

The effects of implanting various high energy ions into Ti and Ti–6Al–4V

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Abstract

Samples of titanium and the alloy Ti–6Al–4V were implanted with five different types of ions (C, Si, Ti, Pt and Au) at energies between 1.5 and 9 MeV. In all cases, a new hexagonal close-packed (hcp) structure, previously reported only in the Au ion implantation, was observed using glancing angle X-ray diffraction. The diffraction shows the known hcp α -Ti structure, and, in addition, the new hcp structure with lattice parameters increased by 10.7%. This new structure appears at fluences near and above 10^{20} ions/m², and for beam flux densities of the order of 1.5×10^{16} ions/m²s. The appearance of this structure with implanted ions of such varying masses and energies excludes chemical effects and suggests that the mechanism by which it is formed is independent of nuclear stopping.

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1. Introduction

Applications of titanium and its alloys in the biomedical sciences are common due to their good corrosion resistance and biocompatibility. Any modification of their surface properties, by ion implantation or other techniques, could increase the possibilities of new uses.

The appearance of a new hcp structure with expanded lattice parameters in titanium and the alloy Ti–6Al–4V, when implanted with 9 MeV Au ions, was reported by our group [1]. This structure does not correspond to any of those reported in the phase diagram of titanium, which shows the α phase (hcp), the β phase (bcc) at high temperatures, and the ω phase (simple hexagonal) at high pressures (see, for instance, Ref. [2]).

In this paper, we report that the new hcp structure appears in titanium and the alloy Ti–6Al–4V when they are implanted with other ions, for values of energy transfer (below about 4.5 keV/nm) considerably lower than those required for other comparable transformations.

Heavy ion implantation of titanium at higher energies with U ions has produced the $\alpha \rightarrow \omega$ phase transformation [2]. The explanation, based on the Coulomb explosion model, is associated with an energy transfer of 33 keV/nm. This same direct $\alpha \rightarrow \omega$ transformation has been produced in high power (29 MW/cm²) irradiation with H and C ions [3]. Metastable hcp phases also appear in ion mixing experiments; of particular relevance to the present experiment is an hcp structure observed in the Ti–Au system [4].

2. Experimental conditions

The Ti samples consisted of slices cut from 9.5-mm-diameter rods. They were 99.6% purity, the main impurities quoted by the manufacturer (Goodfellow) being Al, Cr, Mn, Ni and V at 500 ppm. They were annealed in argon at 675 °C by the manufacturer. After cutting, they were polished with Emery paper and 1- μ m diamond compound. The Ti–6Al–4V alloy samples were similarly cut from 10.0-mm-diameter rods. The maximum impurity, quoted by the same manufacturer, is 650 ppm of oxygen. After cutting, they were also polished with Emery paper and 1- μ m diamond compound.

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Table 1
Implantation conditions for both Ti and the Ti–6Al–4V alloy

Type of ion	Energy (MeV)	Beam flux density (ions/m ² s)
Au ⁺³	9.00	0.5 to 1.5×10 ¹⁶
Pt ⁺³	9.00	1.1 to 1.5×10 ¹⁶
Ti ⁺²	3.50	0.4 to 1.2×10 ¹⁵
Si ⁺¹	2.12	1.3 to 1.9×10 ¹⁶
C ⁺¹	1.53	1.3 to 1.5×10 ¹⁶

C, Si, Ti, Pt and Au ions were produced by the Instituto de Física 3MV 9SDH-2 Pelletron Accelerator. The implantations were all carried out at room temperature, and, in each case, the beam was rastered over the whole sample. Table 1 summarizes the ion energies and charge states used and the intervals of beam flux density. The ion energies were chosen so that the projected range, as calculated using the SRIM code [5], was, in all cases, about 1.4 μm. For each type of ion, various values of fluence were studied, varying between 0.5×10^{20} and 6.5×10^{20} ions/m².

In order to estimate the sample temperature during implantation, separate thermocouple temperature measurements were made on the same type of sample, using the same sample holder used in the implantations and different beam currents. The results indicated that, over the whole experiment, the sample temperatures never exceeded 100 °C.

Grazing angle X-ray diffraction (GXR) was used to analyze the samples. The grazing angle measurements were performed on a Siemens D5000 diffractometer with a grazing incidence attachment and LiF crystal monochromator in the secondary beam path, using Cu(K_α) radiation. The diffraction patterns were taken with the sample fixed at angles of incidence $\alpha=1^\circ$ and 3° . The detector scanned from $2\theta=20^\circ$ to 80° , (θ is the diffraction angle) in steps of 0.02° . For angle of incidence $\alpha=1^\circ$, 90% of the scattered intensity comes from a depth less than $\approx 1 \mu\text{m}$.

3. Results

The hexagonal close-packed (hcp) polycrystalline structure of Ti was confirmed in the reference samples by the presence of the eight known diffraction peaks in this angle interval, with lattice parameters $a=0.2950$ nm and $c=0.4686$ nm [1]. The measured spacing between adjacent planes d agree well with the reported reflections [6] from the α phase of unimplanted Ti. In the reference Ti–6Al–4V alloy samples, the parameters of the hcp phase are $a=0.2925$ nm and $c=0.4670$, and, in addition, a peak corresponding to a vanadium-enriched bcc phase with $a=0.3230$ was observed. These values were measured in a control sample.

A total of 36 implantations were carried out. GXR patterns were taken for all the Ti and Ti–6Al–4V alloy samples plus reference samples. For all five implanted ions, in addition to the regular α phase hcp structure, a new hcp

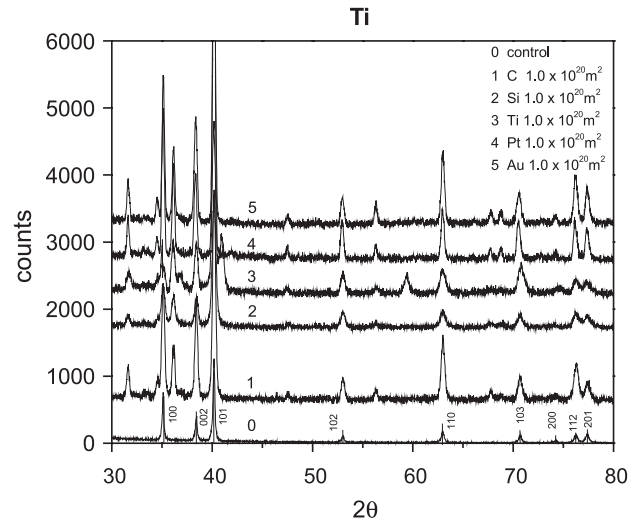


Fig. 1. GXR spectra of Ti implanted with C, Si, Ti, Pt and Au ions, and control sample. The unmarked peaks in the implanted spectra correspond to the new hcp structure, with values of 2θ and d listed in Table 2. In the Ti ion case, there are three conspicuous unidentified peaks that do not appear in any other spectra.

structure appeared with lattice parameters a and c 10.7 % larger than the original, in both Ti and the alloy. This was observed for fluence above approximately $\geq 10^{20}$ ions/m².

In Figs. 1 and 2, for Ti and the alloy, respectively, are included spectra implanted with C, Si, Ti, Pt and Au ions at the fluence of 1.0 or 1.5×10^{20} ions/m², showing the similarity between spectra, with the peaks of the new structure appearing at the corresponding same angles. The bottom spectrum indicates the original α -Ti structure peaks. In the other spectra, the unmarked peaks correspond to the new hcp structure, with values of 2θ and d

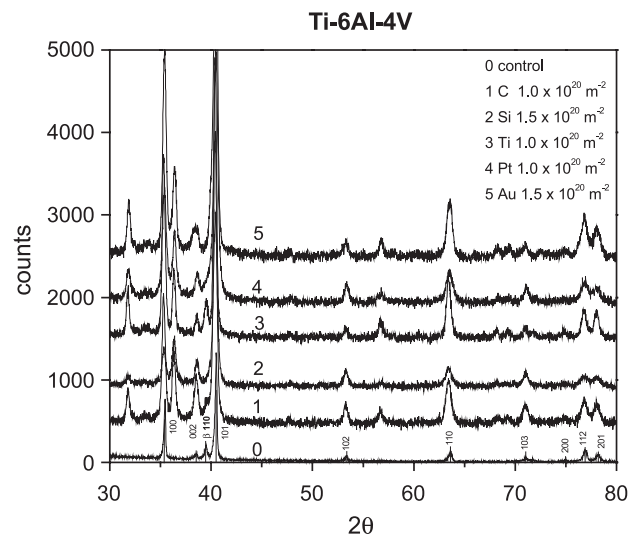


Fig. 2. GXR spectra of the Ti–6Al–4V alloy implanted with C, Si, Ti, Pt and Au ions, and control sample. The unmarked peaks in the implanted spectra correspond to the new hcp structure, with values of 2θ and d listed in Table 3.

Table 2

Diffraction angles (2θ) and adjacent plane spacings d for unimplanted Ti (columns 2 and 3) and for the new structure reported here (columns 4 and 5)

hkl	Unimplanted		Implanted	
	2θ	d (nm)	2θ	d (nm)
100	35.093°	0.2556	31.615°	0.2827
002	38.421°	0.2341	34.550°	0.2594
101	40.170°	0.2243	36.144°	0.2483
102	53.004°	0.1726	47.525°	0.1912
110	62.949°	0.1475	56.306°	0.1633
103	70.661°	0.1332		
200	74.157°	0.1277		
112	76.218°	0.1248	67.753°	0.1382
201	77.366°	0.1232	68.813°	0.1363

The values for the new structure are averages over all the spectra measured, for the five different implanted ions. Missing values are peaks obscured by other reflections.

listed in Tables 2 and 3. It must be pointed out that the diffraction maxima did not shift gradually to the new positions, but appeared directly at the new positions. In all cases, the original α -Ti peaks were always present. In the particular case of Ti ions implanted in Ti, there are three conspicuous unidentified peaks that do not appear in any other spectra.

For the new structure, the value of the lattice parameter a was calculated for each spectrum from the measured value of the interplanar spacing d from the (100) peak. An average value $\langle a \rangle_{100}$ over all the spectra (all five ions and all values of fluence) with its corresponding standard deviation is reported in Table 4. The same procedure was used to obtain $\langle c \rangle_{002}$ and $\langle a \rangle_{110}$. A relevant parameter for hcp structures is c/a , so the value $\langle c \rangle_{002} / \langle a \rangle_{100}$ is reported, and is close to the value of 1.633 for spheres in contact (the value reported in the literature for α -Ti is 1.587). Combining these values for a and c , the spacings d for all other peaks were calculated, giving excellent agreement with the experimental values. Table 4 contains the values for Ti and also for Ti-6Al-4V obtained using the same procedure. The average

Table 3

Diffraction angles (2θ) and adjacent plane spacings d measured for the unimplanted Ti-6Al-4V alloy (columns 2 and 3) and for the new structure reported here (columns 4 and 5)

hkl	Unimplanted		Implanted	
	2θ	d (nm)	2θ	d (nm)
100	35.351°	0.2537	31.826°	0.2809
002	38.542°	0.2334		
101	40.434°	0.2229	36.357°	0.2469
102	53.244°	0.1719	47.784°	0.1902
110	63.348°	0.1467	56.758°	0.1621
103	71.031°	0.1326		
200	74.678°	0.1270		
112	76.589°	0.1243	68.246°	0.1373
201	77.850°	0.1226	69.303°	0.1355

The values for the new structure are averages over all the spectra measured, for the five different implanted ions. Missing values are peaks obscured by other reflections.

Table 4

Lattice parameters (in nm) obtained by averaging measured values over all implanted ions and all fluences

	Unimplanted	Implanted
Ti	$a=0.29505$ $c=0.46826$ $c/a=1.587$	$\langle a \rangle_{100}=0.3266 \pm 0.0003$ $\langle c \rangle_{002}=0.5186 \pm 0.0006$ $c/a=1.588$
Ti-6Al-4V	$a=0.2925$ $c=0.4670$ $c/a=1.597$	$\langle a \rangle_{100}=0.3243 \pm 0.0004$ $\langle c \rangle_{002}=0.5171 \pm 0.0006$ $c/a=1.595$

For comparison, the accepted values from the literature for unimplanted α -Ti, and the values obtained experimentally for unimplanted Ti-6Al-4V are given.

values of a , c and c/a , together with the small values of the standard deviations, verify the presence of the same hcp structure in each material for all types of ion, energies and values of fluence studied.

Various values of fluence were accumulated in different samples of both metal and alloy in order to determine the onset of the new structure and the amount produced, compared with the original hcp structure. The values of percent new structure vs. ion fluence are summarized in Fig. 3 for all implanted ions in Ti, with lines connecting the values of corresponding ions to guide the eye. Except for the Au ion case, the threshold for appearance of the structure is below 0.5×10^{20} ions/m². The percent new structure was obtained directly from the spectra as (counts in all the new peaks/total counts) $\times 100$. Where the structure appears, its intensity is almost always between 15% and 20%. A similar effect occurs in the alloy, as shown in Fig. 4.

An extensive study of Vickers microhardness (25 g load for 20 s, and 10 indentations per point) was performed on reference samples and on all the implanted samples, using a

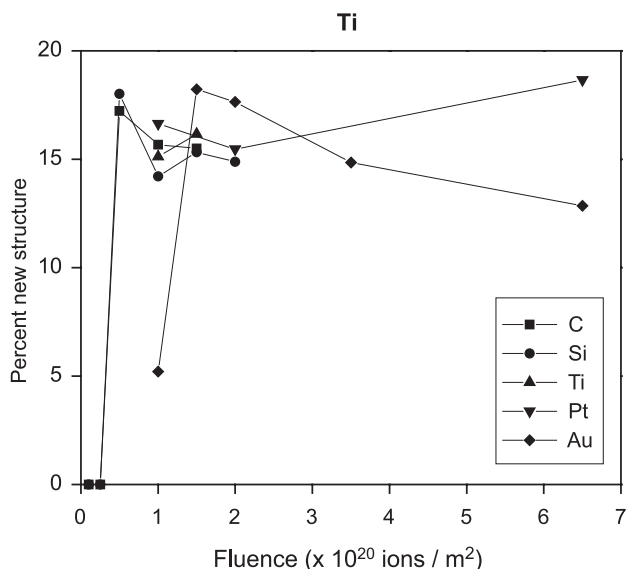


Fig. 3. Percent new structure vs. ion fluence for all implanted ions in Ti, with lines connecting the values of corresponding ions to guide the eye.

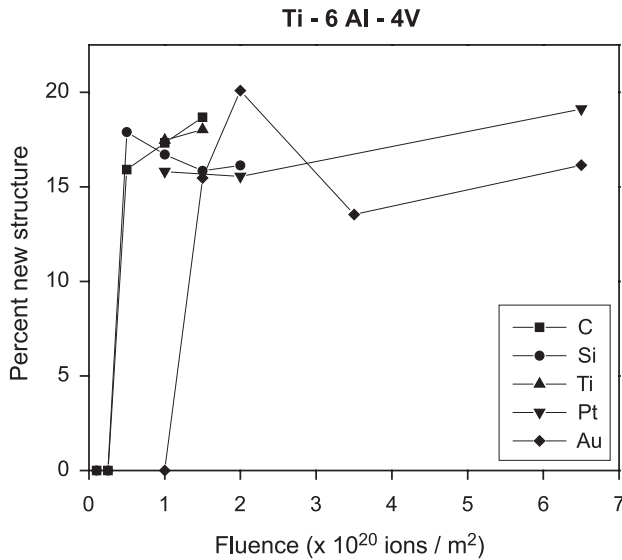


Fig. 4. Percent new structure vs. ion fluence for all implanted ions in the Ti-6Al-4V alloy, with lines connecting the values of corresponding ions to guide the eye.

Matsuzawa MHT2 microhardness tester. The penetration of the diamond indenter in the samples was chosen so the indenter penetration was slightly larger than the implantation depth of 1.4 μm . There is a general tendency for microhardness to increase with fluence. For all the samples, several loads were tried, and the square of the measured penetration was always proportional to the load, as expected [7], giving assurance that the measurements were correctly performed. The results for a load of 25 g are summarized in Figs. 5 and 6. Vickers microhardness values for the reference samples were consistently $H_V=220$ for Ti, and $H_V=330$ for the alloy, for different loads. The uncertainty in

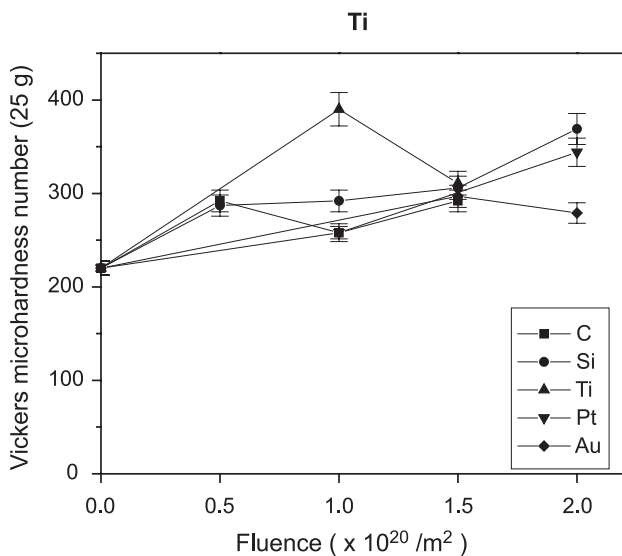


Fig. 5. Summary of Vickers microhardness measurements of Ti implanted with five different types of ions, using a load of 25 g, as a function of ion fluence. The values for the reference samples were consistently $H_V=220$.

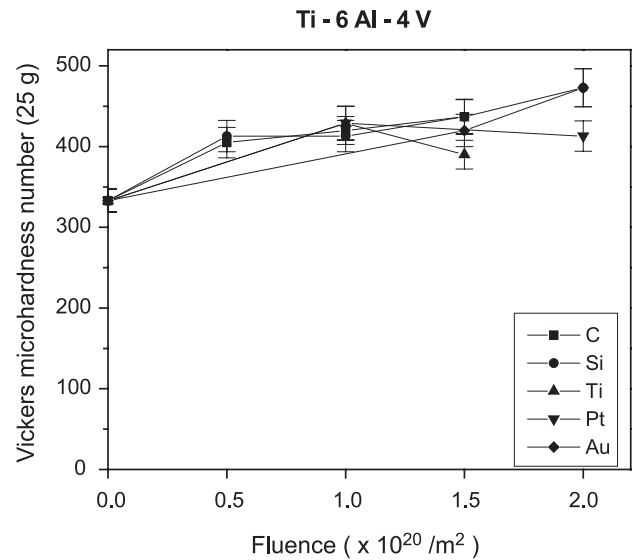


Fig. 6. Summary of Vickers microhardness measurements of the Ti-6Al-4V alloy implanted with five different types of ions, using a load of 25 g, as a function of ion fluence. The values for the reference samples were consistently $H_V=330$.

Vickers microhardness measurements is estimated to be about 4%.

4. Discussion

In the mechanism for formation of the new structure, chemical processes are ruled out because it appears when five different types of ions are implanted. No chemical compound diffraction peaks were observed, with the exception of one that coincides with a AuTi_3 line [1] in the Au implantation.

Rutherford backscattering (RBS) spectra of Au- and Pt-implanted samples were measured using 6-MeV He ions. The positions of the observed Au and Pt distributions were in agreement with distributions calculated using the SRIM [5] code. The measured FWHM, however, were close to 0.62 μm , as opposed to the calculated value of 0.22 μm . The RBS spectra also showed a thin (a few tens of nm) oxide surface film and some carbon contamination, in both reference and implanted samples. The oxide films, that are always present, are too thin (of the order of 30 nm) to appear in the diffraction spectra, even at grazing angles. The diffraction spectra did not contain any peaks that could be identified with the known oxides of titanium.

The appearance of the new structure in approximately the same amounts, independent of the type of implanted ion, indicates very little dependence on nuclear stopping. For the energy intervals employed, the nuclear stopping for Au and Pt ions is about two orders of magnitude larger than that for the lighter ions. Therefore, differences in the production of vacancies and structural damage and any ensuing effect would be markedly different for different ions [8].

One effect that is always present is sputtering, with calculated coefficients of 2.2 for 9 MeV Au ions and 0.0062 for 1.53 MeV C ions [9]. In all cases, the ions penetrated more than 1 μm , so a very small fraction of the energy is used in sputtering. Optical and SEM inspection of the samples indicated a difference in the erosion of samples bombarded with different ions: the Au and Pt produce a greater erosion than the C and Si.

The number of displacements per atom (dpa) also depends on nuclear stopping, and can be estimated using a SRIM calculation. For 9 MeV Au ions on Ti, a fluence of 10^{16} ions/cm² produces an average of 62 dpa in the sample, whereas the same fluence of 1.53 MeV C ions produces 1.1 dpa. In no case was amorphization apparent in the GXR D spectra.

From these arguments, it appears that the production of the new structure does not depend on nuclear stopping. The relative insensitivity to type of ion, energy and rate of energy deposit follows more the behavior of electronic stopping, so a mechanism triggered by electronic stopping at the relatively low value of 4.5 keV/nm is more feasible.

5. Conclusions

It has been shown experimentally that when Ti and the alloy Ti–6Al–4V are implanted with high-energy ions (in the MeV range), a new hcp structure is produced that has lattice parameters 10.7 % larger than the original Ti structure. This takes place with ions of very different masses (C, Si, Ti, Pt and Au), and with very different energies and rates of energy deposit. In general, there is an accompanying increase in microhardness with fluence. The origin of the new structure seems to be electronic stopping and not

nuclear stopping, although the threshold value of electronic stopping power is an order of magnitude lower than for similar previously observed phase changes in Ti.

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Further reading

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