X-ray Diffraction of Titanium Under High Pressures: A Systematic Analysis of the Mechanism for the Alpha to Omega Martensitic Transformation

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Introduction

Structural transformations in titanium have received a great deal of experimental and theoretical attention. Under pressure, titanium transforms from the hexagonal-closed-packed (hcp) structure to the high-pressure omega phase. This phase transition from hcp (α) to omega (ω) is martensitic. Martensitic transformations are abundant in the nature and have tremendous scientific and technological interest. In particular, the pressure-induced martensitic α ® ω transformation in pure titanium (Ti) has significant implications in the aerospace industry because the ω phase formation affects the toughness and ductility of Ti.

The occurrence of the pressure-driven α ® ω transformation was first observed by Jamieson [13] and has since been studied extensively. Room temperature (RT) high-pressure studies of the α ® ω transition show a large hysteresis, with the high-pressure ω phase being retained after pressure is released [2, 3]. The onset of the transition has been observed over a wide range of pressures from 2.9 GPa [4] to 11 GPa [5]. One of the factors that could be responsible for this scatter in the observed transition pressure ($P_{\alpha\rightarrow\omega}$) is possibly the variation in the non-hydrostatic conditions in different experiments. However, the combined results from different experiments are inconsistent with this fact. Then the question is whether the shear stress explanation is correct and whether other factors play a role in the transition. To answer this question, we conducted a series of experiments in a diamond-anvil cell (DAC) using different pressure media.

In this study, we examined the effects of uniaxial stresses on the α ® ω transition of Ti using synchrotron x-ray powder diffraction. Experiments were performed using a DAC and four different pressure media, which provided different hydrostatic conditions. We clearly demonstrated that the presence of uniaxial stresses has a significant effect on the structural stability of Ti. We also observed that short-term laser-heating of Ti lowers $P_{\alpha\rightarrow\omega}$.

Methods and Materials

The structural stability of Ti under compression was studied up to 16 GPa by angle dispersive powder x-ray diffraction (ADXRD). In order to analyse systematically the effects of uniaxial stresses on the α ® ω transition of Ti, we performed four different sets of experiments using a symmetric DAC with the sample loaded under four different pressure transmitting media (argon, 4:1 methanol-ethanol mixture, NaCl, and without pressure medium). Ti samples, compressed from commercial powder (Alfa Aesar) of stated purity 99.9 %, with a diameter of 50 μm and a thickness of approximately 5 μm were loaded in stainless steel gaskets to perform the studies reported here. The experiments were performed using a monochromatic synchrotron radiation source (λ = 0.3875 or 0.4246 Å) at the 16-IDB beamline of the HPCAT facility at the Advanced Photon Source. The monochromatic x-ray beam was focused down, using multilayer bimorph mirrors in a Kickpatrick-Baez configuration, to 10 μm by 10 μm. Diffraction images were recorded with a MarCCD detector, being the sample-detector distance ≈ 210 mm. Indexing, structure solution, and refinements were performed using the POWDERCELL program. The ruby fluorescence technique was applied to measure the pressure.

Discussion

Figure 1 shows ADXRD patterns of Ti at selected pressures measured from a sample loaded in a 4:1 methanol-ethanol pressure medium. The six diffraction peaks observed in trace (a) corresponds to the diffraction pattern of the α phase of Ti (α-Ti) at 1 GPa. On increasing pressure, at 10.2 GPa (trace (b)) six new Bragg peaks appear, showing the coexistence of the α and ω phases of Ti at this pressure. The $\alpha \rightarrow \omega$ transition is completed at 14.7 GPa as shown in trace (c). After pressure release the observed transition is not reversible (see trace (d)) in agreement with previous results [3].

In contrast with the behavior observed in Fig. 1, in the sample studied using NaCl as pressure medium, the onset of the $\alpha \rightarrow \omega$ transition was observed at 6.2 GPa and the transition was completed at 14.2 GPa. In addition, in this sample after pressure release, a mixture of the α and ω phases is recovered. The other two samples studied under different pressure media also show differences regarding the pressure for the first observance of the ω phase, the pressure range of coexistence of both phases, and the crystalline structure of the recovered samples after decompression. The sample studied under argon shows similar results to those of the one studied under a 4:1 methanol-ethanol mixture, the onset of the transition occurring at 10.5 GPa. On the other hand, in the sample studied without pressure medium the results are similar to the results obtained under NaCl but the starting pressure of the transition is the lowest (4.9 GPa).

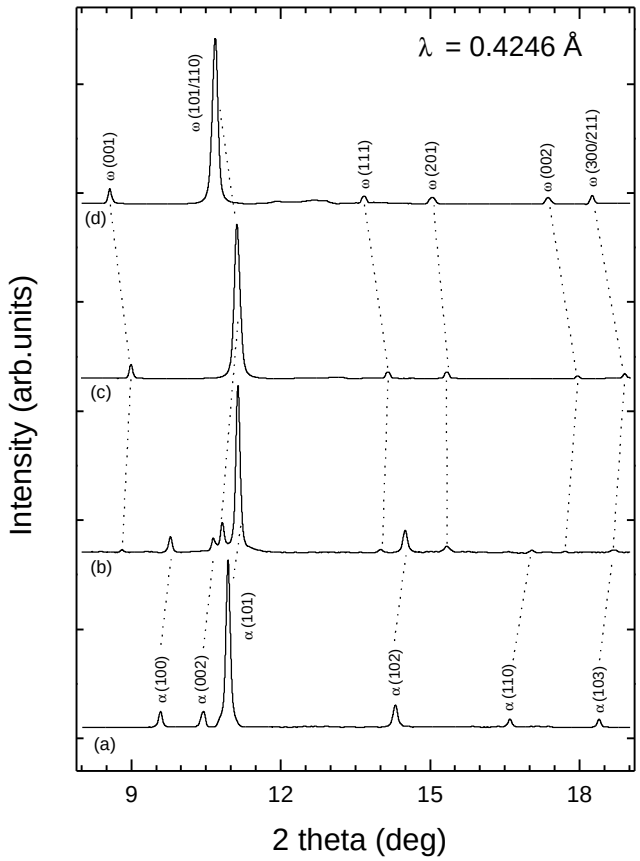

Figure 1: *x-ray diffraction patterns of Ti at different pressures: (a) 1 GPa, (b) 10.2 GPa, (c) 14.7 GPa, and (d) 1 GPa after pressure release. The sample was loaded using 4:1 methanol-ethanol as pressure transmitting medium. Miller indices corresponding to the a and w phases of Ti are indicated.*

We now turn our attention to the different behaviors that have been observed for Ti in the range 2 - 15 GPa to show that they can be ascribed to different pressure conditions. In order to analyse the effect of uniaxial stresses on the $\alpha \rightarrow \omega$ transition we calculated the volume fraction of the ω phase of Ti (ω-Ti) as a function of pressure in the four samples here studied. The results obtained are shown in Figure 2. There it can be seen that in those samples studied under less hydrostatic media (no medium or NaCl) the transition starts at lower pressures than in the other samples and the pressure range of the transition is wider. In addition, by comparing all the x-ray diffraction patterns measured under different pressure enviroments, we observed that the diffraction peaks exhibit larger full width at half maximum values in those experiments performed under less hydrostatic conditions (see Ref. 6). It has been documented that this broadening of the diffraction peaks is due to more pronounced pressure gradients and to uniaxial stresses. All these facts support our idea that uniaxial stresses play an important role on the pressure-driven $\alpha \rightarrow \omega$ transition of Ti. The metastability of the α and ω phases observed in shock-wave experiments [5] in the range 10.7 – 14.3 GPa is also in good agreement with our results.

Several transition mechanisms have been proposed for the $\alpha \rightarrow \omega$ transformation [7]. Among them, Silcock's [8] and Usikov's [9] pathways have been the most invoked to describe the $\alpha \rightarrow \omega$ transformation. According to Silcock's mechanism, in each α stacking plane, three of six atoms shuffle by 0.74 Å along $[\bar{1}\bar{1}20]_\alpha$, while the other three shuffle on the opposite direction $[11\bar{2}0]_\alpha$. This shuffle is accompanied by a strain e_{xx} = 0.05 along $[1\bar{1}00]_\alpha$ and a strain e_{yy} = 0.05 along $[11\bar{2}0]_\alpha$ to produce a hexagonal ω cell with the correct *c*/*a* ratio. In contrast with the direct mechanism proposed by Silcock, Usikov proposed a mechanism with two variants (both having the same strains but different shuffles) which involves a metastable intermediate β (bcc) phase (i.e. $\alpha \rightarrow \omega$ is predicted to proceed as $\alpha \rightarrow \beta \rightarrow \omega$). On the other hand, recently Trinkle *et al.* proposed for the $\alpha \rightarrow \omega$ transformation two pathways (related to Usikov's variants) called TAO-1 ("titanium alpha to omega") and TAO-2 [7]. The TAO-1 mechanism is a direct mechanism in which in the α cell four atoms shuffle by 0.63 Å and two atoms by 0.42 Å, combining this shuffle with strains of e_{xx} = -0.09, e_{yy} = 0.12, and e_{zz} = 0.02 to produce a final ω phase from the α phase [7].

The fact that our experiments systematically demonstrate that uniaxial stresses play an important roll in the $\alpha \rightarrow \omega$ transformation suggests that Silcock´s mechanism (which involves the smallest strains) is not appropriate to describe this transformation. In addition, this mechanism involves considerable reconstruction of the lattice, being this fact also in contradiction with the martensitic nature that we and previous authors [4] have observed for the $\alpha \rightarrow \omega$ transformation. On the other hand, in our studies we did not find any evidence of the existence of a metastable β phase during the $\alpha \rightarrow \omega$ transformation, ruling out Usikov's mechanism. Therefore, our measurements give support to the TAO-1 pathway, as the most likely transition mechanism, in agreement with recent energy barrier calculations [7].

Another interesting phenomenon to note is the fact than when shear forces are important (no medium or NaCl medium) the $\omega \rightarrow \alpha$ transition is observed after some hysteresis under decompression. However, the same fact is not observed in those samples studied under nearly hydrostatic conditions (4:1 methanol-ethanol medium or argon medium), wherein the ω phase is recovered after complete pressure release. According to Sikka *et al.* [10] retention of the high-pressure ω phase is only possible if the uniaxial stress component of the stress tensor is considerably smaller than the transition pressure. This is qualitatively in agreement with the fact that in our case, those samples with narrower diffraction peaks (i.e. smaller uniaxial stresses) do not transform back to the α phase under decompression.

Based upon our results, it is expected that shear stresses present in DAC experiments will also affect the $\alpha \rightarrow \omega$ transition in zirconium and hafnium thereby explaining the observed scatter of the transition pressures reported. In addition, it may be also expected that uniaxial stresses will influence the phase transitions observed at very high pressures in Ti, being the cause of the contradictory results reported by different authors [2, 11, 12]. Experiments reporting the β, δ, and γ phases of Ti were performed without

pressure medium and therefore metastable phases could be formed due to shear stresses as suggested by FP-LAPW calculations [13].

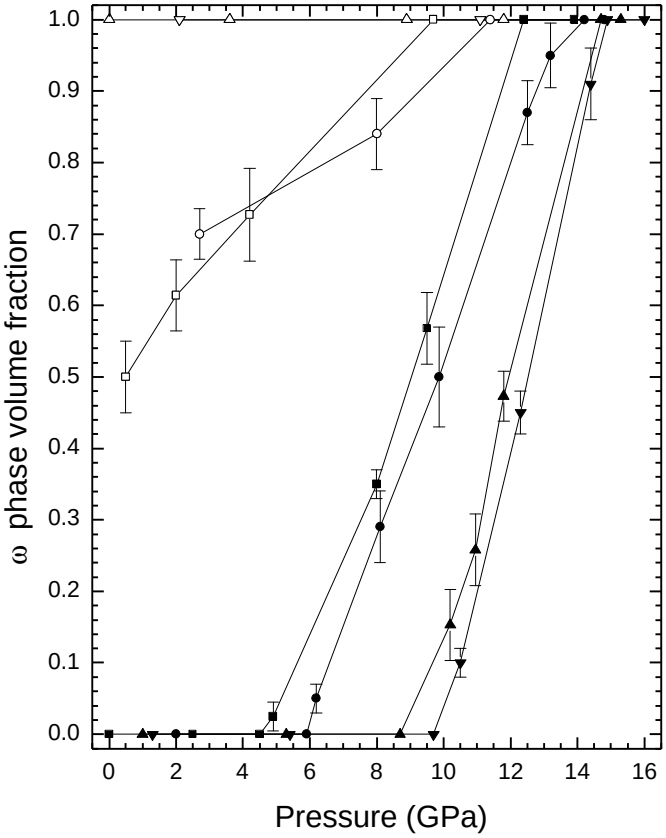

Figure 2: *Relative amounts of w-Ti to a-Ti at high pressures clearly showing that completion of the a-to-w transition depends on the sample environment. (squares) No pressure medium, (circles) NaCl pressure medium, (up-triangles) 4:1 methanol-ethanol, and (down-triangles) argon pressure medium. It contains the data obtained during compression (solid symbols) and decompression (empty symbols). Solid lines are just a guide to the eye.*

From our data we also obtained the pressure dependence for the lattice parameters for both faces, α and ω (See Ref. 6). Within the experimental errors there is no observable effect of pressure medium on the measured unit cell parameters. We observed that for both phases the lattice compression is anisotropic, with the *a*-axis being clearly more compressible than the *c*-axis. As a consequence of this, the *c*/*a* ratios of both phases increase with pressure. For the ω phase, the *c*/*a* ratio raises from 0.609 at ambient pressure to the ideal ratio, 0.613, at 16 GPa. The *c*/*a* ratio of the α phase increases from 1.583 at ambient pressure to 1.622 at 14.5 GPa. Our pressure-volume data also yield a third-order Birch-Murnaghan EOS with $B_0 = (117 \pm 9)$ GPa, $B_0' = 3.9 \pm 0.4$, and $V_0 = 10.66 \pm 0.03$ cm^3/mol for α-Ti, and $B_0 = (138 \pm 10)$ GPa, $B_0' = 3.8 \pm 0.5$, and $V_0 = 10.48 \pm 0.05$ cm^3/mol for ω-Ti, respectively.

Finally, it is interesting to mention that at 5 GPa, two different Ti samples (α phase) loaded under a NaCl pressure medium were double-sided laser-heated with the radiation of two Nd:YLF lasers (Photonics GS40, 85 W, TEM_{01} mode, λ = 1053 nm) available at the HPCAT [14]. The aim of these two experiments was the retrieving of the β (bcc) phase of Ti to study its pressure behaviour. In one case, the Ti sample was heated to the stability region of the high-temperature β phase, T = 1750 K, and quenched. In the second case, the Ti sample was heated to a temperature just above the melting [15], T = 2150 K, and quenched. In both cases, samples were laser-heated for approximately one minute, however we could not succeed in quenching the β phase of Ti. In contrast, a mixture of the α and ω phases was obtained at a pressure where only the α phase was observed in RT experiments performed under the same pressure environment. This lowering of the equilibrium transition pressure after heating suggests that thermal fluctuations induced by the heating could have the same effect as uniaxial stress on the α → ω transformation of Ti. This phenomenon is consistent with the fact that ω embryos can be stabilized as defects at high temperatures under conditions where the β phase is thermodynamically stable. Upon quenching, the β phase of Ti reverts to the α phase, but the ω embryos could remain stable favouring the onset of the α → ω transition at lower pressures than in unheated samples.

Acknowledgments

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