Phase transformations during high-pressure torsion (HPT) in titanium, cobalt and graphite

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Abstract. Several elements were processed by high-pressure torsion and phase transformations were investigated. Titanium exhibited a transition from hcp to an ω phase at pressures higher than 4 GPa, while the transition was facilitated with increasing the shear strain. The stability of ω phase appeared to decrease with decreasing the grain size to the nanometer level (e.g., by processing at cryogenic temperatures and/or by consolidation of powders). Cobalt exhibited a transition from metastable fcc to hcp until the grain size reached the submicrometer level, but the fcc phase appeared to be more stable with decreasing the grain size to the nanometer level. Graphite exhibited a transition to diamond-like carbon (DLC), while the formation of DLC was facilitated with increasing the pressure, temperature and strain.

1. Introduction

Phase transformation during high-pressure torsion (HPT), a severe plastic deformation method as schematically shown in Fig. 1 [1-11], has been of interest for many years since the earliest works by Bridgman [1], who introduced the principles of HPT in 1935, to numerous recent works [11-20]. Phase transformation during HPT is influenced by many parameters such as pressure, shear strain, lattice defects and grain size. In this paper, we review our recent results on phase transformations in pure titanium, pure cobalt and graphite. Detailed results were presented in Refs. [21-23].

Figure 1. High-pressure torsion (HPT): (a) as described by Bridgman [1] and (b) current form.
Titanium exhibits a phase transformation from $\alpha$ with the close-packed hexagonal (hcp) structure to $\beta$ with the body-centered cubic (bcc) structure at temperatures above 1155 K under ambient pressure [24]. It also exhibits a phase transformation from $\alpha$ to the hexagonal $\omega$ phase under pressures well above 2 GPa at ambient temperature [24]. There are also several reports that Ti with the face-centered cubic (fcc) structure is formed at ambient conditions when the grain size is well below 10 nm [25].

Cobalt exhibits a martensitic phase transformation from a $\gamma$ phase with the fcc structure to an $\varepsilon$ phase with the hcp structure at temperatures below ~673 K [26]. Whereas Co exists mainly in the form of hcp at room temperature, many papers reported the metastability of the fcc phase at room temperature [26]. Furthermore, the fcc phase becomes thermodynamically less stable in Co with increasing the pressure [27].

Graphite and diamond are two main allotropes of carbon with $sp^2$ and $sp^3$ bonds, respectively. The graphite-diamond transition pressure is theoretically estimated as $P\,(\text{GPa}) = 0.71 + 0.0027\,T\,(\text{K})$ [28], which indicates that graphite should transform to diamond at ambient temperature under pressures higher than 2 GPa. However, since the energy barrier of the transformation is quite high, the transition was not experimentally reported at 2 GPa and at the temperatures lower than 1200-1700 K [28]. Besides the crystalline diamond, pure carbon forms as thin films of diamond-like amorphous carbon (DLC) with high fractions (40-90%) of $sp^3$ bonds and high concentration of lattice defects using methods such as chemical vapour deposition (CVD) [29].

It is important to examine the possible effects of grain size on dynamical stability of different phases in Ti and Co under high pressures. High-pressure torsion (HPT), can be employed as an ideal process to control the grain size under high pressures [1-11]. Furthermore, although Bridgman could not detect any phase transformation in graphite during HPT [1], it is interesting to examine the possible phase transformations in HPT-processed graphite using new analytical techniques. In this study, pure Ti, pure Co and graphite are torsionally deformed by HPT and the effect of processing on phase transformations is investigated.

2. Experimental procedures

In order to control the grain size under high pressures, this study used discs of high purity Ti (99.9%) with 10mm diameter and 0.8mm thickness (annealed for 1 h at 1073 K), powders of Ti with particle sizes less than 45 μm, powders of Ti mixed with 20 wt.% Al$_2$O$_3$, discs of high purity Co (99.99%) with 10mm diameter and 0.8mm thickness (annealed for 1 h at 1073 K), Co powders with particle sizes less than 2 μm and powders of mixed with 89 wt.% tungsten carbide, WC. HPT was carried out on the bulk discs, powders and powder mixtures for 10 turns with a rotation speed of 1 rpm under a pressure of 6 GPa at room temperature (300 K) and at cryogenic temperatures (100 K) in liquid nitrogen.

In order to investigate the phase transformation during HPT, HPT was performed on chips of pure graphite (99.99% C) at 298 and 773 K for 0.25-50 turns and the discs with 0.8mm thickness and 5 and 10mm diameters were produced under the pressures of 20 and 6 GPa, respectively.

The HPT-processed Ti and Co samples were first examined with X-ray diffraction (XRD) analysis to detect any occurrence of the phase transformations. Second, for transmission electron microscopy (TEM), thin foils were prepared from the positions at 3-4 mm away from the disc center and examined for microstructure observation and for recording selected-area electron diffraction (SAED) patterns. Third, crystal orientation analysis and phase mapping were performed using a scanning transmission electron microscope (STEM) with an automated crystal orientation mapping system. Fourth, in order to examine the transition temperatures, electrical resistivity measurements were conducted during heating. Fifth, in order to examine dynamical stability of different phases, first-principles phonon calculations, were made under 0 and 6 GPa using VASP (Vienna Ab initio simulation package) [30] using phonopy code [31].
All graphite samples were examined by XRD analysis using the Cu Kα radiation, X-ray photoelectron spectroscopy (XPS) using the Mg Kα radiation, Raman spectroscopy using a 488nm argon ion laser, STEM observation, SAED analysis, and electron energy-loss spectroscopy (EELS).

3. Results and discussion

3.1. Titanium

STEM crystal orientation mappings and phase mappings are shown in Fig. 2 for the bulk Ti sample after HPT processing. Observation shows that the microstructure after HPT at room temperature consists of mainly submicrometer grains, but the grain size is reduced well to the nanometer level by HPT processing at cryogenic temperatures. The fraction of the ω phase also decreases with decreasing the processing temperature from room temperature to cryogenic temperature. This trend is not consistent with the phase diagram of Ti, which predicts a higher stability of the ω phase at cryogenic temperatures [24]. This contradiction may arise because of the effect of grain size on the phase transformation.

Figure 2. STEM automated crystal orientation maps (left) and phase maps (right) for bulk Ti samples processed by HPT at (a, b) room temperature and (c, d) cryogenic temperature in liquid nitrogen [21].

Figure 3(a) summarizes (a) the ω-phase fraction for the bulk Ti samples, Ti powders and Ti+Al2O3 powder mixtures after HPT processing at room and cryogenic temperatures. The ω-phase fraction was calculated from the XRD results. Figure 3(a) indicates that the ω-phase fraction decreases when HPT was operated at cryogenic temperatures, when HPT was applied to powders instead of bulk samples or when HPT was applied to powder mixtures with Al2O3 particles. We consider these trends are due to grain size effect. Electrical resistivity measurements also confirm that the temperature range
for the stability of \( \omega \) phases decreases with processing at cryogenic temperatures, i.e., with decreasing the grain size.

The \( \omega \)-phase fraction is plotted in Fig. 3(b) as a function of the grain size, showing that the \( \omega \)-phase fraction decreases monotonically with decreasing the average grain size and reaches zero when the average grain size is \( \sim \)20 nm. Therefore, the \( \alpha \) phase with the hcp structure, which is stable at high temperatures under 6 GPa, becomes stable at room and cryogenic temperatures by reducing the grain size to the nanometer level, but the \( \beta \) phase with the bcc structure, which is stable at temperatures higher than 1155 K [24], remains unstable.

In order to examine dynamical stability of the three crystal structures in Ti, first-principles phonon calculations, were made. The most striking feature in the first-principles phonon calculations was the presence of imaginary phonon modes only in the \( \beta \) phase, which implies that the \( \beta \) phase is neither stable nor metastable and should spontaneously transform to another structure. However, the other two structures (\( \omega \) and \( \alpha \)) did not show any imaginary modes.

It should be noted that the earlier works showed that the formation of \( \omega \) phase is accelerated with increasing the shear strain during HPT [13-18].

3.2. Cobalt

An optical micrograph of the bulk sample of Co after annealing but before HPT is shown in Fig. 4(a) and TEM results are shown in Figs. 4(b-d) for the same sample after HPT, where (b) is a bright-field image and (c) and (d) are corresponding dark-field image and SAED patterns, respectively. Observation shows that the microstructure after annealing consists of many twins within large grains with an average grain size of \( \sim \)2 mm. The microstructure after HPT processing is refined and consist of submicrometer grains with an average grain size of \( \sim \)120 nm. The grains after the HPT processing have only an hcp structure as evident from the SAED in (d). Close examination of Figs. 4(b,c) reveals that twins can rarely be seen.

![Figure 4. Optical micrograph for annealed bulk sample of Co with coarse grains and (b-d) TEM results in same sample after HPT, where (b) is bright-field image, (c) corresponds to dark-field image taken with diffracted beam indicated by arrow in (d) SAED pattern. Grains are refined to submicrometer level after HPT and hcp phase is only detected [22].](image)

![Figure 5. Microstructures of Co+WC powder mixtures after HPT: (a) bright-field image, (b) bright-field image with twins indicated by arrows, (c) lattice image of twins, and (d) SAED pattern of fcc phase. Grains are refined to nanometer level (~20 nm) after HPT and significant amount of fcc phase with nanotwins is formed [22].](image)

In order to reduce the grain size of Co to the nanometer level (<100 nm), Co+WC powder mixtures were processed by HPT. Microstructures are shown in Fig. 5 for the HPT-processed powder
mixtures, where (a) is a high-resolution image of Co grains surrounded by WC particles, (b) is a bright-field image of Co with twins indicated by arrows, (c) is a lattice image of the twins and (d) is an SAED pattern corresponding to (b). Examination of Fig. 5 indicates several important points. First, nanograins with an average grain size of ~20 nm with high angles of misorientation were formed after HPT. Second, the SEAD pattern indicates the presence of fcc. It is then concluded that the fcc phase in Co which is stable at high temperatures becomes stable at room temperature by nanograins formation during HPT. Third, {111} deformation twins were formed within the fcc nanograins.

In consistency with the current results on Co, molecular dynamic simulation suggested that the deformation of nanocrystalline Co with a grain size of 10 nm is mainly controlled by partial dislocation slips, leaving accumulation of stacking faults [32]. The continuous accumulation of stacking faults thus leads to the formation of fcc. Once the fcc nanograins are formed, deformation proceeds by dislocation slip and {111} deformation twinning [32].

3.3. Graphite

XPS profiles together with the peak positions for $sp^2$ and $sp^3$ bonds are shown in Fig. 6. Although all peak position matches the $sp^2$ binding energy, the peaks are broadened and extended to higher energies after HPT, indicating that appreciable amounts of $sp^3$ bonds are formed. This broadening becomes more prominent with increasing the processing temperature and with increasing the distance from disc center (i.e., with increasing the shear strain).

Raman spectra together with the peak positions for the G, D and G' peaks are shown in Figs. 7. A peak broadening occurs after HPT, indicating the lattice defects are formed. The broadening becomes more prominent with increasing the distance from the disc center (i.e., increasing shear strain). The G peak shifts to lower values with increasing the shear strain, but it shifts to high values again at very large shear strains (i.e., at $r = 4$ and 5 mm), indicating that an amorphization and formation of DLC phase should have occurred.

**Figure 6.** XPS results corresponding to 1s electron configuration in carbon atom ($C_{1s}$) for samples processed at 298 K and 773 K for 50 turns under 6 GPa including as-received sample. Positions of $sp^2$ and $sp^3$ bonds are included and $r$ indicates distance from disc center [23].

**Figure 7.** Raman spectra for as-received graphite sample and HPT-processed samples after processing at 773 K for 50 turns under 6 GPa at different distances from disc center. D, G and D' peaks are indicated in plots. $r$ indicates distance from disc center [23].

Inspection of Carbon K edge EELS spectra in Fig. 8(a) which were obtained by two repeated measurements for each HPT processing condition indicates three important points. First, the intensity of $\pi^*$ peak become weak after HPT, whereas the intensity of $\sigma^*$ peak becomes prominent after HPT,
indicating that the fraction of $sp^3$ bonds increases. Second, three representative spectra, A, B and C are detected corresponding to the crystalline graphite, amorphous carbon and DLC, respectively, but no spectrum for crystalline diamond could be detected. Third, Formation of DLC appears to be facilitated with increasing the temperature, pressure and shear strain.

![Figure 8](image)

**Figure 8.** Electron microscopy results. (a) Carbon K edge of EELS spectra for three HPT-processed samples including as-received graphite sample. A, B and C indicate spectra corresponding to graphite, amorphous carbon and DLC, respectively. TEM high-resolution image and corresponding SAED pattern for (b) as-received graphite sample and (c) sample processed under 6 GPa for 50 turns at 773 K. (d) STEM-HAADF image and corresponding EELS mapping for DLC for sample processed under 6 GPa for 50 turns at 773 K. Analyses were conducted at 4.5 mm and 2 mm from disc center for samples processed under 6 GPa and 20 GPa, respectively [23].

TEM results are shown in Fig. 8(b) for the as-received sample and in Figs. 8(c,d) for an HPT-processed sample. Observation shows that the HPT-processed sample consists of nanograins as marked D in (c) and onion-like carbon as marked E in (c) together with amorphous phase. The ring-shape halo pattern in the SAED analysis in (c) confirms the presence of amorphous phases. The EELS mapping together with the corresponding STEM-HAADF (High-Angle Annular Dark-Filed) image in (d) indicates that the microstructure consists of mainly graphite phase and partly DLC phase. The formation of DLC during HPT contrasts with conventional CVD method where DLC is produced in the form of thin films by rapid cooling of carbon atoms in vacuum [29].

### 4. Conclusions

1. Although transition from hcp to an $\omega$ phase at high pressures is accelerated with increasing the shear strain during HPT, the stability of $\omega$ phase appears to decrease with decreasing the grain size to the nanometer level during the HPT processing.
2. The fcc phase in Co, which is usually stable at high temperatures and low pressures, appears to be more stable with decreasing the grain size to the nanometer level during the HPT processing.
3. Graphite exhibited a transition to diamond-like carbon (DLC) during HPT processing, but no evidence for the formation of crystalline diamond during HPT could be found.
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References
[1] Bridgman P W 1935 Phys. Rev. 48 825
[2] Valiev R Z, Islamgaliev R K and Alexandrov I V 2000 Prog. Mater. Sci. 45 103
[3] Zhilyaev A P, Lee S, Nurislamova GV, Valiev R Z and Langdon TG 2001 Scripta Mater. 44 2753
[4] Zhilyaev A P, Nurislamova G V, Kim B K, Baro M D, Szpunar J A and Langdon T G 2003 Acta Mater. 51 753
[5] Valiev R Z, Estrin Y, Horita Z, Langdon T G, Zehetbauer M J and Zhu Y T 2006 JOM 58(4) 33
[6] Zhilyaev A P and Langdon T G 2008 Prog. Mater. Sci. 53 893
[7] Pippan R, Scheriau S, Taylor A, Hafok M, Hohenwarter A and Bachmaier A 2010 Annu. Rev. Mater. Res. 40 319
[8] Kawasaki M, Figueiredo R B and Langdon T G 2011 Acta Mater 59 308
[9] Valiev R Z, Sabirov I, Zhilyaev A P and Langdon TG 2012 JOM 64(10) 1134
[10] Zhang N X, Kawasaki M, Huang Y, Langdon T G 2013 J. Mater. Sci. 48 4582
[11] Estrin Y and Vinogradov A 2013 Acta Mater 61 782
[12] Ivanisenko Yu, MacLaren I, Sauvage X, Valiev R Z and Fecht H J 2006 Solid State Phenom. 114 133
[13] Kilmametov A R, Khristoforov A V, Wilde G and Valiev R Z 2007 J. Kristallogr. Suppl. 26 339
[14] Todaka Y, Sasaki J, Moto T and Umemoto M 2008 Scripta Mater 59 615
[15] Perez-Prado M T, Gimazov A A, Ruano O A, Kassner M E and Zhilyaev A P 2008 Scripta Mater. 58 219
[16] Edalati K, Matsubara E and Horita Z 2009 Metall. Mater. Trans. A. 40 2079
[17] Edalati K, Horita Z, Yagi S and Matsubara E 2009 Mater. Sci. Eng. A 523 277
[18] Zhilyaev A P, Sabirov I, Gonzales-Doncel G, Molina-Aldarequia J, Srinivasarao B and Perez-Prado M T 2011 Mater. Sci. Eng. A 528 3496
[19] Straumal B B, Gornakova A S, Mazilkin A A, Fabrichnaya O B, Kriegel M J, Baretzky B, Jiang J Z and Dobatkin S V 2012 Mater. Lett. 81 225
[20] Straumal B B, Gornakova A S, Fabrichnaya O B, Kriegel M J, Mazilkin A A, Baretzky B, Gusat A M and Dobatkin S V 2012 High Temp. Mater. Proc. 31 339
[21] Edalati K, Daio T, Arita M, Lee S, Horita Z, Togo A and Tanaka I 2014 Acta Mater. 68 207
[22] Edalati K, Toh S, Arita M, Watanabe M and Horita Z 2013 Appl. Phys. Lett. 102 181902
[23] Edalati K, Daio T, Ikoma Y, Arita M and Horita Z 2013 Appl. Phys. Lett. 103 034108
[24] Srik K, Vohra Y K and Chidambarram R 1982 Prog. Mater. Sci. 27 245
[25] Chatterjee P and Sen Gupta S P 2001 Philos. Mag. A 81 49
[26] Betteridge W 1979 Prog. Mater. Sci. 24 51
[27] Tonkov E Y and E. G. Ponsyatovsky 2005 Phase Transformation of Elements Under High Pressure (Boca Raton: CRC Press)
[28] Bundy F P, Bassett W A, Weathers M S, Hemley R J, Mao H K and Goncharov A F 1996 Carbon 34 141
[29] Robertson J 2002 Mater. Sci. Eng. R 37 129
[30] Kresse G 1995 J. Non-Cryst. Solids 193 222
[31] Togo A, Oba F and Tanaka I 2008 Phys. Rev. B 78 134106
[32] Zheng G P, Wang Y M and Li M 2005 Acta Mater. 53 3893