A discussion of the behavior of titanium under high energy ion implantation

J. Rickards
Instituto de Física, Universidad Nacional Autónoma de México
Ap. Postal 20364, México, D.F. 01000, México

Ion implantation of metals has been used routinely for more than 30 years. In this period a great amount of information has been collected on the physical processes involved in ion implantation in solids, in which connected topics such as stopping power, radiation damage, sputtering, ion mixing, defects, diffusion, are studied. Many models, like the spike model, have been developed to explain these processes, and detailed calculations have been made, for instance, using molecular dynamics and Monte Carlo techniques. In spite of the copious knowledge that has accumulated, new effects are still being observed, partly due to increasing the energy regime, but also to the availability of new more sensitive experimental techniques. Recent results of the formation of a new phase in titanium and the alloy Ti-6Al-4V when they are bombarded with different MeV energy ions is discussed, and their relation to various models. The appearance of the new phase does not depend on type of implanted ion (C, Si, Ti, Pt and Au), so chemical effects are ruled out. The amount of the new phase produced does not follow the regular behavior of the nuclear stopping power, which in this energy regime is orders of magnitude stronger for heavy ions than for light ions. The application of the displacement and thermal spike model, the Coulomb explosion, as well as the model of "freezing by heating" in driven mesoscopic systems, are discussed.

Keywords: Ion implantation; Metallic alloys; Binary collisions

1. The ion implantation process

Ion implantation in metals has been used both as a research tool and in applications for several decades. The primary mechanisms of ion implantation up to MeV energies in different materials are reasonably well understood [1], using as a basis the theory of passage of energetic heavy charged particles through matter. Some of the basic ideas are that each projectile loses energy gradually through multiple interactions with the electrons and nuclei of the absorber (stopping power), following a certain trajectory until it loses all of its energy and comes to a stop (range, typically of the order of nm to μm). Since experiments entail large numbers of projectiles, there is a distribution of ranges with a certain variance (straggling). These quantities depend on the implantation parameters: the type of projectile and its energy, and the composition of the implanted material and its density.

It is generally accepted that primarily the incoming ion transfers energy to the material through two basic mechanisms: interactions with the electrons of the material (electronic stopping), and interactions with the whole atoms (nuclear stopping). The electronic stopping produces ionization and excitation of the absorber; the nuclear stopping gives rise to atomic displacements, and therefore to structural damage. These events can be calculated using published data tables, or more effectively using computer codes like SRIM [2], that, applying the Monte Carlo technique, yields ion range, ion distribution, ionization distribution, damage distribution, vacancy production, and sputtering, all dependent on the implantation parameters. The two types of interaction are treated separately and normally yield very different values of stopping powers (or energy transfers), depending on the ion energy. For instance, in the few MeV ion energy interval the electronic loss in titanium of very different ions (C to Au) give comparable values of electronic stopping power. However, the nuclear stopping power shows great variations among the different ions, up to three orders of magnitude in the same energy interval.

For the case of ion implantation in metals, it is generally assumed that the electronic interactions only heat the target through electronic plasma oscillations, besides ionizing and exciting. However, the nuclear interactions can produce much more noticeable effects, basically due to atomic displacements that give rise to structural defects. In this case heavy ions are more efficient in transferring energy to the target atoms through atomic collisions than light ions. The binary collisions of ions with atoms are described by a screened Coulomb potential, in which a high atomic number yields a high collision cross section.

A straightforward consequence of binary collisions is the generation of point defects in the crystal lattice. If the energy transfer to the target atom exceeds the displacement energy, which is of the order of a few tens of eV, a vacancy is produced. The displaced atom travels a distance which depends on the transferred energy, and eventually is lodged into the lattice as an interstitial. A combination of a vacancy and an interstitial is a Frenkel defect. Other types of point defects can be produced as well, since the lattice is strongly disrupted in the region struck by the bombarding ion. Each incident ion typically has enough energy (MeV) to produce a large number of point defects. Some vacancy and interstitial pairs can recombine and disappear, with no further effects on the material. However, other point defects can diffuse within the bulk of the target, accumulating at sinks like extended defects or grain boundaries, or aggregating to form new extended defects. These processes can alter the macroscopic properties of the solid in the implanted region and sometimes beyond this region [3].

Complementing this view, the result of each primary binary collision is a couple of energetic ions, the projectile and the recoil atom, both of which can have enough kinetic energy, dictated by classical collision kinematics, to originate new collisions. Sequential collision cascades are thus produced, with each recoil giving rise to cascades of

self atoms [4]. Within the cascade, the average kinetic energy per moving atom is gradually reduced and the corresponding mean free path between collisions is reduced as well, while the number of moving atoms increases. When the mean free path of the particles between collisions is of the order of the atomic spacing, the cascade develops into a small volume (typically a few nm^3) of the target where essentially all of the target atoms are moving, with energies sufficient to still produce further displacements. This happens at a critical energy which depends on the mass of the moving atoms. The corresponding volume is called a displacement spike, whose center is rich in vacancies and its outer edge rich in interstitials.

The atoms continue to lose velocity on the average, grow in number, and share their energies, until velocities are reached and numbers are sufficiently large so that an energy distribution may be assumed approaching a Maxwell-Boltzmann distribution, from which a local temperature can be calculated. This regime is called a thermal spike. Temperatures of the order of 10^4 K are calculated within the spike volume, so local melting would be expected. Once this high temperature is reached, it is followed by a cooling stage that depends strongly on the thermal conductivity of the metal. Cooling rates up to 10^{12} K/s have been estimated.

In a typical ion implantation experiment a large homogeneous area coverage is desired, so the beam is often rastered over the whole area of interest, giving smooth implanted regions. However, this smoothness is the result of a very large number of events, each of which can be considered initially independent of the rest, and may overlap in space, but not in time. In the experiments discussed here, a total fluence (sometimes called dose) of the order of 10^{16} ions/cm^2 is normally reached, and experiments take some 10^4 seconds to perform, depending on the beam current, giving a beam flux density of 10^{12} ions/cm^2s. Considering a monolayer as 10^{15} atoms/cm^2, each surface atom would be struck on the average every 10^3 seconds. If one considers a cascade region to have a cross section of $(100\ nm)^2$ (10^{-10} cm^2), each one of these regions would be struck 10^2 times per second.

Now it is relevant to estimate the duration of a typical cascade event [1]. Due to the high ion velocities involved, it has been considered that the displacement spike lasts approximately 10^{-14} s after the initial ion arrival. The thermal phase appears after about 10^{-12} s. After this, cooling begins, and temperature-driven processes (diffusion, phase transitions, chemical effects) start to take over. Characteristic times for interstitial diffusion are 10^{-6} s, and for vacancy diffusion 1 s. Therefore, for the experiments discussed here, no time overlap of cascades, displacement and thermal spikes can be expected, but subsequent thermal effects can overlap. It is important to note that the values given here are approximate. There are no clear-cut times involved, since the processes evolve gradually. In addition, they could vary considerably depending on the experiment parameters.

A phenomenon associated with ion implantation is sputtering, that is the ejection of target atoms from the surface. Sputtering is believed to consist of a collisional stage and a thermal stage, associated with the displacement and thermal spikes. The sputtering yield increases with projectile energy, goes through a maximum, and then decreases when most of the energy is deposited deep within the target and far from the surface.

2. Ion implantation in Ti and the alloy Ti-6Al-4V

Until 1995 no ion implantation facilities were available in Mexico. In March of that year a National Electrostatics 3 MV Model 9SDH-2 Pelletron Accelerator was installed at the Instituto de Física, National University of Mexico. It is a two-stage machine, and has two negative ion sources: one for He ions, and a cesium sputtering source for all ions except noble gases. The two stages allow a choice of several charge states in the second stage, depending on the type of ion, so energies up to 10 MeV or higher can easily be achieved. One of the beam lines is designed for ion implantation; it has a beam rastering system, a deflecting system for the elimination of neutrals, and a current integrating system with secondary electron suppression.

Implanting ions at these high energies opens up the possibility of observing effects that have not been seen before, since most implantations have been carried out at energies of tens or hundreds of keV. MeV ions typically penetrate μms into the target, and most of their energy that goes into displacements is deposited at these depths, rather than near the surface. Therefore sputtering is diminished. One of the limitations of lower energy implantation is that the surface recedes due to sputtering, and when this effect reaches the implantation depth, no more ions can be implanted, since an equilibrium is reached of implanted ions and ions lost by the receding surface. At higher energies, the surface receding may be minimized due to the high penetration and the lower sputtering, so the amount of ions that can be implanted may be higher.

One of the first experiments performed was the ion implantation of Ti and the alloy Ti-6Al-4V with Au ions at 9 MeV, due to the interest in improving surface properties of these metals for orthopedic implants [5]. The result was the observation of a new phase near the surface in both metals, with a consequent increase in hardness and, in the case of Ti, considerable disruption of the originally smooth surface.

99.6% purity Ti samples were used. Metallographic tests and scanning electron microscopy revealed a grain structure of approximately 100 μm size; glancing angle x-ray diffraction (GXRD) indicated an additional mosaic structure with sizes of 56 nm at 1 μm depth, in addition to the crystallographic hcp α-phase structure with lattice parameters a = 0.2950 nm and c = 0.4686 nm. The phase diagram of Ti (6) shows the α phase present up to a temperature of 1155 K at which it transforms to a bcc β phase. The melting temperature of Ti is 1933 K. The alloy Ti-6Al-4V consisted of 10-15 μm α-phase grains depleted in V, in a β-phase matrix rich in V. The size of the mosaic structure was 71 nm, and the hcp α-phase structure had

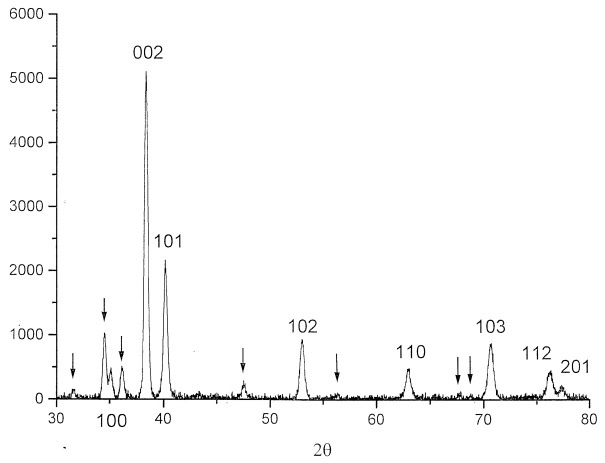

Figure 1.-Glancing angle x-ray diffraction spectrum of a Ti sample after implanting with Au ions. The labeled peaks correspond to the original hcp structure; the arrows show the new hcp structure. Each original peak is reproduced in the new structure with lattice parameters increased by 10.7 %.

lattice parameters a = 0.2925 nm and c = 0.4670 nm. All the polished samples had a thin (≈ 30 nm) oxide layer, measured by the Rutherford backscattering (RBS) technique.

Besides implanting with Au ions, samples were implanted with Pt, Ti, Si and C ions. The energy of each type of ion was selected so the range of the bombarding ions in the target was 1.5 μm. In this way GXRD results are comparable between samples, because the geometry of the diffraction is always the same, in particular the degree of penetration of the x-rays. However, this means that the ion energies were very different, ranging from 1.5 MeV for C ions to 9 MeV for Au ions, and this must be considered when analyzing the results.

In all cases a new hcp phase was observed (Figure 1) using GXRD with lattice parameters a and c 10.7% larger than the unimplanted materials, regardless of the type of ion and the projectile energy, at values of ion fluence of the order of 10^{16} ions/cm^2 [7]. The fraction of the new phase produced is similar in all cases, reaching a saturation value between 15 and 20%. The SEM measurements of the Ti samples showed a surface structure very different from the original, suggesting an ordered swelling of the α phase. The alloy, on the contrary, showed very little change in appearance, presumably because the β phase can absorb the dimensional changes of the swollen α phase.

3. Discussion

Since the appearance of the new phase does not depend on type of ion, chemical processes are ruled out in explaining the mechanisms involved. In fact, the density of ions implanted (the equivalent of about 10 monolayers), spread out over an interval of several tenths of a μm (the straggling in the ion distribution calculated using the code SRIM), is too small for a significant formation of compounds. In only one case of 6.5×10^{16} Au ions/cm^2 in Ti was a small peak observed in the diffraction spectrum that could be associated with the compound $AuTi_3$.

Neither is there any apparent dependence of the amount of new phase produced on nuclear stopping, which gives rise to defects, structural damage, collision cascades and spikes. The calculated values of nuclear stopping power of C, Si, Ti, Pt and Au ions in Ti yield differences of up to three orders of magnitude, the heavier ions being more liable to be stopped by collisions, and therefore producing more damage. The corresponding SRIM calculations for the ions and energies employed indicate that, in the region analyzed by GXRD, ten times more vacancies per unit total energy available are produced by Au and Pt ions than by C ions. This is not reflected in the amount of new phase produced by the different ions. For reference, the electronic loss in titanium of these ions give comparable values of electronic stopping power.

On the other hand, conditions are met for amorphization of the material [8], though none was observed in the diffraction spectra. The SRIM calculation for a fluence of 10^{16} Au ions/cm^2 indicates a damage profile which peaks near the ion projected range, with some 35 displacements per atom (dpa) at the peak, that is, taking into account collision cascades with the possibility of replacement collisions, with this fluence each atom of the damaged region is struck and displaced an average of 35 times. Although this is a static calculation, it indicates the high degree of disorder that can be achieved, and therefore one would expect amorphization of the implanted region. The amorphization would take place in two steps: production of disorder, and its stabilization.

For the application of the spike model to this experiment one must assume a value for the volume of the cascade [1]. One also must estimate the mean free path of the particles between collisions, using some type of interaction between particles, and from there the critical energy and the distribution of subcascades. At the high energies involved in these experiments, the damaged region is composed of many subcascades, the critical energy being of the order of a few hundred eV for Ti. Since the displacement energy of Ti is 25 eV, only a few atoms would be in motion in each subcascade, hardly enough to define a temperature. Under these conditions the development of a thermal spike would not follow a displacement cascade of binary collisions, but would need the input of a larger number of atoms in motion though not necessarily displaced (subthreshold collisions). This process has become evident in molecular dynamic calculations , in which the motion of one atom can be rapidly transmitted to neighboring atoms, particularly along low index directions.

With the model of local melting and fast cooling in thermal spikes, amorphization would be expected as happens in the splat quenching technique, in which typical cooling rates are of the order of 10^6 K/s. Indeed, amorphization has been observed to be the result of some ion implantation experiments. Another phenomenon that has been observed is recrystallization [9], that is a return to the original crystal structure. Molecular dynamics

calculations have been made of recrystallization in times of a few ps. The experiments described here would be a case of recrystallization on quenching, but not to the original phase, rather to a new hcp phase, that does not appear in the known phase diagram of Ti, with lattice parameters 10.7% larger than the original.

Another model that has been used to explain structural changes in bombarded materials, in particular insulators, is the Coulomb explosion model. In this model the primary ion leaves a wake of positive charges (ionized atoms) in the absorber, which produces a very unstable region due to electrostatic repulsion. This can produce a shock wave that modifies the solid structure. In metals it would be expected that the conduction electrons would partly neutralize this process, but the model has been used to explain some structural changes observed, particularly in Ti [6]. In this case, the pressure wave produced by the electrostatic repulsion gives rise to a transition between the α phase and the ω phase which happens at high pressure. The condition proposed for this transition is an electronic energy loss higher than a threshold value of 33 keV/nm. In the experiment described in reference [6], this was achieved with 2.2 GeV uranium ions. The experiments we are discussing here were performed with a maximum electronic energy loss of 4.5 keV/nm, only an order of magnitude below the proposed threshold. The transition to the ω phase was not observed, but rather another hcp phase was obtained. However, the relative insensitivity of the experiment to ion mass is a parameter that agrees with the Coulomb explosion model.

In the computer study of far from equilibrium processes in a mesoscopic system, attention has been given recently [10] to driven systems, where the driving force is either external or the particles are self-driven. These systems have been calculated to give rise to new ordering procedures, outside of the realm of commonly understood equilibrium processes. A model has been proposed which exhibits a transition from a disordered state to an ordered (crystallized) state by raising the number of particles and fluctuations--the so-called “freezing by heating” model. This 2D calculation predicts the formation of lanes in which particles move in opposite directions, followed by a stable compact ordered structure, which persists even after the temperature is lowered. The conditions are: a large number of similar particles, a hard core interaction between them, a driving force, and confinement of the system.

If one accepts that the 2D calculations of the "freezing by heating" model can be generalized to 3D, then many of the features of the “freezing by heating” model are reproduced in the present experiment.

First, a large number of particles is involved, with a high density determined by the initial Ti hcp structure. Since most collisions are produced by Ti recoils, the mass of essentially all the particles is the same.

Second, although the potential acting between Ti atoms is not exactly a hard core, at small separations in binary collisions a screened Coulomb type is regularly assumed, determining a practical repulsive core where particles, especially low energy ones, are rarely allowed.

Third, there is a driving force, initially due to the energetic projectile, which after multiple collisions is distributed among the target atoms, and can be considered to be shared by most of the particles within the cascade volume. Along the cascade, the initial momentum in the incident direction is distributed to all collision pairs, so there is a general tendency of the particles to move in this direction. In each collision the high energy product will tend to move forward, and the low energy product laterally. In the detailed cascades many directions are involved, but there is an initial well defined direction that could contribute to the formation of lanes.

Fourth, the volume of the cascade would be equivalent to the confinement region, the borders of the cascade being a (soft) wall.

Fifth, a close-packed structure is obtained experimentally, in analogy to the hexagonal 2D structure predicted by the “freezing by heating” model.

Sixth, the structure is maintained when the temperature is lowered, consistent with the hysteresis predicted by the model. The supposition here is that quenching is fast enough (~10^{12} K/s) in each of the spikes to congeal the structure, a reasonable assumption, given the thermal conductivity of the metal. Therefore the new hcp structure is maintained until another nearby event takes place, for which the first may even act as a seed for the growing crystal structure.

Seventh, the total energy of the system is increased, as evidenced by the increase in the measured lattice parameters.

Although there is no way of directly proving the applicability of the model in the present experiments, and conceded that the step from 2D to 3D in the calculations could alter the results significantly, there is still a significant resemblance between the experiment and the model predictions.

4. Conclusions

Experiments on the implantation of various ions in titanium, in which a new crystalline hcp phase is observed, have been discussed, in the light of currently accepted models of radiation effects in metals. Chemical and direct damage processes cannot explain the appearance of the new phase, and the thermal spike model would require an additional energy input, that could come from prior subthreshold collisions. The Coulomb explosion model has been previously used to explain a phase transition in Ti, but in a higher energy loss regime. Finally, similarities are pointed out between the experimental results and calculations of the model of the “freezing by heating” in driven mesoscopic systems.

Acknowledgements

The author wishes to acknowledge the help of R. Trejo-Luna, L.R. de la Vega, C. Falcony and Ma. Jergel for helpful discussions, and K. López, J. Cañetas, M. Galindo, F. Jaimes, M. Guerrero, and L. Baños for help in performing the experiments. CONACYT grants G0010-E and F036-E9109 are also gratefully acknowledged.

References

[1] M. Nastasi, J.W. Mayer, and J.K. Hirvonen, *Ion-Solid Interactions: Fundamentals and Applications*, Cambridge University Press, 1996.
[2] J.F. Ziegler, J.P.Biersack and U Littmark, *The Stopping and Range of Ions in Solids*, Pergamon Press, 1985.
[3] L.K. Mansur, Mechanisms and Kinetics of Radiation Effects in Metals and Alloys, in *Kinetics of Non-Homogeneous Processes*, Ed. G.R. Freeman, John Wiley & Sons, 1985.
[4] D.A. Thompson, Radiation Effects **56,** 105 (1981).
[5] R. Trejo-Luna, L.R. de la Vega, J. Rickards, C. Falcony and M. Jergel, J. Mater. Sci. **36**, 503 (2001).
[6] H. Dammak, A. Dunlop and D. Lesueur, Phil. Mag. A **79**, 147 (1999).
[7] L.R. de la Vega, R. Trejo-Luna, J. Rickards, C. Falcony and L. Baños, *to be published*.
[8] P. Ziemann, Mater. Sci. and Engineering **69**, 95 (1984).
[9] D.M. Follstaedt, Nucl. Instruments and Methods in Phys. Research B **7/8**, 11 (1985).
[10] D. Helbing, I.J. Farkas and T. Vicsek, Phys. Rev. Letters **84**, 1240 (2000).