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ω phase in individual latent tracks induced by irradiation of α-titanium with MeV fullerenes*

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ABSTRACT

Evidence is obtained for the existence of a hexagonal ω phase in individual latent tracks (i.e. in the vicinity of the ion paths) induced in h.c.p. α-titanium after irradiation at 80 K at low fluences with 30 MeV C_{60} ions. The orientation relationships between the α and ω phases are those previously observed (Dammak *et al*.1993) when the ω phase is obtained after irradiation at *high* fluences with GeV monomers at low temperature (i.e. $(002)_\alpha \parallel (2\bar{1}0)_\omega$ and $[100]_\alpha \parallel [001]_\omega$). Parallel moiré fringes, due to the overlapping of the structure of the ω phase with the α matrix, are observed in bright-field images obtained with $(020)_\alpha$ ($\parallel(030)_\omega$) reflection conditions. The spacing of these fringes is very close to the value of 3.2 nm expected from the inter-planar distances $d^{\alpha}_{(020)}$ and $d^{\omega}_{(030)}$. After irradiation at 300 K such fringes are also observed but the track structure cannot be established unambiguously. This dependence of the irradiation temperature is related to the temperature-pressure structural properties. The present TEM observations are compared to those obtained (Dammak *et al*. 1996,1999) in the case of irradiation with GeV monomers for which it has been established that an overlapping of tracks is necessary to induce the α→ω transformation.

1. INTRODUCTION

Since 1991 (Dunlop *et al*. 1991) it has been established that titanium is, among pure metals, the most sensitive to high rates of linear energy deposition in electronic processes (LED) during swift heavy-ion irradiations (typically GeV Xe to U ions). Transmission electron microscopy (TEM) observations of titanium foils irradiated at 90 K by 0.9 GeV Ta ions at low fluences (10^{11} cm^{-2}) show alignments of small 'objects' located in the surroundings of the ion paths (Henry *et al*. 1992). The 'objects' present black and white contrasts resembling those observed for dislocation loops. The alignments were called 'discontinuous tracks' with 3-5 nm diameter. The spatial overlap of tracks during irradiation at 20 K by 2.2 GeV U ions up to a fluence of 6×10^{12} ions cm^{-2} leads to displacive phase transformation from the h.c.p. α-phase to the hexagonal ω-phase (Dammak *et al*. 1993). A study of the structural modifications by TEM observations after irradiations performed under various conditions (Dammak *et al*. 1996) showed that the complete α→ω phase transformation is obtained: (*i*) during irradiation at low temperature (20-90 K), (*ii*) for LED levels higher than 33 keV nm^{-1} and (*iii*) for fluences higher than 10^{12} ions cm^{-2}. This latter condition was confirmed later by using in situ electrical resistance and length measurements during irradiation at 20 K by 2.4 GeV U ions (Dammak *et al*. 1999). Authors showed that: *i*) at low fluences (i.e. in each track) the damage creation is identified by TEM observations as the formation of dislocation loops and *ii*) the incubation fluence above which ω domains are formed in the α matrix is about 1.2×10^{12} ions cm^{-2}.

On the other hand during irradiations at 300 K under the same conditions (LED level~35 keV nm^{-1}), the ω phase is not formed for fluences up to 10^{13} cm^{-2} (Dammak *et al*. 1996). In this case TEM observations show a dense dislocation structure in the α matrix caused by the spatial overlap of tracks.

* Irradiations were performed on the tandem accelerator, I.P.N. Orsay (France)

The mechanism proposed for the phase transformation during irradiation by GeV monomers (Dammak *et al*. 1999) is based on the propagation of localized displacement waves of the $[100]_\alpha$ close-packed rows. The creation of dislocation loops or stacking faults in a track is assumed to be due to a shearing of neighbouring $(010)_\alpha$ prismatic planes. The formation of ω domains at low temperature (20-90 K) requires a spatial overlap of these tracks and is assumed to be the result of a local rearrangement. The deduction of the existence of stacking faults arising from a disorder in the transverse displacements in $(010)_\alpha$ prismatic planes takes into account the diffuse intensity lines observed in the electron diffraction pattern. At room temperature the spatial overlap of tracks leads to a partial recovery and so to a dense dislocation structure.
However, it has been recently established that, using 10-40 MeV C_{60} ions for which the LED levels are slightly higher than those obtained by using GeV monomers, the resulting structural modifications were extremely important in titanium (Dammak *et al*. 1995). In fact 18 MeV C_{60} ions create quasicontinuous tracks of about 20 nm diameter. The important resulting structural modification is thought to arise from the very strong localization of the deposited energy.
In the following we present the influence of the irradiation temperature on the structural modification in titanium during irradiation by MeV C_{60} ions using TEM observations.

2. EXPERIMENTAL

High-purity polycrystalline titanium ribbons of 11 μm thickness were annealed in vacuum (3×10^{-4} Pa) for 17 h at 1090 K in a furnace containing titanium sponge: the ribbons were then slowly cooled down to room temperature. From the ribbons 3 mm diameter discs were punched out which were ground and electrochemically thinned up to electron transparency by a double-jet technique using a perchloric acid electrolyte at 240 K and an applied voltage of 17.5 V.
The discs were irradiated with 30.2 MeV C_{60}^{2+} ions either at room temperature or in a liquid- nitrogen-cooled cryostat at the Orsay tandem accelerator : the fluences were chosen in order to avoid overlapping of the damaged regions, with values around 5×10^{9} ions cm^{-2}.
At such incident energies, when hitting the target surface, the C_{60} clusters will break up into single ions or small assemblies of ions. During the slowing-down of this flow of neighbouring projectile constituents, a spatial separation of the fragments occurs as a consequence of Coulomb repulsion between charged fragments and multiple scattering by elastic collision processes. A detailed description of these effects was given by Dunlop *et al*. (1997). The range of 30.2 MeV C_{60}^{2+} in titanium (~ 700 nm) is much larger than the thickness (< 100 nm) of the regions observed by TEM, so that in this work we deal only with the regions of correlated slowing-down of the fragments in which energy loss occurs mainly through electronic excitation and ionization.
The microstructure of the irradiated samples was examined using a Philips CM30 transmission electron microscope operated at 300 kV.

3. RESULTS

The analysis of the images obtained in the microscope shows that the observed damaged zones (tracks) go entirely through the sample thickness with an almost constant ‘diameter’. The absence of halos and thin rings in the electron diffraction patterns shows that the damage cannot be associated with an amorphous phase nor to micro-crystallized matter. In the following we show that orientation relationships exist between the new phase and the h.c.p. α-matrix.

3.1. Irradiations at 300 K

For the samples irradiated at room temperature, tilting around $g = (010)_\alpha$ (i.e. prismatic planes of α-Ti remain parallel to the electron beam in the microscope) in the diffraction patterns, extra spots indexable as $(030)_\omega$ along the direction of the $(0h0)_\alpha$ spots (figures 1(a) and 1(b)), are associated with the tracks. The bright-field images (figure 1(c)) taken in orientations such that a row of $(0h0)_\alpha$ reflections are excited, show that fringes parallel to the $(010)_\alpha$ planes with a spacing of about 3 nm are associated with the tracks. These fringes have been identified as parallel moiré fringes - a double-diffraction effect due to an overlapping of the structure of the tracks with the α matrix. The spacing of the fringes

is very close to the value of $\delta = 3.2$ nm expected from the lattice spacing of $(030)_\omega$ and $(020)_\alpha$ ($1/\delta = 1/d^{\alpha}_{(020)} - 1/d^{\omega}_{(030)}$).

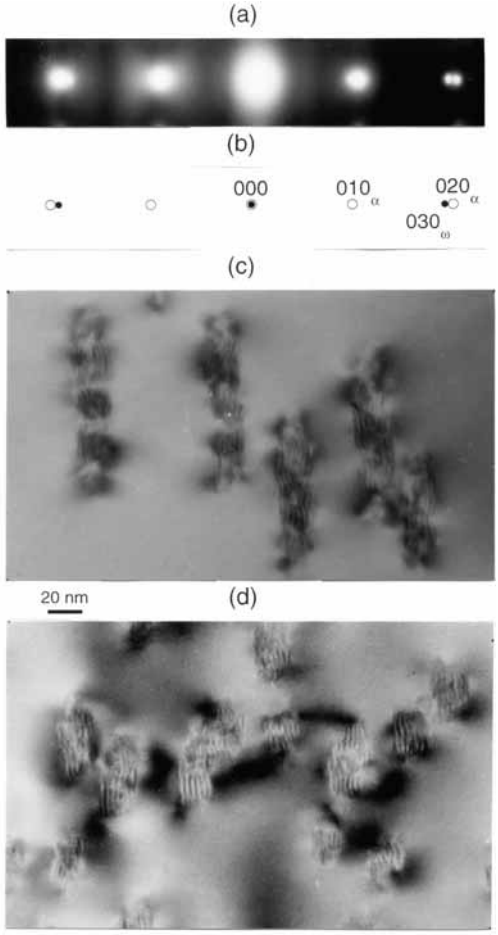

Figure 1. Titanium irradiated at 300 K (fig. 1a-c) and 80 K (fig. 1d) with 30 MeV C_{60} ions. (a) electron diffraction pattern showing the $(0h0)_\alpha$ row. (b) index of the diffraction pattern showing the $(030)_\omega$ extra spot. (c) and (d) bright-field images of tilted tracks, bserved after irradiations respectively at 300 K and 80 K, showing fringes perpendicular to the $(0h0)_\alpha$ row. The spacing of the fringes is very close to the value of $\delta = 3.2$ nm expected from the lattice spacing of $(030)_\omega$ and $(020)_\alpha$ ($1/\delta = 1/d^{\alpha}_{(020)} - 1/d^{\omega}_{(030)}$). The tilt angle of the tracks is respectively about 35° and 13° for (c) and (d).

Other diffraction effects related to the structure of the tracks were seldom found and it was not possible to establish unambiguously the crystallographic structure of the tracks. In fact the observed extra spot can also be indexed in the b.c.c. β-phase as $(111)_\beta$ with $\delta = 3.2$ nm, and in the h.c.p. α-phase as $(103)_\alpha$ with $\delta = 3.1$ nm.

3.2. Irradiations at liquid-nitrogen temperature

In samples irradiated at liquid-nitrogen temperature, the diffraction patterns (figures 2 and 3) show the coexistence of both α and ω phases with the orientation relationships $(002)_\alpha \parallel (2\,\bar{1}\,0)_\omega$ and $[100]_\alpha \parallel [001]_\omega$ previously found after irradiation with GeV monomers at high fluences (Dammak *et al.* 1993). Figure 2 shows the electron diffraction pattern corresponding to the superposition of the $[320]_\alpha$ zone axis with the $[\bar{1}\,\bar{2}\,3]_\omega$ zone axis and $(002)_\alpha$ parallel to $(\bar{2}\,10)_\omega$. The evidence of the ω phase in this case is confirmed by the observation of the $(111)_\omega$ reflection (figure 2(b)) for which there is no equivalence in the β or α phases.

The bright-field image given in figure 1(d) taken with the same diffraction conditions of those of figure 1(a), shows fringes spaced by 3 nm as found in the samples irradiated at room-temperature. It is important to note that the parallelism of $(010)_\alpha$ with $(030)_\omega$, which is also observed after room-temperature irradiation, is coherent with the α/ω orientation relationship. The dark-field image (figure 3(a)), made with a beam diffracted by the structure associated with the tracks and corresponding to $(121)_\omega$, show the ω-phase in the 'cylindrical' region surrounding the ion path. It is interesting to note that despite the fact that the moiré fringes extend continuously all over the tracks, the dark-field images show small transformed domains. The structure of the track seems to be continuous parallel to the $(010)_\alpha$ (i.e. $\parallel [120]_\alpha$) and defective normal to $(010)_\alpha$ (i.e. $\perp [120]_\alpha$).

The average lateral size of tracks measured on figure 3(a) is equal to 21±2 nm. On the other hand, using figures 1(c) and 1(d), the number of fringes is about 6 for both room-temperature and liquid-nitrogen irradiations. The lateral size of tracks is then about

6 δ ~ 19 nm. The images of figures 1 and 3 obtained by tilting tracks around two different directions give approximately the same measured lateral size of the track. The tracks have an approximately cylindrical morphology.

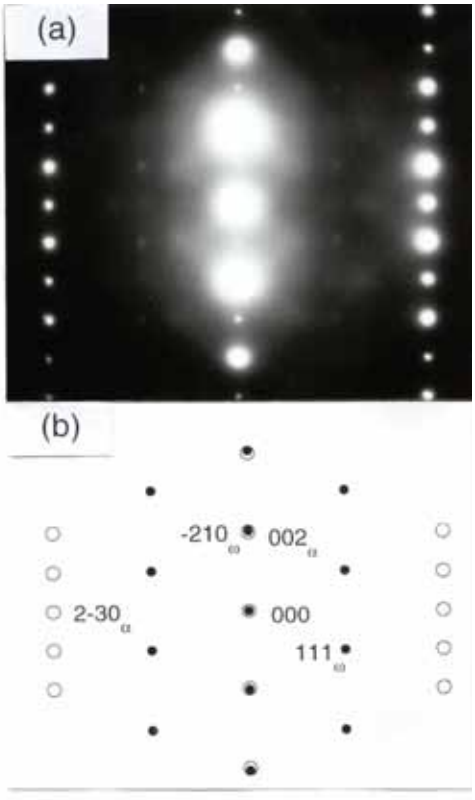

Figure 2. Titanium irradiated at liquid-nitrogen temperature with 30 MeV C_{60} ions. (a) electron diffraction pattern showing the superposition of the $[320]_\alpha$ zone axis with the $[\bar{1}\bar{2}3]_\omega$ zone axis. (b) index of (a) using the orientation relationship $\{(002)_\alpha \parallel (2\bar{1}0)_\omega$ and $[100]_\alpha \parallel [001]_\omega\}$.

4. DISCUSSION AND CONCLUSIONS

On the basis of these observations it is possible to say that the end product of 30 MeV C_{60} irradiation is a highly defective ω-phase along the ion paths. The absence or weakness of ω reflections other than $(030)_\omega$ in samples irradiated at room temperature could to be due to the presence of many faults in the stacking of the $(030)_\omega$ planes. After irradiations at 300 K, we find the same orientation relationship of the $(030)_\omega$ planes as after low-temperature irradiation.

These results should to be compared to those (see Introduction) obtained under the same conditions by GeV monomers (Table 1).

Comparing 10-40 MeV C_{60} ions and GeV monomer ions, for which the LED levels are similar, the resulting structural modifications in titanium are extremely different. The enhancement of the resulting damage after cluster ion irradiations is expected to be due to the very strong localization of the deposited energy (Dammak *et al*. 1995). The transport of the energy away from the ion path is governed by the ejected δ electrons, which have an angular and kinetic energy distribution related to the projectile velocity. The volume in which the energy is deposited is related to the radial range of secondary electrons. Using GeV Pb or U ions the radial range of δ-electrons is of some 1000 nm, whereas using a few 10 MeV C_{60} ions, this radial range falls to a few interatomic distances. In this latter case the deposited energy density can reach values as high as 100 eV/atom. The relaxation of such a high-energy density induces very strong structural modifications around the ion path.

Table 1 shows that after irradiations with 30 MeV C_{60} ions, the volume of the regions in which structural modifications takes place is temperature independent: the *cross-section diameters* of the tracks are approximately the same for both room-temperature and liquid-nitrogen irradiations. But the *nature of structural modifications* (i.e. the resulting latent damage) is temperature dependent (table 1). It seems that the deposited energy density threshold above which the ω-phase is obtained in a track increases when the irradiation temperature increases.

This temperature effect is similar to that observed for the α→ω phase transformation induced by applied static or dynamic pressure. From the pressure-temperature phase diagram of titanium (Zil'Bershteyn *et al*. 1973, Sikka *et al*. 1982), the athermal martensitic start pressure $P_{Ms}^{\alpha\to\omega}$ (above which the α→ω transformation occurs) also increases when the temperature increases. Kustar and German (1979) show that no ω-

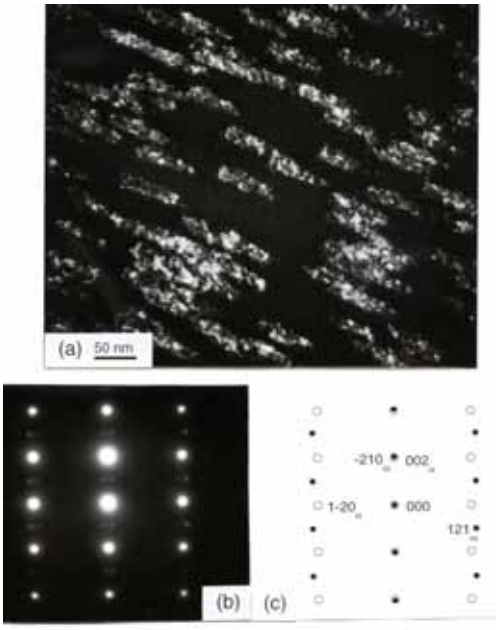

Figure 3. Titanium irradiated at liquid-nitrogen temperature with 30 MeV C_{60} ions up to a fluence of 5×10^{9} ions cm^{-2}. (a) dark-field image of tilted tracks. (b) electron diffraction pattern showing the superposition of the $[210]_\alpha$ zone axis with the $[\bar{1}\bar{2}5]_\omega$ zone axis. (c) index of (b) showing the spot $(121)_\omega$ selected to make the dark-field image (a). The double weak spots result from double reflection.

phase is formed in titanium samples shock-loaded at 290 K with pressures in the 12-50 GPa range. At 120 K, the ω-phase is formed and the amount of this increases (from 6 to 54%) when the shock pressure amplitude increases from 12 to 50 GPa. This temperature effect is related by the authors to an increase of the shock residual temperature above the back transformation temperature $T^{\omega\rightarrow\alpha}$ (~ 400K at atmospheric pressure).

When the cluster fragments slow-down in a material, the energy is deposited in a very short time in a highly non-equilibrium process, so that the resulting damage can be compared to the results of the shock experiments. In fact, the time taken by a 30 MeV C_{60} ion to travel a distance of 10 nm in the material is of the order of 10^{-14} s, which is much smaller than the characteristic time for the lattice motion (10^{-13}-10^{-12} s). However for the phase transition under shock conditions, Duvall and Graham (1977) show that the brief duration (<1 μs) for which the pressure pulse is applied rules out the possibility of any diffusion-assisted growth. Recently Lavrentiev *et al*. (1999) show that the ω-phase is formed during surface irradiation of titanium by 800 keV electron beam with a pulse duration of 10 ns. The explanation of this result by the authors is based on stress waves, which arise in such exposures.

Hence it can be expected that, in the vicinity of the C_{60} ion path, the transformation has to proceed rapidly and directly because the brief duration of the excited state cannot allow the formation of nucleation centres through creation and motion of defects. A collective and coherent movement of atoms is necessary to obtain the observed structural modification in the tracks; the $\alpha\rightarrow\omega$ phase change may be realized by a transformation of the martensitic type. The phase transition may proceed as described by the direct mechanism proposed by Rabinkin *et al*. (1981) which is based on the shearing of the prismatic planes and developed recently in a phonon description to explain the structural modifications induced with GeV monomers (Dammak *et al*. 1999).

The relaxation of the high deposited energy density generates around the C_{60} ion path strong stress waves leading to structural modifications. At a low temperature (liquid nitrogen) the remaining displacements are correlated leading to ω-phase formation in the track. At room temperature the remaining lattice displacements are only correlated along $(010)_\alpha$, leading to the $(030)_\omega$ reflection in the electron diffraction pattern. The effect of the irradiation temperature is related to the temperature-pressure structural properties.

Irradiation temperatures	GeV U ions	MeV C_{60} ions
300 K	- discontinuous tracks with 3-5 nm cross-section diameter. - no ω-phase, even after high irradiation fluences.	- quasicontinuous tracks with ~20 nm cross-section diameter. - only $(030)_{\omega}$ reflection is observed.
80 K	- discontinuous tracks with 3-5 nm cross-section diameter. - ω-phase observed only after high irradiation fluences.	- continuous tracks with ~20 nm cross-section diameter. - ω-phase is formed in individual tracks.

Table 1. Structural modifications in titanium observed by TEM after irradiation at room and liquid-nitrogen temperatures. A comparison between the previous results using GeV U ions (Dammak *et al*. 1995, 1996, 1999) and the present results using 30 MeV C_{60} ions.

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