Blistering in alloy Ti–6Al–4V from H⁺ ion implantation

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Abstract. The effect of H⁺ ion implantation on surface morphology of the titanium alloy, Ti–6Al–4V, was studied, following H⁺ ion implantation of 150 keV and 250 keV energy to fluence of $2.6 \times 10^{18} \text{ cm}^{-2}$ and $2.5 \times 10^{19} \text{ cm}^{-2}$, respectively at ambient temperature. No detectable change was observed in surface features of either of the above specimen immediately after the implantation. However, vein like features (VLF) were observed to appear on the surface of the sample, implanted at 150 keV to a fluence of $2.6 \times 10^{18} \text{ cm}^{-2}$, following natural ageing at room temperature for 150 days. Subsequent annealing of the above naturally aged sample, at 423 K for 150 min under vacuum (10^{-3} torr), led to development of a macroblister.

In sharp contrast in the other sample, implanted by H⁺ ions of higher energy (250 keV) to higher fluence of $2.5 \times 10^{19} \text{ cm}^{-2}$, neither there was any effect of natural ageing following the implantation nor that of subsequent annealing at 423 K and ageing on its surface morphology.

Keywords. H⁺ ion implantation; blisters; surface modification; Ti–6Al–4V alloy.

1. Introduction

Titanium and its alloys assume much importance in space technology owing to their high specific strength and corrosion resistance. Structural components in space technology experience different types of radiations, therefore, their stability in such environments becomes an important consideration for their suitability. Stability of titanium and its alloys against H⁺ ion irradiation is of concern in view of their application as first wall and a diverter material because of their low induced radio activities and small cooling effects by sputtering. A number of investigations have been carried out on the effect of environmental and charged hydrogen on physical properties of titanium alloys and the processes like stress corrosion cracking (SCC), sustained load cracking (SLC), subcritical crack growth (SCG) and fatigue dwell-time effect in these materials (Nelson *et al* 1972; Meyn 1974; Bernstein and Thompson 1976). However, little attention has been paid on the influence of energetic ionized hydrogen on surface degradation of titanium alloys through the process of blistering. The effect of energetic H⁺ ions is expected to be quite different from those of the environmental and charged hydrogen, in view of the radiation damage caused by them. The effect of H⁺ ion implantation on blistering behaviour of some metals and alloys has been reported (Das and Kaminski 1976; Gittus 1978). Takeu-

chi *et al* (1988) studied trapping mechanism of energetic hydrogen ions in titanium.

The present investigation was undertaken to study the influence of irradiation by H⁺ ions of 150 keV and 250 keV energy to fluences of $2.6 \times 10^{18} \text{ cm}^{-2}$ and $2.5 \times 10^{19} \text{ cm}^{-2}$, respectively, on surface degradation of the titanium alloy, Ti–6Al–4V.

2. Experimental

The alloy Ti–6Al–4V was obtained from the Indian Space Research Organization in the form of a sheet of 3 mm thickness. Rectangular pieces of $2 \times 1 \text{ cm}$ were mechanically polished and subsequently electropolished to remove surface roughness, if any, and produce strain free surface.

H⁺ ion implantation was carried out under vacuum (2×10^{-6} torr) using AN 400 Van de Graaff Accelerator. The experimental details are given elsewhere (Shrinet *et al* 1983). Magnetically analysed, focussed and collimated beam of 3–5 mm diameter was made incident normal to the electropolished flat surface of the specimen. Two specimens were irradiated by H⁺ ions, one with energy of 150 keV and the other of 250 keV separately, to fluences of 2.6×10^{18} and $2.5 \times 10^{19} \text{ cm}^{-2}$, respectively. The respective current densities during implantation by 150 and 250 keV H⁺ ions were 17.8 and $25 \mu\text{A cm}^{-2}$ and the corresponding equivalent fluxes were 11.2×10^{13} and $15.6 \times 10^{13} \text{ H}^+ \text{ cm}^{-2} \text{ s}^{-1}$. The implanted samples were kept at room temperature and examined frequently under opti-

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cal and scanning electron microscope to study the changes on their surfaces, resulting from natural ageing at room temperature (*RT*). The implanted samples naturally aged at *RT*, were annealed at 423 K for 150 min under vacuum (10^{-3} torr) and the modifications in the surface features, resulting from subsequent ageing at *RT* were examined, following ageing for different periods.

3. Results

3.1 Microstructure

The initial microstructure of the alloy Ti-6Al-4V, prior to H^+ ion implantation, is shown by the SEM micrograph

Figure 1. SEM micrographs showing microstructure of the alloy Ti-6Al-4V: (a) unirradiated, (b) irradiated by 150 keV H^+ ions (fluence $2.6 \times 10^{18} \text{ n cm}^{-2}$) and (c) irradiated by 250 keV H^+ ions (fluence $2.5 \times 10^{19} \text{ n cm}^{-2}$).

in figure 1a. The microstructure consists of two phases, the light phase (alpha) and dark phase (beta). The beta phase has different shapes and is distributed in the alpha matrix. Alloy Ti-6Al-4V is a well known alpha + beta type alloy to exhibit dual phase microstructure of alpha and beta phases (Polmear 2006).

3.2 150 keV H^+ ion implantation

Surface topography of the specimen, immediately after implantation by 150 keV H^+ ions to a fluence of $2.6 \times 10^{18} \text{ H}^+ \text{ cm}^{-2}$, is shown by SEM micrograph in figure 1b. It may be seen that surface features, immediately after implantation by 150 keV H^+ ions are similar to those of the unimplanted one, however, the volume fraction of the beta phase as well as its average size is seen to be relatively higher in the implanted specimen. The implanted specimen was examined after the intervals of 10 days and no detectable change was observed on its surface features, during the initial period of natural ageing of five months. However, vein like features (VLF) and a few microblisters, were observed to develop after five months (figure 2). These vein like features and the microblisters could be detected only at high magnifications. The 150 keV H^+ ion implanted sample, following natural ageing for 5 months, was annealed at 423 K for 150 min under vacuum (10^{-3} torr). Subsequent ageing of this sample at room temperature led to development of several interesting features. A microblister of nearly 1.13 mm diameter was observed to form in the central region of the implanted area, from ageing at room temperature, for the first seven days. Further ageing for the next seven days caused growth of the central blister as well as development of new annular array of blisters around it (figure 3a). In general, the blisters in the annular array, were elongated and arranged in sequence one after the other, like beads in a necklace.

Figure 2. SEM micrograph showing microblisters and vein like features on surface of the 150 keV H^+ ion implanted Ti-6Al-4V alloy and aged at *RT* for five months.

The growth of the central macroblister led to rupture of its dome in the central region (figure 3b). It may be seen that the substrate of the bursted macroblister shows features similar to that of the unirradiated specimen (figure 1a). Concurrent with appearance of the macroblister, vein like features were observed on its dome. Number density of VLF increased with the time of ageing at *RT*, however, their distribution was inhomogeneous. There was relatively higher concentration of VLF of the blisters at the crest and slant surface of the blisters. It was observed that

during the early stage of ageing, following the annealing treatment at 423 K, VLF were confined mainly to the central region, enclosed within the annular array of blisters and their distribution was inhomogeneous. However, later they were observed to spread up to the boundary of the implanted region. On long ageing, VLF were observed to cross the circumference of the implanted region. Further, the shape and size of the VLF also changed with ageing (figure 5).

3.3 250 keV H^+ implantation

The sample implanted at 250 keV to a fluence of $2.5 \times 10^{19} H^+ cm^{-2}$ was also examined at intervals of 10 days, however, no detectable change was observed on its surface, following natural ageing for a period of five months at room temperature.

It may be seen that surface features of the 250 keV implanted sample (figure 1c) are similar to that of the unimplanted one (figure 1a). It is important to mention here that no change was detected on surface features of the 250 keV implanted sample, also after annealing under vacuum (10^{-3} torr) at 423 K for 150 min and subsequent ageing at room temperature.

4. Discussion

4.1 Post implantation changes in surface features

Implanted H^+ ions diffuse faster than atomic hydrogen, in the target alloy Ti-6Al-4V, without much differentiation between the alpha and beta phases, because of their extremely small size ($10^{-5} \text{ \AA}$). During the process of penetration the energetic H^+ ions produce lattice defects. Once their energy is reduced to the level of thermal energy they get neutralized to atomic hydrogen capturing electrons from the target material. Thus the concentration

Figure 3. SEM micrographs showing surface features of the 150 keV H^+ implanted Ti-6Al-4V, following ageing at 423 K for 2.5 h and aged at *RT*: **a.** growth of central blisters and development of an annular array of blisters, **b.** merger of the surrounding blisters with central blisters at some regions and **c.** rupture of the dome of the central blisters.

Figure 4. SEM micrograph showing substrate of an exfoliated central blisters resulting from 150 keV H^+ implantation, annealing at 423 K and ageing at *RT*.

of atomic hydrogen is increased in the implanted region at the depth of penetration. The atomic hydrogen resulting from H^+ ion implantation gets distributed in different forms like solid solution, molecular hydrogen and hydride. Takeuchi *et al* (1988) studied trapping behaviour of hydrogen, implanted into 99.5% pure polycrystalline titanium, at an energy of 10 keV per nucleon from 77 K to 400 K, over the fluence of $6.3 \times 10^{16} - 3.3 \times 10^{19} H^+ cm^{-2}$. They have shown that trapping mechanism of hydrogen, implanted into titanium, depends both on the temperature as well as the fluence. When the implantation was carried out at a temperature sufficiently higher than 273 K hydrogen moved from the surface to an underlying bulk and precipitated as hydride, irrespective of the fluence (Takeuchi *et al* 1988).

The major share of the implanted hydrogen in the alloy Ti-6Al-4V gets absorbed in the beta phase in preference to the alpha phase because of its higher solubility and diffusivity in the beta phase (Wasilewski and Kehl 1954). During the initial stage of implantation, when the concentration of implanted hydrogen is low, hydrogen atoms are trapped by vacancies and there remains little possibility of hydride formation at ~ 273 K. However, during the later stage of implantation, when the atomic ratio of H/Ti becomes close to the stoichiometric value of TiH_2 , there is a likelihood of hydride formation. Also there is a possibility of formation of molecular hydrogen at internal defects like small voids, resulting from coalescence of radiation induced vacancies. Accumulation of molecular hydrogen in such voids gives rise to formation of gas filled bubbles. Absence of any apparent change in the surface morphology, immediately following H^+ ion implantation, is due to extremely small size of the internal gas filled bubbles and low pressure of the gas in them. The development of microblisters in the implanted area, resulting from natural ageing at room temperature for a period of nearly five months, prior to annealing at

423 K, is from growth of the tiny voids from increasing accumulation of hydrogen. When the concentration of hydrogen reaches to a level to cause formation of TiH_2 , vein like features of titanium hydride develop. The higher number density of hydrides on the bulged surface of the blisters as compared to those in the unswelled regions may be attributed to stress induced diffusion and accumulation of hydrogen in the swelled regions (Dutton 1978).

4.2 Vacuum annealing of implanted sample and development of macroblister

The changes in surface morphology of the 150 keV implanted sample, following vacuum annealing at 423 K for 150 min may be due to strong temperature dependence of solubility of hydrogen in the alpha phase from 293 K to 423 K, increased instability of some hydrides and enhanced diffusion of hydrogen. Solubility of hydrogen in the alpha phase titanium is considerably higher at 423 K than that at room temperature (Lenning *et al* 1954). On the other hand, there would be relatively less effect of temperature on the solubility of hydrogen in the beta phase. The marked increase in solubility of hydrogen in alpha phase at 423 K leads to redistribution of hydrogen in the two phases because of enhanced diffusion of dissolved hydrogen from the beta to alpha phase. However, the subsequent cooling of the implanted sample at room temperature, following the annealing treatment at 423 K, leads to drastic reduction in solubility of hydrogen in the alpha phase. Part of the excess hydrogen, beyond the solid solubility limit of the alpha phase, precipitates out as titanium hydride in the alpha phase and the remaining excess hydrogen atoms diffuse to vacancies and voids and form bubbles. The growth and coalescence of the internal voids cause localized bulging of the irradiated regions, and lead to formation of macroblister. Absence of any detectable change on surface features of substrate of the exfoliated macroblister suggests that the effect of implanted hydrogen is confined essentially to surface region of the specimen (figure 4).

The concentration profile of 250 keV energy would be different from those of the 150 keV energy H^+ ions like that of He in copper (Moreno and Eliezer 1997). It is well established that while the depth of penetration increases with energy of implantation, the concentration of implanted gas decreases with increase in energy of the projectile. Formation of blister depends on mechanical properties of the material and near surface concentration of the implanted gas. In case of gases like hydrogen which have high permeability in metals, the critical dose of implanted ion for blister formation is generally higher than for inert gases like helium (Kaminsky and Das 1973).

In general, blister diameter, blister density, blister skin thickness and the critical dose for blister appearance

Figure 5. SEM micrograph showing vein like features (VLF) on macroblister, resulting from 150 keV H^+ implantation, annealing at 423 K and ageing at RT. Change in the shape of VLF may be noted.

increase with increase in projectile energy in several target projectile systems. Blisters form when the internal pressure of accumulated gas below the surface exceeds yield strength of the overlying material and causes plastic deformation. The absence of blisters in the 250 keV H^+ implanted sample may thus be attributed to low concentration of accumulated gas, below the critical level, due to higher range of implanting H^+ ions of 250 keV, insufficient to cause bulging of the overlying material by plastic deformation.

5. Conclusions

The following conclusions may be drawn from the present investigation:

- (I) No detectable blister formed on the surface of either of the 150 keV or 250 keV H^+ ion implanted Ti-6Al-4V, immediately after implantation.
- (II) A few microblisters and vein like features of titanium hydride appeared on the surface of the 150 keV H^+ ion implanted specimen, on natural ageing at room temperature for a period of nearly 150 days.
- (III) Vacuum annealing of the naturally aged samples at 423 K for 150 min and subsequent ageing at room temperature caused surface bulging only of the 150 keV H^+ ion implanted specimen and there was no effect of it on the 250 keV implanted sample.
- (IV) No blisters formed on surface of the 250 keV H^+ ion implanted sample, either from natural ageing at room

temperature for 150 days or from vacuum annealing at 423 K for 150 min and subsequent ageing at room temperature, in spite of the fluence level of H^+ ions being higher by one order of magnitude than that of the 150 keV implanted sample.

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