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$\alpha \rightarrow \omega$ phase transformation induced in titanium during ion irradiations in the electronic slowing-down regime

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ABSTRACT

This letter shows that the displacive phase transformation from the h.c.p. α-phase to the hexagonal ω-phase can be triggered in titanium targets in an unusual way during swift heavy ion irradiations†. This unexpected result is a consequence of the high level of energy deposition in electronic excitation. A model based on the Coulomb explosion mechanism can account for such a phase transformation.

§ 1. INTRODUCTION

A new and unexpected mechanism of defect production has been evidenced recently in some metallic targets irradiated by swift heavy ions (Dunlop and Lesueur 1992a): such GeV ions deposit their energy mainly in the targets via electronic excitations. This so-deposited energy is transferred to the lattice in such a way that defect creation becomes possible. The available experimental results do not allow us to settle the question of the mechanism by which such energy conversion occurs. Two theoretical approaches have been proposed:

(i) the first one is based on the thermal spike concept in which the energy carried out by the excited electrons returns to the lattice via efficient electron–phonon coupling leading to a local melting followed by a quench (Toulemonde, Paumier and Dufour 1992); and

(ii) the second one is based on the Coulomb explosion concept in which the electrostatic potential energy of the ionized atoms along the projectile wake is converted into kinetic energy (Lesueur and Dunlop 1992). It has been shown that such collective and coherent motions of neighbouring atoms can generate a shock-wave.

Among the metals studied, the most spectacular effects are found in titanium (Dunlop *et al.* 1991, Dammak, Lesueur, Dunlop, Legrand and Morillo 1992). For example, during an irradiation at 20 K with 4·5 GeV lead ions (corresponding to a linear rate of energy deposition in electronic excitation $(dE/dx)_e \approx 29\,keV\,nm^{-1}$):

(i) the cross-section attributed to damage production by electronic excitation $\sigma_e \approx 6 \times 10^{-16}\,cm^2$ is twenty times higher than the cross-section for damage production by solely elastic collisions (Dunlop *et al.* 1991, Dunlop and Lesueur 1992b); and

† Irradiations performed on the GANIL accelerator—Caen, France.

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(ii) after an irradiation up to a fluence of $2{\cdot}4 \times 10^{13}$ ions cm^{-2}, room temperature electron microscopy observations reveal the existence of alignments of small objects along the ion beam direction (Henry, Barbu, Leridon, Lesueur and Dunlop 1992). Such striated contrast has never been observed in other metals irradiated under similar conditions.

In order to increase the linear rate of energy deposition in electronic excitation, titanium was irradiated with GeV uranium ions. The results presented here show unambiguously that a phase transformation takes place: the sample evolves from the equilibrium h.c.p. α-phase to another hexagonal phase, the so-called ω-phase. To our knowledge, this is the first time that a phase change has been observed during irradiation of a pure metal.

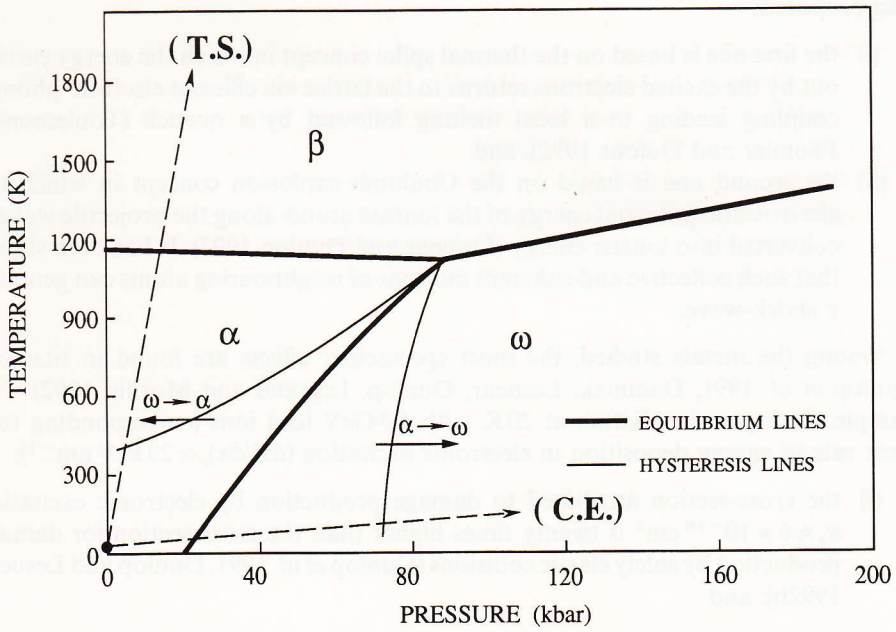
This ω-phase is usually obtained from the α-phase of titanium when either a static or a dynamic pressure is applied as shown by the equilibrium phase diagram given on fig. 1 (Sikka, Vohra and Chidambaram 1982). Moreover, the displacive $\alpha \rightleftharpoons \omega$ transformation is characterized by a wide hysteresis that allows the ω-phase to be retained in a metastable state at room temperature and atmospheric pressure.

The orientation relationships between the α and the ω-phases have been established by pure crystallographic considerations by Usikov and Zilbershtein (1973) and have two different variants:

$$\begin{cases} (001)_\alpha \parallel (011)_\omega \\ [100]_\alpha \parallel [\bar{2}\bar{1}1]_\omega \end{cases}, \tag{1}$$

$$\begin{cases} (001)_\alpha \parallel (2\bar{1}0)_\omega \\ [100]_\alpha \parallel [001]_\omega \end{cases}. \tag{2}$$

Fig. 1



Equilibrium pressure–temperature phase diagram of titanium (after Sikka, Vohra and Chidambaram (1982)).

Transmission electron microscopy observations have been performed after application of high hydrostatic pressure in titanium and zirconium targets (the pressure–temperature diagram of Zr is similar to that of Ti). In each experiment, either one or the other orientation relationship is observed:

(*a*) variant (1) has been observed in Ti and Zr by Usikov and Zilbershtein (1973)
(*b*) variant (2) has been observed in Zr by Rabinkin, Talianker and Botstein (1981) and in Ti by Sargent and Conrad (1971).

§ 2. Experimental

A pure 11 μm thick titanium ribbon was annealed in a good vaccum (3×10^{-4} Pa) at 820°C for 17 h in a furnace containing titanium sponge. It was then slowly cooled down to room temperature. An X-ray diffraction pattern was registered on the virgin titanium.

The sample was then irradiated at 20 K with uranium ions: the average projectile energy and corresponding $(dE/dx)_e$ were respectively 2·2 GeV and 39 keV nm^{-1}. *In situ* electrical resistivity measurements were performed. To avoid sample heating during irradiation the ion flux was kept below 5×10^7 ions cm^{-2} s^{-1}. After an irradiation fluence of 6×10^{12} ions cm^{-2}, the sample was heated up to room temperature.

X-ray diffraction patterns were taken. The sample was then electrochemically thinned under 17·5 V by a double jet technique using a perchloric acid electrolyte at −30°C. The thinned specimen was then examined by transmission electron microscopy in a Philips CM30 microscope operating at 300 keV.

§ 3. Results

The X-ray diffraction patterns obtained at room temperature before and after irradiation are shown in fig. 2. The diagram of the unirradiated sample exhibits only the characteristic lines of the h.c.p. α-phase: the width of these peaks indicates a good crystallinity of the virgin sample. After irradiation the intensity of the α-phase peaks has dramatically decreased, whereas new peaks corresponding to the hexagonal ω-phase of titanium are observed. The determined lattice parameters ($a_\omega = 4{\cdot}62 \pm 0{\cdot}01$ Å and $c_\omega = 2{\cdot}83 \pm 0{\cdot}01$ Å) are consistent with those cited by Sikka *et al.* (1982).

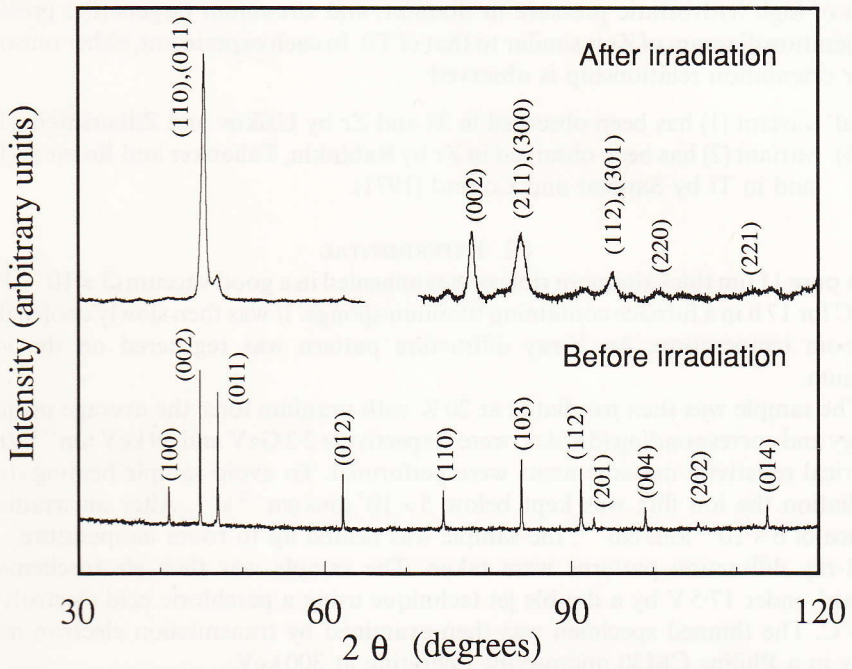
Typical electron diffraction patterns of the irradiated titanium are shown on fig. 3 (*a*1 and *a*2). Analysis of these diffraction patterns reveals the coexistence of ω and α phases and that orientation relationship (2) is obeyed.

Figure 3 (*b*2) is a dark field image obtained using the $(010)_\alpha$ spot of fig. 3 (*a*2): it shows that the remaining α-phase consists now of small regions of average size 10 nm. Figure 3 (*b*1) is a dark field image obtained using the $(001)_\omega$ spot of fig. 3 (*a*1): the morphology of the ω-phase platelets is very intricate and the average grain size is also of 10 nm which is in agreement with the width of the X-ray peaks (fig. 2).

§ 4. Discussion and conclusions

Let us first comment on the observations of lead irradiated titanium (Henry *et al.* 1992) cited in the introduction in which 3 nm diameter platelets lying in the prismatic planes have been observed. These platelets were aligned along the ion beam direction and have been then interpreted as being small dislocation loops. The assumption of an α→ω phase transformation was rejected by using only the experimental observations of Usikov and Zilbershtein (1973), i.e. the sole orientation relationship (1), Taking into

Fig. 2



X-ray diffraction patterns (Co $K_{\alpha 1}$ wavelength) of a titanium sample registered at room temperature before and after irradiation with 2·2 GeV uranium ions up to a fluence of 6×10^{12} ions cm^{-2}. Before irradiation, all the observed diffraction lines belong to the h.c.p. α-phase and are indexed in the lower part of the diagram. After irradiation, new peaks appear: they all correspond to the hexagonal ω-phase and are indexed in the upper part of the diagram.

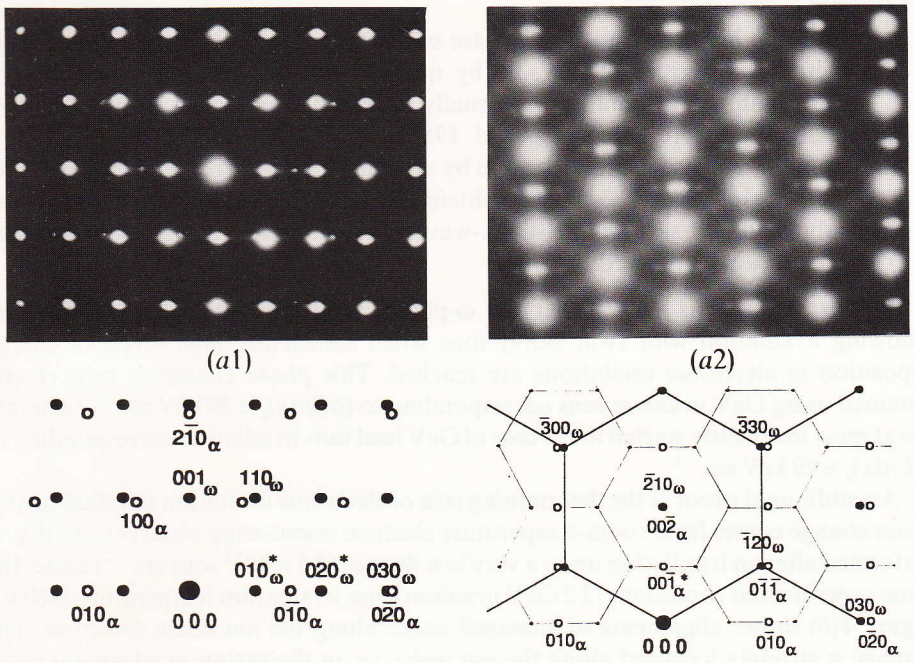
account the two possible orientation variants and the results presented here following uranium irradiations ($(dE/dx)_e \approx 39$ keV nm^{-1}), the platelets observed after lead irradiation (Henry *et al.* 1992) ($(dE/dx)_e \approx 29$ keV nm^{-1}) might well be premonitory signs of the α→ω transformation.

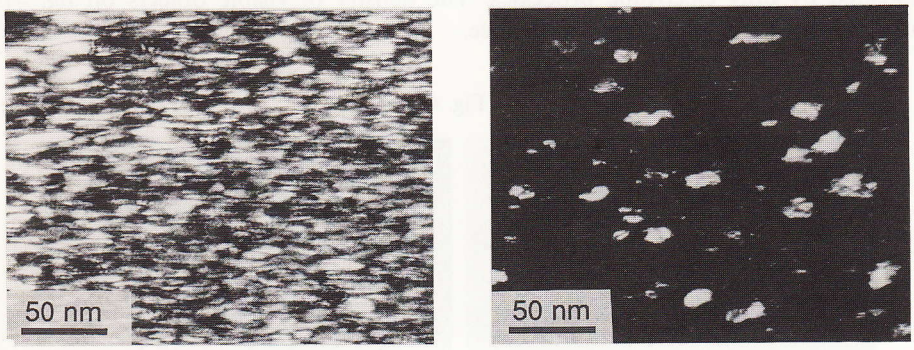
The α→ω phase change which is clearly evidenced in the present letter by X-ray diffraction and electron microscopy observations also strongly influences the electrical resistivity measurements:

(i) at the end of the irradiation with uranium ions the observed increase, $\Delta\rho_i$, of electrical resistivity ($\rho_{20K}^{\text{after irradiation}} - \rho_{20K}^{\text{before irradiation}}$) is 70 μΩ cm and is far from saturation. Such a high value cannot be related solely to the creation of lattice defects: indeed, after an irradiation with MeV electrons the saturation resistivity increase is only 24 μΩ cm. Unfortunately, the electrical resistivity of the ω-phase is known only at room temperature (Jayaraman, Klement, Kennedy and Kennedy 1963); this work suggests that at low temperature the presence of ω-particles in an α-matrix greatly increases the electrical resistivity of titanium.

(ii) after heating up to about 250 K, only a small part of the damage is annealed: the electrical resistivity increase ($\rho_{20K}^{\text{annealed}} - \rho_{20K}^{\text{before irradiation}}$) is still 85% of $\Delta\rho_i$. This has to be compared to the results of similar thermal treatments following

Fig. 3





(*a*): Electron diffraction patterns of the uranium irradiated titanium: (*a*1) zone axis $[001]_\alpha$ and $[100]_\omega$; and (*a*2) zone axis $[100]_\alpha$ and $[001]_\omega$. The general indices of the very weak spots are $(hk0)_\omega$ with $h-k\neq 3n$. The stars indicate that the spots result from double reflection. (*b*) Corresponding dark field images obtained using: (*b*1) the $(001)_\omega$ spot of (*a*1); and (*b*2) the $(010)_\alpha$ spot of (*a*2). The orientation is respected between each diffraction pattern and its corresponding image.

irradiations with electrons or light ions (Legrand *et al.* 1992), for which the electrical resistivity is restored to its initial value $\rho_{20\,K}^{\text{before irradiation}}$. This observation is consistent with the metastability of the ω-phase at room temperature and atmospheric pressure (fig. 1).

When ω – Ti was obtained:

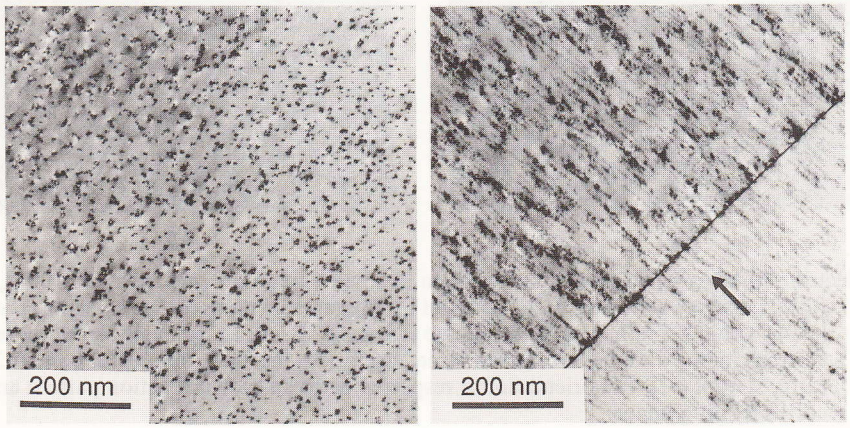
(i) from the high-temperature β-phase of titanium containing small amounts of metallic impurities (Nb, V,...) by quenching (Silcock 1958, Sass 1972): ω precipitates in a β-matrix are usually observed. Sometimes an additional α′ phase is also present (Sikka *et al.* 1982).

(ii) from the α-phase of pure titanium by applying a hydrostatic pressure (of about 100 kbar) (Usikov and Zilbershtein 1973, Rabinkin *et al.* 1981) or by submitting the sample to a shock-wave (Sikka *et al.* 1982): ω precipitates in an α-matrix are observed.

In this paper, it is shown that the ω-phase can be obtained from α-titanium following irradiation with swift heavy ions when sufficiently high levels of energy deposition in electronic excitations are reached. This phase change is now clearly obtained using GeV uranium ions corresponding to $(dE/dx)_e \approx 39\,\text{keV nm}^{-1}$, whereas it is at most incipiently started in the case of GeV lead ions irradiation corresponding to $(dE/dx)_e \approx 29\,\text{keV nm}^{-1}$.

An additional proof of the determining role of electronic excitation in inducing this phase change comes from room-temperature electron microscopy observations (fig. 4) performed after an irradiation up to a very low fluence ($2{\cdot}5 \times 10^{11}$ ions cm^{-2}) under the same experimental conditions (2·2 GeV uranium ions; irradiation temperature = 20 K). Figure 4(*b*) shows alignments of damaged zones along the ion beam direction. The damage is strongly localized along the ion wake, i.e. in the region in which energy is deposited by only electronic processes. The density of visible objects on fig. 4(*a*) corresponds to the impinging ion fluence.

Fig. 4



(*a*) (*b*)

Bright field image of a titanium sample irradiated with 2·2 GeV uranium ions up to a fluence of $2{\cdot}5 \times 10^{11}$ ions cm^{-2}: (*a*) the ion beam direction is perpendicular to the image plane; and, (*b*) the ion beam direction is tilted by about 10° from the normal to the image plane. The arrow indicates the projection of the ion beam direction.

Let us now come back to the possible mechanisms by which the energy deposited in electronic excitation can can cause a displacive phase transformation:

(i) in a thermal spike mechanism, the sample history could follow an almost vertical line denoted by T.S. in fig. 1. This could lead to an $\alpha \rightarrow \beta$ transformation.

(ii) in a Coulomb explosion mechanism, a radial shock-wave is generated around each ion path, so that the sample history could follow an almost horizontal line denoted by C.E. in fig. 1. This would lead to an $\alpha \rightarrow \omega$ transformation. This phase transformation indeed occurs as shown in the present work. It has to be emphasized moreover that in such a mechanism, although only a small fraction of the energy deposited in electronic excitation is converted into atomic motion, the collective and coherent characters of the induced atomic movements (Lesueur and Dunlop 1992) fit well with displacive phase transformations.

The Coulomb explosion mechanism appears thus to provide the better explanation for electronic excitation induced damage in metallic targets.

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