C, the rate of loss was very slow but steady as represented by the slope of the degradation curve and an approximate weight loss of about 12% occurred in this step. In the third step the rate of degradation is fast and its onset and end set may be considered as 350 ^{0}C and 425 ^{0}C respectively, beyond which the filled adhesive system was resistant to degradation and



(a) Unmodified titanium surface (b) Modified titanium surface

Fig. 4 Optical microscopic images of titanium surface before and after plasma treatment approximate weight of about 60% is left behind as the residue. In contrast, the unfilled system undergoes degradation right from the beginning that is from approximately 50 ^{0}C and proceeds at a very fast rate till a temperature of 350 ^{0}C is reached subsequent to which these exhibit a faster degradation rate and finally leaving a residue of only about 27%. From the narration above it is quite distinct that the nano filled adhesive system used in the study possesses much higher thermal stability than the non-filled one. The present investigation of the nano adhesive bonding of titanium by dispersing nano powder in high temperature epoxy adhesive shows a considerable improvement of thermal properties of adhesive even when there is a loading of only 5% of nano silicate powder in the basic epoxy resin.

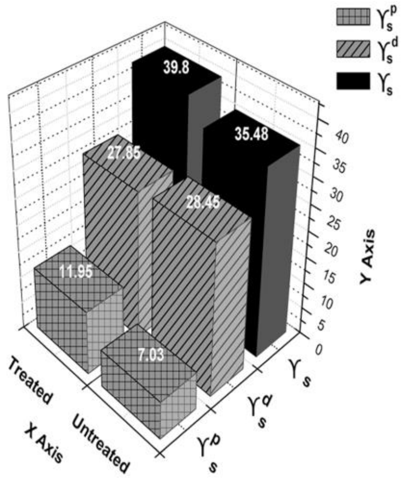


Fig. 5 Comparison of surface energy, polar and dispersive components of titanium materials before and after plasma treatment

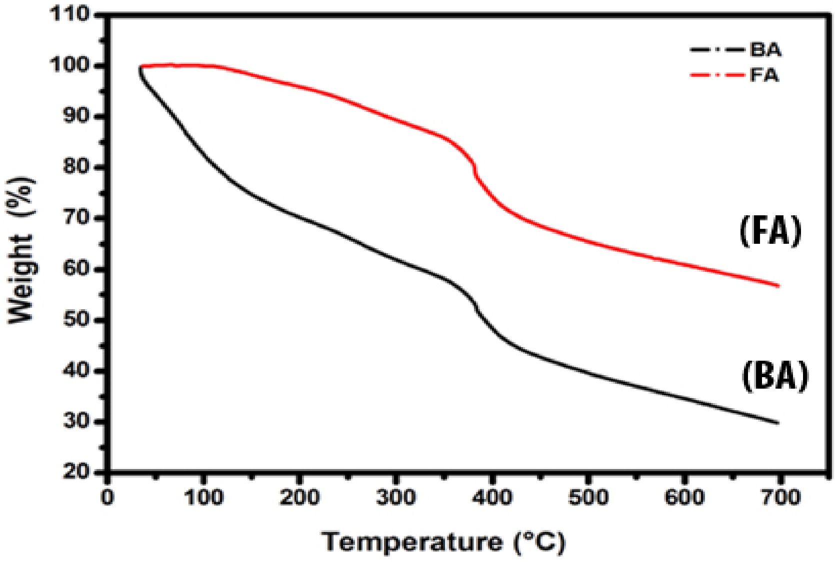
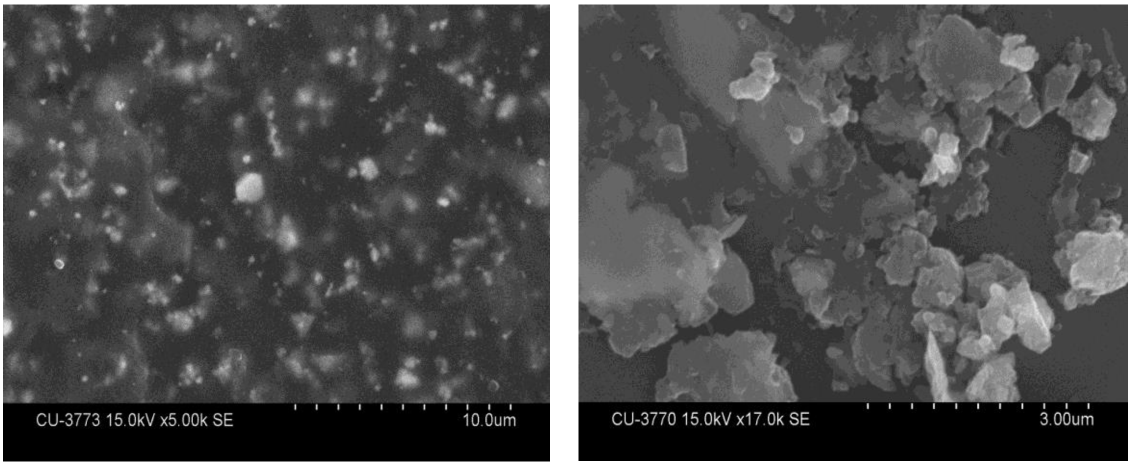


Fig. 6 TGA results of cured basic adhesive (BA) and nano reinforced filled (FA)epoxy adhesive



(a) Epoxy adhesive film (b) Nano reinforced epoxy adhesive film

Fig. 7 Scanning electron microscopic images of cured basic and nano reinforced epoxy adhesive film

3.5 Scanning electron microscope (SEM) studies on high temperature adhesive and nano adhesive

The analysis of scanning electron micrographs on both unfilled and nano filled epoxy adhesive system was performed to investigate the dispersion of nanosilicates reinforcing material and are shown in Fig. 7(a)-(b). The figure clearly demonstrates a different feature with the inclusion of silicate nano powder. Nano silicate particles have very high surface area that essentially influences the overall performance of the adhesive(Jha *et al.* 2010). The SEM image of the unfilled adhesive shows a uniform distribution of mineral filler in the epoxy matrix as supplied. The further incorporation of the nanosilicate material invokes a tendency of agglomeration of the mineral filler-nano filler, nano filler-nano filler and mineral filler-mineral filler interaction within the epoxy matrix. The cumulative effect is the generation of a blend of different phases of filler particles over which the epoxy matrix can anchor and get the possibility of stress transfer through them in a much improved fashion contrast to the epoxy system containing only the mineral filler.

3.6 Lap-shear tensile properties of adhesive bonded titanium laminate

Lap shear tensile testing was carried out to evaluate the effect of plasma nitriding on the adhesive bond strength. Four laminates samples; two with untreated native titanium alloy; (one of them getting laminated with the mineral filled epoxy adhesive system as supplied and the other being bonded with epoxy adhesive containing both mineral filler and reinforcing nanosilicate filler) and the other two, with plasma nitride titanium alloys being bonded (as previously with mineral filled epoxy adhesive and in the other case nanosilicate and mineral filled adhesive). Lap-shear test results for titanium before and after plasma nitriding treatment are shown in Fig. 8. Five specimens for each variety were subjected to such tests and the average mechanical values were considered.

The Fig. 8 reveals that the adhesive joint strength of the titanium-titanium is 10MPa when mineral filled adhesive as supplied is used and the strength increases to 15MPa when nano silicate

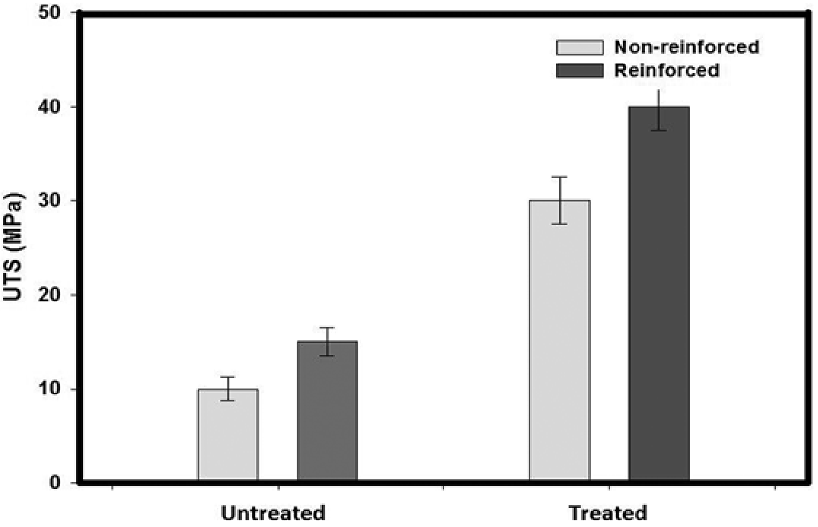
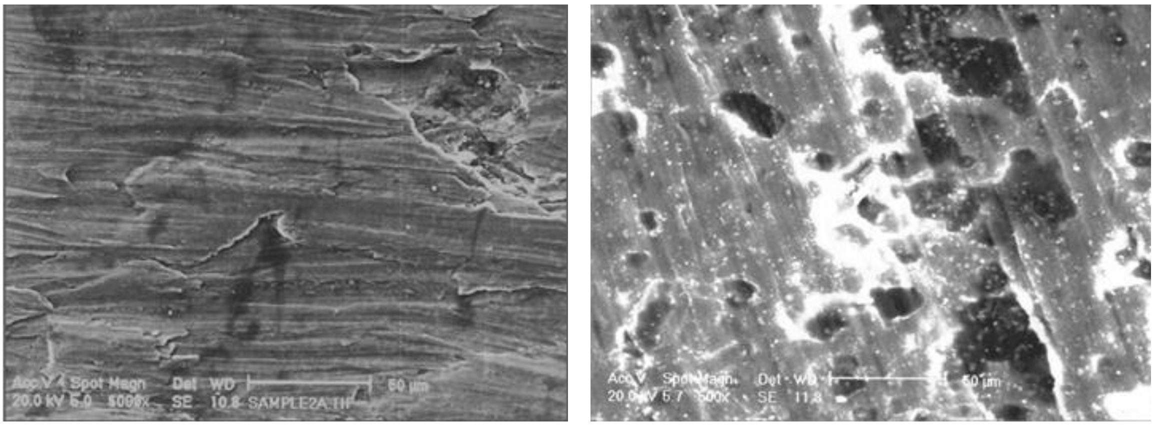


Fig. 8 Lap shear test results of untreated and plasma treated titanium adhesive joint

reinforced epoxy adhesive containing original mineral filler is used. In the second case, when surface modified titanium is used, the joint strength is increased to 30MPa with the adhesive as supplied (mineral containing filler). It is observed that there is considerable increase in joint strength to 40MPa, when the plasma nitriding titanium laminate is prepared with nano silicate epoxy adhesive (mineral containing filler). Frauehiger and Schlottig (2004) have revealed that anodic plasma chemical processes essentially modify the chemical and morphological properties of the titanium surface. Ramaniand Zhao (2004) have also emphasized that surface modification of titanium, especially by plasma sputtering and sodium hydroxide anodization, proves beneficial for the joint under severe chemical climates. It has been reported that when plasma sputtering modifies titanium surfaces, the durability of adhesive joints of titanium improves under the wedge cleavage test (Sautrot *et al.* 2005). In line of the present investigation, Bhowmikand coworkers (Bhowmik *et al.* 2006) have revealed that adhesive joints of plasma nitrided or anodized titanium essentially failed cohesively within the adhesive. Hanawaand coworkers (Hanawa *et al.* 2002) have emphasized that surface properties can also be changed through laser or electron beam thermal treatment without adding or removing material. The layer is grown electrochemically from the bulk of the metal and modified by heat treatment, this essentially enhancing the durability of adhesive bonding of titanium when subjected to corrosive environments. Zingerand Chauvy (2003) have modified titanium surface by plasma sputtering and anodization. They also reveal that electrochemical properties of titanium surface improve due to this modification. A remarkable improvement of tensile properties is observed of titanium-titanium adhesive joints due to modification by Plasma ion implantation technique (Bhowmik *et al.* 2009).

In light of the above discussion it may be inferred that due to formation of a mixture of nitrides like Ti_3N, Ti_2N and TiN respectively there was tremendous increase in polarity to the titanium surface, which imparted the necessary adhesion force that surpassed force of cohesion. This is possible because the protective coating of nitrides of titanium surface generated under plasma nitriding helps in reducing the interfacial tension between titanium and the adhesive. Also the extra boost in lap shear tensile strength (about 10MPa) for Nano silica reinforced plasma treated



(a) Bare titanium surface (b) Plasma treated titanium

Fig. 9 Scanning electron micrograph showing interfacial failure and cohesive failure for bare titanium and plasma treated titanium surfaces respectively

titanium laminates may be considered to be due to synergistic action of both nanosilica reinforcement and the surface modification.

3.7 SEM Fractographic analysis of titanium adhesive joint

The failure analysis of adhesive joints of titanium as shown in Fig. 9(a)-(b) which confirmed that adhesive joints for unmodified titanium laminates fail from titanium-adhesive interface resulting in low joint strength. Adhesive bonded joints can fail by a variety of failure modes. The most common failure modes observed for the adhesive bonded joints are (i) Interfacial failure (ii) Cohesive failure in the adhesive or in the adherend, or (iii) mixed mode failure. The failure mode depends on the materials of the adherends, adhesive, and joint preparation (Iqbal *et al.* 2012). In the present case it is observed that the failure is of cohesive nature, which indicates that titanium adhesive bonding is much higher than the adhesive-adhesive bonding. Moreover, it has been observed that the adhesive applied on one substrate is split almost equally in two halves on the two titanium surfaces when the bonding occurs: a characteristic of good bonding. This is proved by the cohesive failure occurring for this joint, which is well reflected in scanning electron microscopic image of this joint (Fig. 9 (b)).

4. Conclusions

- The proper surface treatment by plasma nitriding is liable to remove the dust, dirt and all sorts of contaminants including any oxide layer which can stand as barrier and increase the Van der Walls distance such that it can maximize the appropriate intimacy between the adhesive and the adherend and strengthen the bonding. The increase in polar constituent of surface energy, as indicated by a reduction in equilibrium contact angle, the spreading and wetting characteristics of the surface have enabled to achieve such high strength. Increase in total surface energy of the solid surface provides greater contact at the boundary of two, titanium metal surface and the adhesive layer.

- The formation of the various nitrides has been exemplified in its XRD, SEM and Optical microscopy studies. From these microscopic studies it was also revealed that the random and haphazard peaks and valleys on the untreated surface of titanium have been made more uniform as if the nitride formation has made land filling as per the requirement and smoothened the surface so as to offer a greater surface area of contact.
- The XRD studies have ensured the crystallographic modifications. The change in surface crystallography and the orientation of the grain boundaries at the surface of titanium have been manifested in the various microscopic studies.
- There is no doubt about the supremacy of the plasma nitrided surface over the untreated one in terms of all rounds performance, namely the adhesive bond strength, the distribution of the adhesive layer and its splitting effect on the two surfaces of titanium almost in identical manner, the enormous improvement in thermal stability etc.
- In order to elucidate the unique effect of the nanofiller, the epoxy adhesive was modified by the inclusion of 5% nano silicate powder and laminate of titanium sheets were made keeping the adhesive coating weight almost identical to unmodified adhesive. Glow discharge plasma nitriding and nanofiller reinforcement gives a synergistic boost in adhesion, which is well described in this paper.

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