Crystallographic structure of Ti-6Al-4V, Ti-HP and Ti-CP under High-Pressure

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Abstract The phase stability of a commercial purity (Ti-CP), high purity (Ti-HP) and Ti-6Al-4V alloy were investigated in a diamond anvil cell up to 32 GPa and 298 K using a polychromatic X-ray beam. The Ti-CP and Ti-HP shown the same HCP ($c/a \approx 0.632$) to Hexagonal ($c/a \approx 1.63$) non reversible martensitic transition at about 9 GPa. The as received Ti-6Al-4V shows a very low relative volume fraction $\beta$-Ti / $\alpha$-Ti. No phase changes were observed in the Ti-6Al-4V alloy in the pressure range of this study. The $\alpha$ phase of the Ti-6Al-4V shows monotonic volume cell pressure dependence. This volume change is reversible and non-hysteretic. The cell of the $\alpha$ phase recovered its original volume when the pressure was released.

1. Introduction
Because their outstanding properties, titanium and titanium alloys, are very useful materials. They are ideal for use in environments, like aerospace, where high strength and low weight are required [1]. Because of their high corrosion resistance hey are also applied in the chemical industry [2]. Thanks to their biocompatibility titanium and its alloys have been used in medical devices and prosthetic components [3].

At ambient pressure and temperature, pure titanium has a close packed hexagonal $\alpha$ (HCP) structure, and at over 890°C a body centered cubic $\beta$ (BCC) one [4]. The $\alpha$ titanium phase has a higher creep resistance; and the $\beta$ titanium phase is more forgeable. For technological applications a combination of $\alpha$ and $\beta$ phases is desired. Then, the pure titanium is alloyed with $\alpha$ and $\beta$ stabilizer elements. For example, in the case of Ti-6Al-4V, the $\beta$ phase is stabilized by vanadium and the $\alpha$ phase by aluminum.
In addition to the alloying elements and temperature influence on the phase stability the pressure effects were studied. By apply a high pressure on the titanium element an atomic rearrangement and a different phase is achieved. At high pressure and room temperature pure titanium shows a $\alpha$ to $\omega$ transformation [5]. The $\omega$ phase has a three atoms hexagonal AlB$_2$ type structure. The $\alpha$ to $\omega$ transformation is very sensitive and can be inhibited by the presence of impurities [6]. However if the $\alpha$ to $\omega$ transformation occur in the Ti-6Al-4V alloy, it will induce mechanical properties degradation.

In order to determine the pressure-volume relationship and any possible change in the crystal structure, the high-pressure room-temperature structure of Ti-6Al-4V alloys was investigated. Moreover, the influence of frequent impurities on the $\alpha$ to $\omega$ pressure induced phase transformation in pure titanium was also studied.

2. Experimental

2.1. X-ray at Ambient and High-Pressure

The X-ray diffraction pattern of the different samples were taken at ambient pressure before the high pressure measurements. The measurements were carried out using Cu-K$_{\alpha 1}$ radiation with a nickel filter and SiO$_2$ monochromator, in the angle range of $2\theta$=20-150°. The high-pressure energy dispersive X-ray diffraction studies were taken at the X17-C beamline of the National Synchrotron Light Source (NSLS).

The pressure (up to ~34.2 GPa) was applied via a Merrill-Bassett type diamond anvil cell (DAC) and a “Tel-Aviv”-type DAC. The experiments were conducted using a polychromatic X-ray beam. The sample dimensions for the high pressure measurements were about 30µm in height and 80µm in diameter.

The energy dispersive data were collected with a high purity germanium detector at a fixed Bragg angle (2$\theta$=12°). The high-pressure X-ray powder diffraction measurements were taken at discrete pressure steps in the range of 0-32.5 GPa. The data was collected by the EDS technique, using the white beam of the superconducting wiggler at the X17-C beamline. The diffraction data was taken for ~15min in discrete steps of pressure. The data was analyzed using a commercial Rietveld analysis software package [7].

2.2. Measurements Results and Data analysis

The X-ray diffraction pattern of the Ti-6Al-4V, Ti-CP and Ti-HP samples were taken at ambient and then at the high pressure range. The Energy dispersive System, EDS, X-Ray spectra were mathematically converted for fitting convenience. The data from the energy dimension was converted to 2$\theta$, as it should be for Cu K$_{\alpha 1}$ radiation $\lambda$=1.54056Å.

Each one of the acquisition data contains three sets of peaks from different origins. The fluorescence lines originated from the elements, the diffraction peaks originated from the crystallography and the escape peak, which is an extra weak peak (~4%), originated from the Ge detector, -9.8KeV away from each original peak.
3. Results

3.1. Ti$_6$Al$_4$V

In figure 1 it can be seen that Ti-6Al-4V keeps the same symmetry as the volume is reduced. We fitted the data to the P 63/m m c (S.G. 194) symmetry. At ambient pressure the unit cell parameters are $a = 2.9216(3)$Å and $c = 4.6698(8)$Å, with G.O.F (Good Of Fitness) of 6.5042%. While increasing pressure there is a decreasing in the unit cell parameters. At the highest pressure reached, 32.4 GPa, the unit cell parameters are $a = 2.7739(2)$Å and $c = 4.4361(9)$Å with G.O.F of 6.341%.

After releasing pressure we obtained the original unit cell parameters within the error uncertainty. No hysteresis was detected during pressure release. As pressure increased to the highest measured, the unit cell parameters decreased monotonically with no phase change. At a pressure of 32.4 GPa volume was reduced by $\sim 14.4\%$. An example of a Rietveld analysis of X-Ray diffraction data at a pressure of 29.2 GPa for the of Ti-6Al-4V sample is given in figure 2.

![Figure 1. X-Ray diffraction of Ti-6Al-4V as function of pressure it the P 63/m m c symmetry.](image1)

![Figure 2. Rietveld X-Ray diffraction analysis of Ti-6Al-4V at 29.2 GPa. The red line is the theoretical calculation to the P 63/m m c symmetry. The fitted parameters are $a = 2.7991(3)$Å and $c = 4.463(1)$Å. The residual of the fitting is indicated below the graph.](image2)
The unit cell parameters are given in figure 3, indicating a monotonic reduction in the unit cell parameter as function of pressure. The unit cell parameters ratio, \( c/a \), remains almost constant, \((1.599)\), over the entire pressure range, as indicated in figure 4.

![Figure 3](image_url)

**Figure 3.** The unit cell parameters \( a \) and \( c \) of Ti-6Al-4V as function of pressure. The results are the parameters from the Rietveld X-Ray diffraction analysis fitted to the hexagonal structure at each pressure.

![Figure 4](image_url)

**Figure 4.** The unit cell parameters ratio \( c/a \) of Ti-6Al-4V as function of pressure.

The volume-pressure curve, calculated from the data is depicted in figure 5. The relationship between pressure and volume change was determined by the Vinet equation of state [8]:
\[ P(V) = 3B_0 \left( \frac{V}{V_0} \right)^{2/3} \left[ 1 - \left( \frac{V}{V_0} \right)^{1/3} \right] \exp \left( \frac{3}{2} \left( B_0 - 1 \right) \left[ 1 - \left( \frac{V}{V_0} \right)^{1/3} \right] \right) \]

\( B_0 \) is the isothermal bulk modulus at room temperature and ambient pressure, and \( B_0' \) is the partial derivative of the isothermal bulk modulus against pressure under the same conditions. The \( B_0 \) parameter was 154 ±11 GPa, with \( B_0' \) 5.4±1.4.

**Figure 5.** The reduction of the \( V/V_0 \) ratio of Ti-6Al-4V as function of pressure. The line is the fit the Vinet [8] equation of state. No phase transition was observed at this pressure range.

### 3.2 Ti-HP and Ti-CP

The Ti-HP (High purity) was of 99.99% purity, while the Ti-CP (commercial purity) was of 99.3% purity. In figure 6a and 6b it can be seen that Ti-HP and Ti –CP do not keep the same symmetry as function of pressure. In response to increasing external pressure the volume was reduced by ~15% at 26.9 GPa, and by 18% at 32.4 GPa, respectively.

The low-pressure phase is in the P 6\( \text{3} \)/\( \text{m} \) \( \text{c} \) (194) symmetry while the high-pressure phase is in the P 6/m m c (191) symmetry, both of them are in the hexagonal structure. There is a change in the \( a \) and \( c \) unit cell parameters, at the low-pressure phase \( a>c \) while at the high-pressure \( a<c \). The unit cell parameters ratio \( (c/a) \) in the P 6\( \text{3} \)/\( \text{m} \) m c symmetry is equal to \( (a/c) \) in the P 6/m m m symmetry.

Upon pressure reduced, a hysterisis is detected. The Ti-HP and Ti-CP samples stay in the high-pressure structure with a volume change of 1.8±0.1% and 1.9±0.1%, respectively. The Ti-CP at ambient pressure before and after introducing pressure, as an example, is depicted in figure 7.
The unit cell volume after compression is reduced by 1.9%.

In figure 8 the unit cell parameters $a$ and $c$ decrease monotonically with increasing pressure. There is no abrupt change or phase transformation up to the maximum measured pressure. The ratio $c/a$ in the two different hexagonal crystallographic structures is given in figure 9. The ratios $c/a$ and $a/c$ are reciprocal between the two structures. In the low pressure phase from the Rietveld analysis $c/a = 1.622$ comparable to the literature 1.607 [9]. In the high pressure phase from the Rietveld analysis $c/a = 0.632$ comparable to the literature 0.608 [10].
Figure 8. The unit a, c unit cell parameters of Ti-HP and Ti-CP as function of pressure in the high pressure phase (a) and low pressure phase (b).

Figure 9. The unit cell parameters ratio c/a of Ti-HP and Ti-CP as function of pressure.

From the Rietveld analysis we derived the volume of the unit cell at a given pressure. We calculated the ratio $V/V_0$, $V_0$ is the volume at ambient pressure and $V$ is the volume at a given pressure. From the volume versus pressure data we derived $B_0$ and $B_0'$ from the fit to the Vinet equation, (see figure 10). We obtained $B_0 = 141.53 \pm 3.88$ GPa from the fitting while $B_0'$ was held constant at 4.0.
4. Discussion

In the pressure range of our experiment we observe many differences between the Ti-HP, Ti-CP and Ti-6Al-4V. Crystallographically there is no difference between the Ti-HP and Ti-CP, both have the same unit cell parameters and unit cell parameters ratio $c/a$. The Ti (HP and CP) crystallize in the P 63/m m c (194) symmetry while the high-pressure phase is in the P 6/m m m (191) symmetry in agreement with the literature [11, 12].

Both Structures are in the hexagonal structure. The unit cell parameters $a$ and $c$ are changing places between themselves. In the P 63/m m c (194) symmetry, $a > c$, meaning that the hexagonal structure is wide and short. In the P 6/m m m (191) symmetry, $a < c$, that means that the hexagonal structure is narrow and high.

The unit cell parameters ratios $c/a$ of the two structures are inversed to each other. In the pressure range of the experiment 0-34.2 GPa there is a reduction of 18% in the unit cell volume. The change in the symmetry is not causing any rapid change in the unit cell volume.

The samples holds the P 6/m m m (191) symmetry from ~9 GPa to the maximum pressure introduced in this experiment, 34.2 GPa. There is a hysteresis when the pressure is release. The Ti-HP and Ti-CP samples stay in the high pressure phase with P 6/m m m (191) symmetry.

From the X-Ray diffraction spectra of Ti (HP and CP) at ambient pressure before and after compression we see a change in the unit cell volume of 1.8% and 1.9%, respectively. The Ti-6Al-4V acts differently then Ti-CP and Ti-HP, which do not show any crystallographic phase change up to 32.4 GPa.

The reduction of the $V/V_0$ ratio of Ti-6Al-4V, Ti-HP and Ti-CP as a function of pressure could reveal the $B_0$ and $B_0'$ by fitting the data with the Vinet [8] equation of state. There are two different equations before and after the phase transition observed at ~9 GPa for the Ti-HP and Ti-CP. $B_0$ is the isothermal bulk modulus at room temperature and ambient pressure, and $B_0'$ for the Ti-6Al-4V are where obtained as 154 ±11 GPa and $B_0'$ 5.4±1.4, respectively. $B_0$ and $B_0'$ for the Ti-CP and Ti-HP are, $B_0$= 141.53±3.88 GPa while $B_0'$ was kept at 4.0 with agreement with literature [9].
5. References

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