



Properties of Ti_3AlH_6 and Ti_3AlD_6 systems at high pressure studied by synchrotron X-ray diffraction analysis



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ABSTRACT

Compressibility of the Ti_3AlH_6 and Ti_3AlD_6 has been studied by X-ray diffraction method using advanced synchrotron technique up to 38 GPa. Significantly higher values of bulk modulus have been revealed for the hydride and deuteride compounds as compared to the initial pure intermetallic compound. The consequences of this observation have been discussed in terms of ductility and strength of obtained materials. Possible explanation of the peculiarity in the equation of states for both compounds is proposed on the base of the difference in repulsion interactions of hydrogen and deuterium species in the metallic lattice. All advantages of the hydrogenation of titanium aluminum compound have been summarized.

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1. Introduction

Titanium and its alloys are considered as the best choice for the designing and producing light and tough devices that can be used in aerospace industry [1]. Therefore, these materials are the objects of interest of numerous studies by the scientists and engineers. The strength and other mechanical properties of titanium can be significantly improved by alloying it with aluminum to form compounds like Ti_3Al or $TiAl$. However, a large loss in ductility is the price paid for such an improvement. Crystal structure is a very important factor for the ductility values as it is determined by number of possible slips in the given structure. In materials science, slip is the process by which a dislocation motion produces plastic deformation. An external force makes parts of the crystal lattice glide along each other, changing the material's shape. Depending on the type of lattice, different slip systems are present in the material. More specifically, slip occurs between planes containing the smallest Burgers vector. The slip planes and slip directions in a crystal have specific crystallographic forms. Slip is an important mode of deformation mechanism in crystals. Slip induces plasticity in most of the metals. Slip in hexagonal close packed (hcp) metals is much more limited than in bcc and fcc crystal structures. This is why the

metals possessing hexagonal structure are so brittle. In this respect it is very desirable to change original hexagonal structure of Ti_3Al to the cubic one that should have more slips and consequently higher ductility.

One of ways to change structure of materials is applying very high pressure. Sahu et al. have published paper on pressure induced phase transformation in Ti_3Al from original Ni_3Sn -type to Ni_3Ti -type structures in the pressure range about 15 GPa [2]. This result has been confirmed by theoretical study by Rajaopalan et al. [3]. However, the detailed studies of Dubrovinskaia et al. [4] conducted up to 25 GPa together with theoretical calculations have revealed no structural transformation in this pressure range.

Another means to change crystal structure of materials is hydrogenation. There are number of papers reporting both experimental and theoretical studies on hydrogen driven phase transitions in Ti_3Al [5–7]. Role of hydrogen in intermetallic systems has attracted a lot of attention due to possibility of using them as hydrogen storage material and because of variety of new hydrogen induced phase transitions. This paper focuses on compressibility of highly hydrogenated and deuterided Ti_3Al compound up to 40 GPa and a search for the pressure induced phase transitions. Comparison of the compressibility of pure Ti_3Al and its hydride and deuteride compounds was an additional stimulus of these investigations as the bulk modulus obtained from such measurements would put some new lights on the strength of material under consideration. The bulk modulus is related to the Young's modulus E via equation:

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$$E = 3K(1 - 2\nu)$$

where K is the bulk modulus and ν represents Poisson's ratio.

Therefore by determination of bulk modulus one can get new information about mechanical properties of material under investigation.

2. Materials and method

Original Ti_3Al compound has been obtained by arc melting of stoichiometric composition of high grade elements in argon atmosphere. Next alloy was annealed in vacuum at temperature of 900 °C. Both "as cast" and annealed samples gave almost the same diffraction patterns showing pure phase of Ti_3Al , space group #194 with $a = 0.57968(5)$ nm and $c = 0.46874(5)$ nm. The hydrogenated and deuterided samples were prepared by exposing thin plates of Ti_3Al to a H_2 or D_2 atmosphere at 7.5 GPa and 300 °C for 24 h followed by cooling under pressure to -150 °C. As a solid H_2/D_2 source, AlH_3 or AlD_3 were used. The method is described in [8]. The H/D content of the samples and the kinetics of the gas evolution were studied by hot extraction into a pre-evacuated volume in the course of heating at a rate of 20 °C/min. Hydrogen evolution from each sample became noticeable above 50 °C and terminated around 650 °C with the major amount of released gas at temperature of about 520 °C. These results are consistent with the preliminary DSC–TGA measurements conducted for Ti_3AlD_6 where the weight drop and the heat uptake occurred at the same temperature range as observed during the hot extraction. From the extraction measurements we obtained values of 5.95 and 6.05 composition for hydrogenated and deuterided samples respectively. Taking the relative accuracy of the measurements as 2% we can conclude that the both Ti_3AlH_x and Ti_3AlD_x samples had $x = 6.0 \pm 0.1$. The X-ray diffraction measurements have been done on powdered samples at room temperature 2 h and five days after retrieval them from liquid nitrogen using $\text{Cu K}\alpha$ radiation. X-ray diffraction analysis have shown pure fcc lattice structure of both hydride and deuteride samples. No additional reflections that can be attributed to the formation of superlattice have been noticed. Lattice parameters of $a = 0.444 \pm 0.0005$ nm and 0.441 ± 0.0005 nm have been determined for hydride and deuteride, respectively, using all reflections indicated in Fig. 2. These values are similar to those obtained by Maeland et al. [5] for both virgin and hydrogenated samples if the influence of additional phases revealed in their paper is taken into consideration.

As one can see the fcc structure presented in Fig. 1 offers eight tetrahedral sites for hydrogen or deuterium species. However even at such a severe conditions as applied here for the synthesis of hydride or deuteride only six of them can be filled, probably due to strong repulsion interactions between adjacent interstitial atoms.

Synchrotron radiation and diamond anvil cell have been used for the high pressure X-ray diffraction structural study. The high pressure X-ray diffraction studies were conducted at X17C beam line of National Synchrotron Light Source (NSLS, BNL) with the X-ray wavelength of 0.04066 nm. Mao-Bell type diamond anvil cell (DAC) [9] with diamond anvils of a culet size 400 μm were used for pressure generation. Samples were loaded into 150 μm hole in the stainless steel gasket (TS302) preindented to a thickness of ~50 μm , along with a small ruby chip at the center of the sample. The pressures were then calculated using the ruby (R_1) fluorescence method. The pressure transmitting medium used in the experiment was silicone oil (Sigma–Aldrich) of viscosity 1000 cP. The 2D diffraction patterns obtained were integrated using Fit2D software [10,11].

3. Results and discussion

The XRD patterns of hydride and deuteride samples were very similar to each other showing the face centered cubic (fcc)

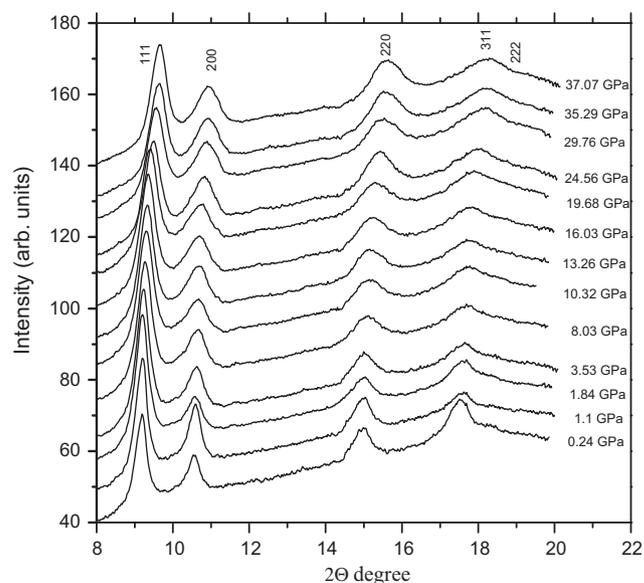


Fig. 2. Synchrotron XRD patterns of Ti_3AlD_6 at different pressures.

structure in the whole pressure range of investigation. Broadening of the diffraction peaks with increasing pressure have been notice probably due to pressure gradient resulting from the nonhydrostatic conditions. After releasing pressure the diffraction patterns have shown full reversibility.

Unit cell volumes as a function of pressure have been fitted to Birch–Murnaghan equation of state:

$$P(V) = \frac{3B_0}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} (B'_0 - 4) \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\}. \quad (1)$$

where B_0 denotes bulk modulus and B'_0 is its pressure derivative.

One set of XRD patterns for the deuteride phase is given below as an example of the measurements.

Unit cell volumes as function of pressure together with the fit to Birch–Murnaghan equation of state for both hydride and deuteride are shown in Fig. 3.

Unit cell volumes and Birch–Murnaghan equation of state parameters for the original compound and its hydride and deuteride phases are shown in Table 1.

From Table 1 one can estimate that the volume increase of the unit cell by uptake of 1 hydrogen atom on 1 metal atom is about 3.2 \AA^3 and density of initial Ti_3Al is decreased by about 30% that makes material substantially lighter.

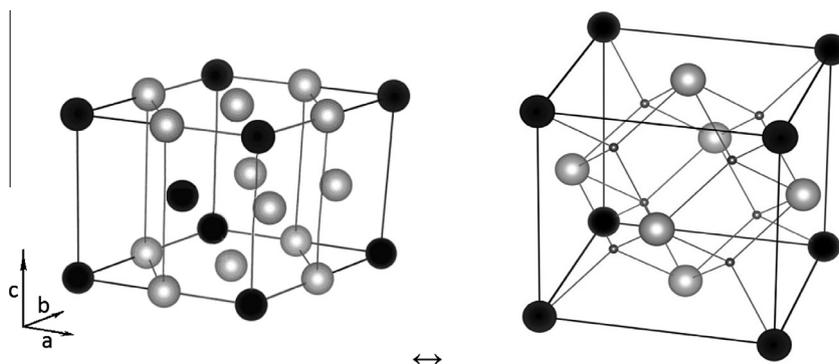


Fig. 1. Hydrogen induced structural transformation in Ti_3Al . Gray spheres represent titanium atoms while black spheres stand for aluminum atoms. Small spheres in cubic structure show tetrahedral position available for hydrogen absorption.

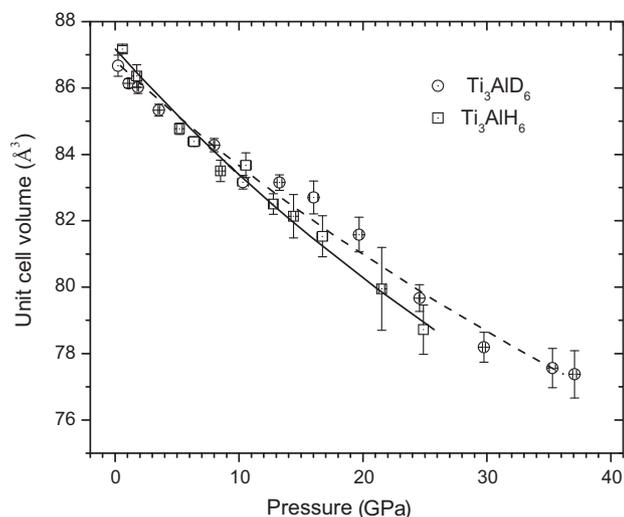


Fig. 3. P–V dependencies for Ti_3AlD_6 and Ti_3AlH_6 . Symbols represent experimental points and lines show fitting of experimental points with 3rd order Birch–Murnaghan EOS.

Table 1

Unit cell volumes and parameters of Birch–Murnaghan equation of state for the original compound and its hydride and deuteride.

Compound	V_0 (\AA^3) (per formula unit)	B_0 (GPa)	B'_0	Pressure range of fitting (GPa)
Ti_3Al [4]	68.2(5)	133(8)	2.6 (8)	0–25
Ti_3AlH_6	87.2(2)	205(9)	4 (fixed)	0–25
Ti_3AlD_6	86.8(2)	249(11)	4 (fixed)	0–38

Relatively high bulk moduli of hydride and deuteride as compared to pure compound have been noticed. This could be crucial factor regarding mechanical properties of the investigated compounds. The fact that the bulk modulus is almost twice as large as for hydrogen less compounds should have huge impact on Young modulus and strength of materials considering corresponding relationships given in the Introduction section. According to Shafrik [12] Young modulus of pure Ti_3Al compound at room temperature is equal about 170 GPa determined by conventional method while calculated from bulk modulus shown in this paper is equal about 160 using value of 0.3 for Poisson ratio, typical value for the most titanium and aluminum alloys. However for the hydrogenated compounds presented here Young modulus can roughly be estimated as about 250 and 300 GPa for the hydride and deuteride respectively. Such modification of mechanical properties of material due to the hydrogenation is another example of the importance of the studies of metal hydrogen systems that could provide us with interesting applications prospects. It should be also noticed that the deuteride and hydride have about 30% smaller density that could be very attractive feature if application in aerospace application would be considered. Another interesting result is the isotope effect in compressibility of both systems. Typically the unit volume of deuteride is smaller than that of hydride. This is due to different oscillation energies of the species in the metal lattice. Observed crossing of the compressibility lines may suggest that the contribution from the Coulomb repulsion interaction with pressure in case of deuteride is higher than that for the hydride resulting in smaller compressibility of the former. For the palladium–hydrogen/deuterium system under high pressure such effect is not observed [13] albeit the lattice parameters of hydride phases in $\text{Ti}_3\text{AlH}/\text{D}_6$ and $\text{Pd}/\text{H}/\text{D}$ are quite similar. However, in the palladium hydride/deuteride system hydrogen

occupies octahedral site while in titanium aluminum hydride/deuteride system there are six hydrogen species distributed randomly in the eight tetrahedral interstitials. This situation could create much bigger electronic interactions between adjacent hydrogen species which are much closely spaced to each other. Assuming ideal placement of hydrogen species in tetrahedral positions, one can calculate average distance between them at adjacent interstices. At normal pressure this distance is about 2.21 Å which satisfies Westlake–Switendick [14,15] criteria of minimal hydrogen–hydrogen distance of 2.1 Å. However at higher pressure this distance is significantly decreased reaching value of 2.14 Å at the limit of our pressure range of investigations. From the equations of state presented here one can estimate that the stability of compound determined by Westlake–Switendick rule will be in danger above the pressure of 50 and 60 GPa for the hydride and deuteride compounds, respectively. Exceeding these pressures would result in possible phase transformation to a structure that could assure proper geometry conditions for hydrogen in metal lattice. Similar situation we have faced while studying pressure induced phase transformations in the number of rare earth trihydrides [16] where hexagonal structure has been transformed to the fcc with much longer hydrogen–hydrogen distance.

At first sight a most probably the body centered cubic structure could be the pick, nevertheless the theoretical calculations on stability of such a phase and extending experimental pressure range would proved such speculations.

4. Conclusions

Compressibility of Ti_3AlH_6 and Ti_3AlD_6 has been determined within the similar pressure range. No phase transitions were observed up to 40 GPa pressure. However the number of interesting observations has been noticed. Rather unusual hardening of material as a result of introducing hydrogen into the metal lattice makes the material more tough and attractive for use in aerospace industry. Also, the substantial, about 30%, decrease of the weight of devices made of Ti_3Al seems to be very attractive property from applications point of view. Another unexpected result is isotope effect in compressibility of hydride and deuteride phases where crossing line of equation of state is observed not present in known metal–hydrogen systems so far.

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