Hydrostatic Compression Behavior and High-Pressure Stabilized $\beta$-Phase in $\gamma$-Based Titanium Aluminide Intermetallics

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Abstract: Titanium aluminides find application in modern light-weight, high-temperature turbines, such as aircraft engines, but suffer from poor plasticity during manufacturing and processing. Huge forging presses enable materials processing in the 10-GPa range, and hence, it is necessary to investigate the phase diagrams of candidate materials under these extreme conditions. Here, we report on an in situ synchrotron X-ray diffraction study in a large-volume press of a modern ($\alpha_2 + \gamma$) two-phase material, Ti-45Al-7.5Nb-0.25C, under pressures up to 9.6 GPa and temperatures up to 1686 K. At room temperature, the volume response to pressure is accommodated by the transformation $\gamma \rightarrow \alpha_2$, rather than volumetric strain, expressed by the apparently high bulk moduli of both constituent phases. Crystallographic aspects, specifically lattice strain and atomic order, are discussed in detail. It is interesting to note that this transformation takes place despite an increase in atomic volume, which is due to the high ordering energy of $\gamma$. Upon heating under high pressure, both the eutectoid and $\gamma$-solvus transition temperatures are elevated, and a third, cubic $\beta$-phase is stabilized above 1350 K. Earlier research has shown that this $\beta$-phase is very ductile during plastic deformation, essential in near-conventional forging processes. Here, we were able to identify an ideal processing window for near-conventional forging, while the presence of the detrimental $\beta$-phase is not present under operating conditions. Novel processing routes can be defined from these findings.

Keywords: high pressure; high temperature; phase transformation; equation of states; plasticity; TiAl; intermetallics; synchrotron radiation; multi-anvil press; in situ diffraction
1. Introduction

Titanium aluminides exhibit significant potential as a low specific weight structural material for high-temperature automotive and aerospace propulsion applications [1-4]. Gamma-based TiAl intermetallics possess high strength and excellent oxidation resistance at half the specific weight of conventionally-employed nickel-based superalloys, up to a temperature range of 1000–1100 K [5]. The drawback, however, of the two-phase (γ + α)/α2 material is the poor ductility, reduced forgeability and a small deformation window for thermo-mechanical processing [3]. To overcome these limitations, material-design focuses on β-solidifying alloys, which are characterized by the presence of a ductile β/β0-phase at the processing temperature. However, through appropriate heat treatments, this ductile phase can be transformed to mechanically-stronger structures at the expected operating temperatures [6]. In addition, heating into a multi-phase field results in sluggish grain growth, while the augmented fraction of β-phase allows for near-conventional forging [7]. This has been partly achieved by alloying γ-based TiAl alloys with β-stabilizing elements, such as Nb and Mo; however, some residual β/β0-phase is still present at the operating temperature [4,8-10].

In the present study, we investigate the influence of pressure on the formation of the ductile β-phase in γ-based TiAl alloys, which is not only of fundamental interest, but is also most relevant to modeling high-pressure deformation techniques, such as high-pressure torsion, in order to achieve severe plastic deformation [11-15] and high-pressure near-net-shape forging [16-19]. These deformation processes operate at pressures up to 7 GPa and forces exceeding 1 GN, respectively. However, to date, no experimental studies have been reported of the attempts to assess the high-pressure performance of this two-phase (γ + α2) TiAl intermetallic, and very little has been done from a theoretical point of view [20]. Examinations of the pure-titanium temperature-pressure phase diagram [21,22] reveal that pressure-dependent phase transformations can be expected to occur, but the exact intermetallic chemistry and the multi-phase fields in the TiAl alloy system can significantly modify these trends.

In the binary, γ-based titanium aluminide alloy system, an ordered, close-packed and not necessarily stoichiometric hcp-based α2 Ti3Al co-exists with the tetragonal γ-TiAl-phase, which is an ordered, close-packed structure, derived from the fcc lattice. The α2-phase disorders to hcp α at the eutectoid temperature Teu and γ fully transforms into α at the γ-solvus temperature Tγ,solv, also referred to as α-transus temperature Tar. This high-temperature single-phase field is prone to excessive grain growth and, on deformation, inherits the anisotropic plastic behavior from the hexagonal lattice [8,23,24]. A variety of alloys based on TiAl with additions of niobium has been developed in the so-called TNB alloy series [5,25-27], where Nb substitutes Ti sites and eventually stabilizes the bcc-based β-phases. In the present study, we have investigated the TNB composition Ti-45Al-7.5Nb-0.25C, which has been produced through a powder-metallurgical route by Gerling et al. [28] using gas-atomization and subsequent hot-isostatic pressing for 2 h at 200 MPa and 1553 K. It is obtained from the same series as extensively characterized by Chladil et al. [29,30] and Yeoh et al. [31], showing globular γ-TiAl/α2-Ti3Al grains with an average size of about 15 µm (see Figure 1b in [29]). In situ investigations revealed conventional transformation behavior for this Ti-45Al-7.5Nb-0.25C alloy, with Teu = 1453 K and Tar = 1565 K, with an additional peritectic (α + β)-phase field at Tper ~1500 K, but no (α + β + γ)-phase field has been observed.

The pure-titanium temperature-pressure phase diagram has been well investigated [21,32]. At atmospheric pressure and Tβ(0) = 1155 K, hcp α-Ti transforms into bcc β-Ti. Under hydrostatic pressure, the β-transus temperature Tβ decreases linearly to meet the triple-point with the hexagonal ω-phase, at about 940 K and 9.0 GPa. Above this pressure, Tβ increases again. The authors also reported that at and above room temperature, the ω-phase occurs only at higher pressure, appearing above 2 GPa. Aluminium, on the other hand, behaves as a simple solid, not transforming from its fcc structure under high pressure [33].

It is not possible to predict the behavior of intermetallic titanium aluminide alloys by using the pure-titanium temperature-pressure phase diagram. However, indications are that phase boundaries
can shift with applied pressure and that the $\beta$-phase can be stabilized because the $\beta$-transus line has a negative slope. Moreover, there is a distinct likelihood that changes in lattice parameters and modified atomic packings, including atomic order and disorder, might influence the phase relationships.

In order to study the phase changes in TiAl intermetallic systems, in situ quantum beam diffraction [34], such as X-rays and neutrons, has been employed. The first in situ X-ray diffraction studies on these intermetallics have been undertaken by Shull and Cline [35], but the real breakthrough came when Liss et al. [36] used high-energy synchrotron radiation [37], to study these alloys. Combined time-resolved and multi-dimensional diffraction in a so-called materials oscilloscope [38] allows determination of the microstructural evolution of multi-phase titanium aluminides during thermo-mechanical processing [7,39]. In situ neutron diffraction is complementary to X-ray studies, due to the negative and positive scattering lengths of Ti and Al, respectively, and is therefore ultimately sensitive to the atomic order in a crystal structure [40,41].

High-pressure diffraction equipment has been well established for a number of decades at synchrotron radiation facilities, mainly driven by the geoscience community, but its application to structural materials science is still in its infancy [42,43]. The most common pressure device is a diamond-anvil cell, capable of reaching pressures up to 200 GPa and temperatures up to 5000 K [44]; however, with a maximum diameter of $\sim$0.2 mm, the total volume of samples is limited. On the other hand, large-volume multi-anvil cells can be used for samples up to an 8-mm side length, with compromises on the maximum achievable pressure of up to approximately 30–50 GPa [45,46], but more typically in the 10-GPa range. Heating can be achieved by building furnaces into the hydrostatic volume, resulting in available sample volumes of $1–2$ mm$^3$.

Because excessive grain growth in titanium alloys becomes a serious problem at very high temperature, a powder diffraction experiment might degenerate into a study of single crystals if the experimentally-accessible reciprocal space volume is collimated [47]. Moreover, studies of microstructural evolution, allowing for the segregation of the elements in a multi-phase field, such as the co-existing $\gamma$- and $\alpha_2$-phases in titanium aluminides, require larger sample volumes. Furthermore, the chemistry of titanium alloys may change at the surface layer, such as the depletion of aluminium, as observed in a vacuum [40] or influenced by the pressure medium, as well as uni-axial stress components [48].

2. Experimental Section

In the current study, diamond anvil cells were deemed unsuitable, and large-volume multi-anvil cells have been utilized in order to ensure that a sufficiently large volume is available to allow for microstructural evolution and segregation. More specifically, the 15-MN force, Kawai-type multi-anvil machine, SPEED-Mk. II, at the SPring-8 bending magnet beamline BL04B1 was utilized. The beamline setup is depicted in Figure 1 [49], and a detailed description of the pressure apparatus was given by Katsura et al. [50]. A 10 mm-thick germanium solid-state detector of CANBERRA industries has been employed for energy-dispersive diffraction at a horizontal take-off angle of $\theta = 5.9827^\circ$. While the detector records energies from 3 keV onwards, the spectrum transmitted through the pressure cell ranges from $\sim$34–140 keV, thereby covering a diffractogram from $\sim$1.8–7.5 $\AA^{-1}$, as shown in Figure 2. Energy calibration of the detector was done by recording the fluorescence lines of Mo, Pb, Au, Ag, Pt, Ta and Cu, before the cell was put into position. In addition to the main detector, a radiography setup was used, implemented by a YAG scintillator (Hamamatsu Photonics K.K., Hamamatsu, Japan), projected to a CCD camera. It images the transmitted beam through the pressure cell and allows for the control of the beam size via a slit system to focus on the sample or the pressure marker. Typical radiographs are shown in Figure 3. In order to reduce the effect of grain size on intensity readings, the whole SPEED-Mk.II apparatus (Sumitomo Heavy Industries, Ltd., Tokyo, Japan), containing the load frame and the pressure cell with the sample, has been oscillated during data acquisition by $8^\circ$, which is an important feature of the instrument used [50].

The heating pressure cell was designed and fabricated by the experimental team, and the details of the design are shown in Figure 4. It consists essentially of a sample space and a pressure marker of a 60MgO-40Au (mass %) mixture, located in a LaCrO$_3$ resistive furnace, contacted by platinum leads
and controlled by an alternate-current power supply. A W-type thermo-couple of W-3Re and W-25Re (mass %) was used for temperature measurements. The remaining space is filled with insulating and pressure propagating ceramics, such as ZrO$_2$, BN and MgO. The furnace assembly sits in a 4.5-mm bore of the pressure octahedron, made of semi-sintered MgO-5Cr$_2$O$_3$ (mass %), which is then installed into the two-stage multi-anvil press (Figure 5). The gasket material is pyrophyllite.

![Figure 1](image1.png)

**Figure 1.** Schematic layout of the beamline. White X-rays emit from the bending magnet (B.M.), which are conditioned by incident slits to enter the high-pressure cell. Transmitted X-rays are used to image the sample cell, converted by a scintillator, YAG, and recorded by a camera, CCD. A fixed diffraction angle, 20, is selected by a collimator and receiving slits in front of the solid state X-ray detector, SSD. After [49].

![Figure 2](image2.png)

**Figure 2.** Full recorded detector spectrum (top axis), translating into a calibrated diffractogram (bottom axis). The bump in the background denotes the useful, transmitted energy spectrum between ~34 and 140 keV, i.e., ~1.8–7.5 Å$^{-1}$. The data shown are the signals off the specimen at 310 K and 0 GPa.

![Figure 3](image3.png)

**Figure 3.** Typical radiographies of the pressure cell for sample alignment. The horizontal and vertical instrument axes show up and right in the figure. Translation of the entire apparatus with respect to the beam allows for different fields of view. The looped thermo-couple is a feature that can be well recognized in the left and central picture. To the right, beam size has been reduced to focus on a particular volume only, here the pressure marker.
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Figure 4. Design of pressure cell 14 M TEL5 (b) and photograph of the individual parts (a, left dish) and specimens (a, right dish).

Figure 5. Ken-ichi Funakoshi and Mark Reid loading the pressure cell and sample into the 15-MN press SPEED-Mk.II at SPring-8 beamline BL04B1.
The serial number of the experimental dataset is M1472. Radiographs were taken to locate the sample and the pressure marker positions and to achieve an optimal beam size of 0.5 × 0.7 mm² (h × v); see Figure 3. Initially, the pressure was ramped stepwise to a target of 10 GPa, while the pressure was accurately determined by the use of the equation of state of the pressure markers [51,52], using the PDIndexer software (V4.32, Yusuke Seto, Kobe University, Kobe, Japan, 2016) [53]. Diffraction patterns were taken while holding at 0, 3.2 and 9.6 GPa, respectively, before the system was heated under maximum pressure.

The measured photon energy E is correlated with the wave number \( k = 2\pi E/h\); \( k(\text{Å}^{-1}) = 0.506768 E \text{(keV)}, \) where \( h \) denotes the Planck constant and \( c \) the speed of light. With Bragg’s relation \( q = 2k\sin(\theta), \) this translates to the scale of momentum transfer or scattering vector in reciprocal space \( q. \) In the present case, the calibration is \( q(\text{Å}^{-1}) = 5.2892 \times 10^{-2} E \text{(keV)}. \)

Figure 6 displays the expanded diffractograms, taken at room temperature during pressurizing pressure steps, while Figure 7 shows all of the data in a zoomed range, both at room temperature and upon heating. A Rietveld refinement, using the MAUD program [54], was utilized for the analysis, allowing for the extraction of lattice parameters and phase fractions.

![Figure 6. Diffraction patterns upon pressurizing. Line shifts to larger scattering vectors can be seen as the unit cell shrinks, accompanied by changes of peak intensity due to phase transformation.](image)

Unless otherwise stated, we used the following choice of unit cell throughout the paper: both \( \alpha \) and \( \alpha_2 \)-phases (\( \alpha/\alpha_2 \)) span a hexagonal lattice with the \( a \)-axis being twice and \( c \) equal to those of conventional \( hcp \). \( \alpha_2 \) and \( \alpha \) differ by an ordered and disordered motif, respectively, the former making up the stoichiometry Ti₃Al. In order to compare the axis ratios, \( 2c/a \) is listed for the \( \alpha/\alpha_2 \)-phases, which directly compares to \( c/a \) of a simple \( hcp \) structure, in its ideal, close-packed case where \( c/a_{hcp} = \sqrt{8/3} = 1.6329932. \) The \( \gamma \)-lattice is constructed from the \( fcc \) structure by altering the Ti and Al...
layers along the $c$-direction. The unit cell is therefore tetragonal and slightly distorted, with a $c/a$ ratio slightly larger than 1. The cubic $\beta$-phase is either disordered and bcc or ordered $\beta_o$ of Strukturbericht designation B2, where the two different kinds of atom sit on the corner and the body center of the cube. Accordingly, the unit cell volumes are $V_{Z,\alpha} = \sqrt{3}/2 \cdot a^2 c$, $V_{Z,\beta} = a^3$ and $V_{Z,\gamma} = a^2 c$. It is of interest to calculate the volume per atom $V_A$ by dividing these volumes by the number of atoms in the unit cell, i.e., 8, 2 and 4, respectively, leading to $V_{A,\alpha} = \sqrt{3}/16 \cdot a^2 c$, $V_{A,\beta} = 1/2 \cdot a^3$ and $V_{A,\gamma} = 1/4 \cdot a^2 c$.

![Figure 7. Zoomed compilation of all diffraction patterns upon pressurizing at room temperature (first 3) and on stepwise temperature ramping at the maximal achieved pressure. Temperature tags are given to the left, serial numbers to the right.](image-url)
3. Results and Discussion

The large diffraction peak around 2.7 Å⁻¹ in Figure 6 corresponds to the close-packed plane-stacking distance and is therefore common to both the fcc-based γ- and hcp-based α-/α₂-phases, indexing 111 and 002, respectively (there is a small irresolvable shift between the two, due to slight deviation from close-packing in each phase). Only α₂ and γ peaks can be identified at room temperature, while β peaks appear at 1381 K and increase in intensity above that temperature. The β-110 peak lies around 2.75 Å⁻¹, representing a near close-packed lattice spacing. The typical fcc peak positions of the γ-phase are split, due to the tetragonal deformation with an axes ratio c/a > 1, by only a few percent. Both the γ- and α₂-phases show superstructure reflections due to atomic order at room temperature, i.e., reflections, which would have vanishing structure factors in fully-disordered lattices, fcc and hcp in the present case.

3.1. Pressure Loading at Room Temperature

Pressure loading at room temperature has been evaluated at {0, 3.2, 9.6} GPa and leads to continuous peak shifts to larger scattering vectors due to the compressive strain on the unit cell. Furthermore, the splitting of the γ-002/200 and γ-112/211 peaks around ~3.1 Å⁻¹ and ~5.2 Å⁻¹, respectively, diminishes slightly, resulting in a decreasing c/a ratio. Furthermore, relative changes in peak intensity are observed throughout the pressurization process. The volumetric strain allows the evaluation of the equation of state in this two-phase system.

3.1.1. Crystallographic Anisotropy, Disorder and Transformation Behavior

Linear lattice strain ε, for a given reflection at position G = G_{hkl} and Miller indices h, k, l, is evaluated in reciprocal space by:

\[ \varepsilon = \varepsilon_{hkl} = \frac{\Delta G}{G_0} = \frac{G - G_0}{G_0} \]  

(1)

where G and G₀ are the strained and unstrained reciprocal lattice vectors, respectively. Here, we select the values of G₀ at ambient conditions (310 K, 0 GPa), the first pattern in Figures 6 and 7. The experimental results for lattice parameters and lattice strains along the crystal axes a and c are shown in Figure 8a–d, for both phases. Linear fittings to the function y = a + bρ with fit parameters a, b and pressure ρ are represented by the continuous lines and numerical results inserted into the figures. To a first approximation, the overall strain response to pressure is \( \varepsilon = \varepsilon (\rho) \) which are presented with fit parameters a, b and c

\( K_{lin} = -V \frac{\partial \rho}{\partial V} \approx -(3\varepsilon (\rho))^{-1} \approx 152 \text{ GPa} \)  

(2)

The crystallographic strain anisotropy is demonstrated by varying c/a ratios, which are presented in Figure 8c,f for both the γ- and α₂-phases. For pure α-titanium, Zhang et al. [55] reported a constant, pressure-independent 2c/a ratio of 1.5868, which agrees well with the generally-accepted value of 1.5871 (from JCPDS Card 44-1294) [56]. Controversially, a large pressure dependence has been reported by Errandonea et al. [48], which Zhang et al. refute and interpret as a response to deviatoric stresses, occurring in their diamond-anvil cell. In alloys, especially titanium aluminides, lattice parameters and c/a ratios of both γ- and α₂-phases depend strongly on the composition of each phase, which varies as a function of temperature and segregation in multi-phase systems [31,57,58]. Increasing 2c/a ratios of [1.60333, 1.60432, 1.60476] with increasing Al content in single-phase α₂-Ti-[24, 28.4, 33.3]Al have been measured by Dubrovinskaia et al. [59]. In the present study, we observed a slight variation of the c/a ratios with increasing pressure, in both phases, as shown in Figure 8e,f. The c/a ratio in the γ-TiAl-phase decreases monotonically at an increasing rate with increasing pressure, towards a c/a ratio approaching unity, the value for a cubic fcc lattice. Such an fcc-Ti structure has been predicted by
ab initio simulations [60,61], but it is energetically unstable and has not been experimentally observed. As a theoretically-postulated phase, it can be asymptotically used to interpret experimental data, such as for interpolating lattice parameters by Vegard’s law [57].

In the case of γ-TiAl with a L10 structure, fully-disordered γ4-TiAl would be fcc, as the break of symmetry is expressed by the order. However, it is lacking even in a massively-transformed γ-phase [36]. It has been reported that γ always tends to order, and when disordered, it transforms to the α-/α2-phase [31]. Moreover, for alloys with no added nucleants, in situ temperature studies on cooling from the disordered α-phase consistently revealed significant undercooling below the α-transus, where the γ-phase should re-appear. Watson et al. [40] correlated the delayed re-appearance
of the latter with the ordering of $\alpha \rightarrow \alpha_2$, where lattice planes first partially order before the stacking sequence changes. Asta et al. [60] argue that for equi-atomic compositions, the hcp-based random alloy is slightly more stable than the fcc-based random alloy, and therefore, the stability of the $\gamma$-phase can be attributed to a stronger tendency to ordering of the fcc lattice. In particular, the ordering energy is larger for the $\gamma$ structure than it is for the $\alpha_2$ structure.

In the present case, a continuous transformation from $\gamma$ to $\alpha/\alpha_2$ takes place with pressure, as presented in Figure 8h, which interestingly scales directly with the $c/a$ ratio of $\gamma$-TiAl, leading to the following scenario: with increasing pressure, atoms in the $\gamma$-phase are pressed towards the optimal close-packed fcc structure, reducing its $c/a$ ratio. Inherent in this behavior is the introduction of disorder between the Ti and Al layers, facilitated by short range diffusion within the size of a unit cell. As disorder increases, the displacive character of the phase transformation $\gamma \rightarrow \alpha/\alpha_2$ becomes viable, in agreement with the arguments above and those advanced in the literature. Long-range diffusion and segregation do not occur at room temperature, while the pressure-driven disorder occurs throughout the bulk of the $\gamma$ grains, leading to the conclusion that ultrafine lamellae form, with thicknesses at the nanometer scale, in a manner very similar to low-temperature annealing of $\alpha$-quenched material [62–64]. The difference is that they may form on all four $\gamma$ [111] habit planes and lead to a Widmanstätten-like or basket-weave arrangement, rather than a lamellar microstructure. Such formation and disorder on a nanometer scale is supported by the micrographs of pressure loaded and unloaded $\gamma$-TiAl-based material published by Srinivasarao et al. [65]. Phase stresses in these ultrafine structured grains build up a large amount of potential energy, preventing further transformation at a given pressure and retaining the given $c/a$ ratio. The remaining disorder at the large density of interfaces leads to the observed decrease of superstructure reflections.

The anisotropic response of the $\alpha-/\alpha_2$-phase is qualitatively different. Its $2c/a$ ratio first increases when atoms are driven to a more ideally close-packed structure similar to the $\gamma$-phase, but then decreases slightly at higher pressure. In contrast to the $\gamma$-phase, the $\alpha-/\alpha_2$-phases are a sink for disorder, both stoichiometrically and crystallographically. According to the phase diagram [66], the $\alpha_2$-Ti$_3$Al-phase is stable over a wide range of concentrations, between roughly Ti-20Al and Ti-35Al, even at room temperature. This indicates that up to 33% of either site can be accommodated by the wrong kind of atom, while the $\gamma$-TiAl formation begins at Ti-47.5Al on the Ti-rich side, allowing only 5% of Ti on Al sites. In the present two-phase system, the compositions of the $\alpha_2$- and $\gamma$-phases are expected to be sitting on the phase boundary lines, i.e., Ti-35Al and Ti-47.5Al, respectively. Furthermore, $\alpha_2$ fully disorders at high temperature (by a eutectoid reaction at $T_{eu}(0) = 1453$ K for our alloy), while $\gamma$ never does.

By considering the experimentally-derived data, the events occurring during pressurization can be clarified: In the first step, while no or little $\gamma$-phase transforms into $\alpha/\alpha_2$, atoms of $\alpha_2$ are pressed into their isotropic positions, i.e., towards ideally close-packed $2c/a$. A high density of the nano-Widmanstätten or basket-weave structure propagates upon further pressure loading throughout the bulk of the grains, to create a relatively isotropic stress state in each volume (as compared to a lamellar microstructure) and introduces disorder, as evidenced by the decrease of the superstructure reflections shown in Figure 8g. Concurrent with a smaller $2c/a$ in $\alpha$-Ti and thermal disorder in $\alpha$-TiAl [31], the $2c/a$ ratio tends to decrease again, an argument that is well supported by the experimental data.

In summary, crystallographic disorder is being introduced into the phases upon loading at room temperature, where no long-range diffusion and annealing can occur. As the $\gamma$-phase disorders, it transforms into the $\alpha-/\alpha_2$-phase, until transformation stresses built up to the extent that further transformation is impeded.

3.1.2. Volumetric Response and Equation of State

From a thermodynamic point of view, response to high pressure is given by the equation of state, relating the volume or density of the matter to pressure $p$, temperature $T$ and potentially other
variables. A well-known equation of state is the ideal gas law. In the case of solids, the interaction potentials of atoms have to be taken into account [67]. Put simply, at constant temperature, atoms sit in the equilibrium position of superimposed attractive and repulsive parts of the potential, defining the bond distance. As hydrostatic pressure is increased, the applied load acts against the repulsive potential, shortening the bond distances and decreasing the volume occupied per atom. An important parameter related to the equation of state is the bulk modulus:

$$K = -V \frac{\partial p}{\partial V}$$

which is evaluated at a given temperature. It relates to the compressibility, mechanical properties, sound velocity, etc. For isotropic, linear strain, this corresponds to Equation (2) and for orthorhombic systems:

$$\frac{\partial V}{\partial V} = \sum_{i=a,b,c} \epsilon_i$$

For solids, there exist a multitude of atomic potential models, corresponding to a multitude of equations of state [68], but all of them should lead to the same bulk modulus $$K_0 = K(p = 0)$$, when properly evaluated at $$p \to 0$$. Physically, $$K(p)$$ is not constant, as a solid is more difficult to compress the further it is compressed. The detail of the potential reflects in the shape of the compression curve $$V(p)$$ as it deviates from linearity. As the non-linearity is small, it suffices to consider:

$$K' = \frac{\partial K}{\partial p}$$

Sometimes, the details lie in the second derivative $$K''$$, for a second and third order fit, respectively.

The current case, with only three measured data points, allows the description of any second order curve in order of $$K'$$, while fitting $$K''$$ would be an under-determined set of equations. Note, however, the change of derivative variable between Equations (3) and (5) and the functional behavior of a given equation of state, so that $$K''$$ may be implicitly determined in that equation. Therefore, the shape of the $$V(p)$$ curve depends on the equation used.

The most commonly-used equation is the Birch-Murnaghan equation of state [69,70], up to 200 MPa [71], although at ultra-high pressure [61], the Vinet equation [72] is probably more accurate. In the present instance, we have fitted both equations and found that there is no significant difference; hence, our subsequent interpretation is not affected, and we present the Birch-Murnaghan approach.

The Birch-Murnaghan equation of state derives from the Helmholtz free energy and is typically Taylor expanded to the $$n$$-th order. The third order expansion is widely employed for the current type of high-pressure studies [48,73,74] and provides three fitting parameters, $$V$$, $$K_0$$, $$K_0'$$:

$$p = \frac{3}{2} K_0 \left\{ \left( \frac{V}{V_0} \right)^{-\frac{7}{3}} - \left( \frac{V}{V_0} \right)^{-\frac{5}{3}} \right\} \left\{ 1 + \frac{3}{4} \left( K_0' - 4 \right) \left( \left( \frac{V}{V_0} \right)^{-\frac{5}{3}} - 1 \right) \right\}$$

Volume occupations per atom have been calculated from the experimental unit cell and are displayed in Figure 9 and listed in Table 1, together with comparable results from the literature. The markers represent the experimental data points for the two phases, as well as for the total volume weighted by the phase fraction, while the continuous lines are fits to Equation (6). For comparison, the $$V(p)$$ behaviors of pure $$\alpha$$-Ti and $$\omega$$-Ti are shown, as taken from Errandonea et al. [48], as well as for $$\alpha_2$$ Ti-33.3Al from the study of Dubrovinskaia et al. [59]. The authors of the cited data also employed the Birch-Murnaghan equation, so that Equation (6) has been applied to the published parameters to compute the literature traces, transferred to volume per atom units.

Phases with a higher Al concentration consistently display a smaller volume per atom, due to the different atomic radii. To a first-order approximation, the compression curve of our $$\alpha/\alpha_2$$ data
coincides very well with Dubrovinskaia’s, which demonstrates that the measurements are accurate. In contrast to all of the examples given in the literature, i.e., α-Ti, ω-Ti and α2-Ti-33.3Al, our curves start with a gentler slope of $V(p)$ and evolve more linearly, expressed by large $K_0$ and small $K'_0$ values. The observed bulk moduli, lying around 146 MPa, are significantly larger than reported elsewhere for related systems. Pure metals have smaller bulk moduli than intermetallic compounds, which have stronger bonds. This is underlined by Asta’s first-principles computation on fcc- and hcp-based Ti-Al compounds, showing that theoretically, γ-TiAl has one of the highest bulk moduli [60] (see Table 1), which still do not reach our experimental values. On the other hand, the presently-observed change of modulus $K'_0$ with pressure is an order of magnitude smaller than otherwise earlier reported values.

**Figure 9.** Atomic volumetric compression behavior of the investigated composition Ti-45Al-7.5Nb-0.25C with Birch–Murnaghan fits (experimental dots with continuous lines), as compared to α2-single-phase compression, and α- and ω-titanium, reported by Dubrovinskaia [59] and Errandonea [48], respectively.

The salient difference between ours and earlier studies is that we are working in the $(\gamma + \alpha_2)$ two-phase field, where phases can transform continuously as a function of composition, temperature [66], disorder (see the discussion above) and pressure (see Figure 8h). A small change of these parameters will affect the relative phase fractions of $\gamma$ and $\alpha / \alpha_2$. All of the other cited pressure studies have been conducted in compositional single-phase fields. Dubrovinskaia et al. reported the absence of any pressure-induced phase transformation in $\alpha_2$ Ti-33.3Al, close to the border line with the $(\gamma + \alpha_2)$ two-phase-field. Therefore, we propose the following:

Upon loading, the atomic volume is reduced in each phase, and the phase transformation occurs, as discussed in Section 3.1.1, building up a nano-Widmanstätten (basket-weave) microstructure. The accumulating inter-phase stresses, highly interwoven and homogeneously distributed over the volumes of the initial grains, build up an additional potential acting against the applied pressure. As a consequence, the volume per atom, in each phase, is less compressed at any given pressure than it would be in its single-phase counterpart. As compression progresses, more and more material transforms, rather than pushing atoms against the repulsive potential, resulting in a seemingly increased bulk modulus. As such, a gradual phase transformation accommodates the response to hydrostatic pressure, rather than an increase of $K$, keeping $K'$ small. It is interesting to note that the
\[ V_{A}^{\text{avg}} = C_{\gamma} V_{A}^{\gamma} + C_{\alpha} V_{A}^{\alpha} \]  

where \( C_{\gamma} \) and \( C_{\alpha} \) are the phase fractions of \( \gamma \) and \( \alpha/\alpha_2 \), respectively, \( (C_{\gamma} + C_{\alpha} = 1) \), and are represented by the black markers and long-short-dashed line in Figure 9. The volume-increasing part \( \gamma \rightarrow \alpha/\alpha_2 \) of the transformation counteracts the volume compression in each phase, so that the total bulk modulus is even larger, and since the transformation rate itself is non-linear, it adds to the non-linearity of \( V \), expressed as a slightly increased total \( K' \), compared to each individual phase; see Table 1.

3.2. Temperature Dependence at High Pressure

The heating experiment was designed to determine if phase field shifts occur under pressure. In the current study, the sample was heated to the point of partial melting and data recorded during heating at various temperature holding points, while the maximum pressure of 9.6 GPa was applied. Figure 7 shows the diffractograms as a function of room temperature loading and subsequent heating under constant load. The phase fractions of the alloy under investigation, Ti-45Al-7.5Nb-0.25C, obtained by Rietveld analysis, are depicted in Figure 10. Also included in the figure is the data of Yeoh et al. for a Ti-45Al-7.5Nb-0.5C alloy. Both alloys have been manufactured at the GKSS research center, Geesthacht, Germany, in a similar way and in consecutive batches [28] in order to study compositional effects only. The thermo-calorimetric and in situ diffraction studies undertaken by Chladil et al. [29] and Yeoh et al. [31] have been combined [30]. For Ti-45Al-7.5Nb-\( x \)C alloys, increasing carbon additions of \( x \in [0, 0.25, 0.5] \% \) increase the eutectoid temperature \( T_{\text{eu}} \) to \( [1432, 1453, 1473] \) K, respectively, but otherwise, the transformation behavior is the same, specifically the \( \gamma \)-solus or \( \alpha \)-transus remains stable at \( T_{\alpha} = 1565 \) K. These expected transition temperatures \( T_{\text{eu}} \) and \( T_{\alpha} \) are marked in Figure 10 for the Ti-45Al-7.5Nb-0.25C used in this study. Although niobium is a \( \beta \)-phase stabilizer, \( \beta \)-containing phase fields were not detected in concentrations up to 7.5 at. \% [31], while higher concentrations above 8% Nb rendered a detectable amount of this phase [30,75].

![Figure 10](image-url)

**Figure 10.** Phase evolution of Ti-45Al-7.5Nb-0.25C under high pressure at 9.6 GPa (continuous lines) in comparison to ambient pressure (\( p = 0 \) and dotted lines for Ti-45Al-7.5Nb-0.5C from Yeoh et al. [31]). The ambient pressure transition temperatures, reported by Chladil et al. [29], are marked for the investigated alloy.
The salient difference between the high and the ambient pressure experiments lies in the appearance of a large fraction of $\beta$-phase above ~1350 K in the high-pressure experiments, while no trace of this phase was experimentally observed in Yeoh’s study [31]. Below 1350 K, only $\alpha$/$\alpha_2$ and $\gamma$-phases are present.

At ambient pressure, the $\gamma$ mass fraction is 81%; it decreases gradually to 78.0% at 600 K before increasing above 1000 K to recover the maximum of 81% at 1250 K. From this temperature, it decreases gradually up to the eutectoid temperature, $T_{\text{eu}}$, then diminishes at a high rate, up to $T_{\text{a}}$, where it becomes fully $\alpha$-phase [31]. The cause of the minimization of the $\gamma$-phase between 600 K and 1000 K is attributed to local stacking rearrangements, where disorder, transitional structures [62,63] or $\beta$-heating, the fraction of $\gamma$ evidenced by the increasing fraction of $\beta$, below 1420 K. It is apparent that in large measure, $\gamma$ at 1250 K, it increases to a maximum of 83.4% at 1420 K. Subsequently, with increasing temperature, both ambient and high-pressure overlap. While at ambient pressure, the $\gamma$ mass fraction is 81%; it decreases gradually up to the eutectoid temperature, $T_{\text{eu}}$, then diminishes at a high rate, up to $T_{\text{a}}$, where it becomes fully $\alpha$-phase [31]. The induced disorder favors the $\gamma$-fraction to show kinetics and planar re-arrangements [62,63]. Subsequently, mass fraction curves at $\alpha$, $\gamma$, and $\alpha_2$ transition, due to the high ordering potential in the $\gamma$-phase [60]. Order is expected to be highest at temperatures between 1200 and 1300 K, resulting in the maximum amount of $\gamma$-phase [31].

Under a pressure of 9.6 GPa, the $\gamma$-fraction was reduced to 77.4% at room temperature; see Section 3.1.1. During heating, it reduces further to 77.1% at 750 K, lying underneath the values of the ambient pressure heating, and then recovers while the difference vanishes at 810 K. As lattice disorder and planar distortions were already induced at room temperature upon pressurizing, the $\gamma$-phase had transformed to $\alpha$/$\alpha_2$, which then reverts between 750 K and 810 K, a temperature region known to show kinetics and planar re-arrangements [62,63]. Subsequently, mass fraction curves at both ambient and high-pressure overlap. While at ambient pressure, the $\gamma$-fraction begins to diminish at 1250 K, it increases to a maximum of 83.4% at 1420 K. Subsequently, with increasing temperature, $\gamma$ monotonically decreases until it vanishes at $T_{\gamma,\text{solv}} = 1590$ K.

### Table 1. Compilation of experimental lattice parameters $a_0$ and $c_0$ under ambient conditions, as well as the derived quantities; their axis ratios and volume per atom $V_A$, compression parameters $K_0$, $K_0'$ (first 3 rows) and data from the literature. The $\alpha$-phase lattice is given in $\alpha_2$ cell notation, and therefore, $2c/a$ is noted. The first $V_A$ column is computed from $a_0$ and $c_0$, while the second results from the fit of pressure data to Equation (6). The original data of Yeoh’s publication [31] has been re-visited to extract the listed values at 300 K. Literature values are reported from their experimental findings, in addition to Ghosh’s first-principles study [61]. Further listed references are Dubrovinskaia [59], Errandonea [48], Asta [60], Zhang [55], JCPDS [56] and Menon [78].

<table>
<thead>
<tr>
<th>Phase</th>
<th>$a_0$</th>
<th>$c_0$</th>
<th>Axis Ratio</th>
<th>$V_A$</th>
<th>$V_A$</th>
<th>$K_0$</th>
<th>$K_0'$</th>
<th>Reference</th>
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<td>4.06542</td>
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<td>16.4138371</td>
<td>16.414</td>
<td>146.34</td>
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</tr>
<tr>
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<td>16.7201111</td>
<td>16.72</td>
<td>145.84</td>
<td>0.55046</td>
<td>this work</td>
</tr>
<tr>
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<td></td>
<td></td>
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<td>1.6047643</td>
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<td>128</td>
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<td>4.07335</td>
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<td>16.815228</td>
<td>16.815228</td>
<td>Yeoh</td>
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</table>

At a pressure of 9.6 GPa, a coexisting, third phase, $\beta$, with $a = 3.20$ Å, appears at 1350 K, in stark contrast to heating at ambient pressure. It is apparent that in large measure, $\alpha_2$ transforms to $\beta$ ($\alpha_2 \rightarrow \beta$), evidenced by the increasing fraction of $\gamma$, below 1420 K. As the fraction of $\gamma$ decreases on further heating, the fraction of $\beta$ increases due to the intermediate formation of $\alpha$/$\alpha_2$. A minimum fraction
of \( \alpha / \alpha_2 \), 2.9% at 1510 K, suggests that a disordering transition \( \alpha_2 \rightarrow \alpha \) occurs at \( T_{eu} \), above which the \( \alpha \)-phase fraction increases again, due to the transformation of \( \gamma \). The suggested transformation sequence \( \gamma \rightarrow \alpha \rightarrow \alpha + \beta \) is evidenced as supported by the rates of transformation: Initially, \( \alpha \) transforms to \( \beta \), then as \( \gamma \) transforms more rapidly, the \( \alpha \)-phase fraction catches up, while the \( \beta \)-formation decreases. When \( \gamma \) disappears abruptly at \( T_{\gamma,solv} = 1590 \text{ K} \), the \( \alpha \)-phase fraction increases sharply, and the \( \beta \)-phase decreases temporarily from 36.9% to 32.4%, which immediately recovers to 53% \( \beta + 47% \alpha \) in the two-phase-field. Above 1660 K, the alloy starts to melt, while the \( \sim 50/50 \) solid-phase ratio is maintained.

The appearance of the \( \beta \)-phase at high pressure has important implications for the deformation behavior of this material, in particular during high-pressure near-conventional forging and shaping. Liss et al. [7] have demonstrated by in situ experiments that the plastic deformation behavior of a \( \beta \)-stabilized Ti-43.5Al-4Nb-1Mo-0.1B alloy in the \( (\alpha + \beta) \)-two-phase field at 1573 K occurs by fast dynamic recovery of the \( \beta \)-phase, while the co-existing \( \alpha \)-grains deform primarily by slip, with slow dynamic recovery and results in even lesser dynamic recrystallization. In this scenario, the dynamically-recovering \( \beta \)-phase allows for deformation to accommodate the harder \( \alpha \)-phase grains embedded therein. Deformation of the same material at 1493 K in the \( (\alpha + \beta + \gamma) \)-phase field leads, qualitatively, to the conclusion that \( \beta \) is the actively deforming phase, while \( \alpha \) and \( \gamma \) grains display greater stiffness [79]. This high kinetic activity of the \( \beta \)-phase is due to phonon softening, relating to extremely high self-diffusion, in the relatively open \( bcc \) lattice [47,80]. This results in rapid dynamic recrystallization, recovery and grain growth, which in essence, eradicates almost any deformation texture of this phase [7]. Microscopic and electron-backscatter-diffraction studies have subsequently confirmed this behavior [79,81].

These compositionally \( \beta \)-stabilized alloys are being developed for near-conventional, near-net-shape forging production since conventional \( (\alpha + \gamma) \) TiAl alloys are prone to brittleness and highly anisotropic plastic behavior, which is related to the strongly ordered \( \gamma \)- and the hexagonal, \( hcp \) \( \alpha \)-phases. Clemens and Mayer [10] proposed the development of an alloy that contains a relatively large fraction of \( \beta \)-phase at processing temperatures, while the fraction of \( \beta \)-phase is minimized at the expected operation temperatures in, for example, a Ti-43.5Al-4Nb-1Mo-0.1B alloy. However, the residual \( \beta \)-fraction would reduce the alloy’s resistance to creep, and it is therefore essential to minimize the amount of \( \beta \) below 1100 K.

Although the \( \beta \)-phase is usually prone to rapid grain growth, Liss [7,39] and Kabra [82] found, by conducting in situ diffraction studies, that grain growth is inhibited in a multi-phase alloy, even in a \( \beta \)-phase containing titanium or zirconium alloy. This is in large part due to segregation, as different phases have distinct compositions and require long-range diffusion for grain growth to occur. Therefore, in two- or multiple-phase materials, the grain size is relatively stable, even at elevated forging temperatures.

Under the conditions pertaining to the present study, all of these requirements are optimally fulfilled, as no \( \beta \)-phase is present in the \( (\alpha/\alpha_2 + \gamma) \) two-phase field, up to \( \sim 1350 \text{ K} \), well above the expected operating temperatures of this material. Conversely, the ductile \( \beta \)-phase is abundant under high pressure in both three- and two-phase regions, potentially giving rise to a large thermo-mechanical processing window. Even a small \( \beta \)-phase fraction, between 5% and 15%, leads to good plasticity in both \( (\alpha + \beta + \gamma) \)- and \( (\alpha + \beta) \)-phase fields [79]. The present study highlights the potential to develop new processing routes by optimizing the fraction of the ductile \( \beta \)-phase by a judicious selection of a temperatures and pressure, in all three \( (\alpha_2 + \beta + \gamma), (\alpha + \beta + \gamma) \)- and \( (\alpha + \beta) \)-phase fields. For example, grains of the ordered structures \( \alpha_2 \) and \( \gamma \) may be largely conserved while being rearranged through plastic deformation of the \( \beta \)-phase. Alternatively, a minimum \( \alpha \) fraction can be chosen for larger and superplastic deformations, minimizing anisotropy, i.e., texture, or even deformation without the \( \gamma \)-phase for extreme and rapid forging.
4. Conclusions

The response of a $\gamma$-titanium aluminide-based, two-phase alloy of composition Ti-45Al-7.5Nb-0.25C to high pressure and temperature has been investigated, leading to unprecedented results, regarding the evolution of lattice parameters, atomic volume and phase transformations.

The pressure-induced appearance of the bcc $\beta$-phase above 1350 K and at 9.6 GPa is the salient result for potential manufacturing applications, such as high-pressure forging, while at conventional pressures, this phase is not abundant under operational conditions, such as in the turbines of a jet-engine. It renders the possibility of good forgeability at achievable processing temperatures coupled with phase stability and creep resistance at the expected operating conditions of the alloy.

The large amount of $\beta$-phase found at high pressure and temperature, supported by the pressure-temperature phase diagram of pure titanium, suggests that this phase is stabilized at much lower concentrations of niobium, and this can ultimately lead to the development of niobium-free, binary titanium aluminides.

Under room temperature pressure loading, $\gamma$-phase gradually transforms to $\alpha/\alpha_2$, driven by local disordering of $\gamma$, while atoms are pressed towards their close-packed fcc positions. Since the $\gamma \rightarrow \alpha/\alpha_2$ transition is largely displacive, planar faults build up on all of the equivalent $\gamma$ {111} planes, producing ultrafine lathes in a nano-Widmanstätten or basket-weave arrangement, introducing more disorder into both co-existing phases.

No phase transformations have been reported in the literature on pressurizing single-phase $\gamma$ or $\alpha_2$ titanium aluminides. The fact that we are working in a two-phase field allows gradual transformation between the two during loading.

Due to the ordering energy in the $\gamma$-phase being the highest, the system is forced to transform, $\gamma \rightarrow \alpha/\alpha_2$, even though the newly-formed product phase occupies a larger volume per atom than the mother phase. However, the total volume of the specimen, when weighted by the phase fraction and the individual bulk moduli, is still reduced with increasing pressure.

A Murnaghan-Birch equation of state has been fitted to the two individual, co-existing phases $\gamma$ and $\alpha/\alpha_2$, as well as to the total weighted volume reduction. With values around 146 MPa, the bulk moduli $K$, fitted to the individual phases, are significantly higher than the values reported in the literature (see Table 1). Conversely, its pressure derivative, $K'$, is an order of magnitude smaller than the values reported in the literature, since the volume response to pressure is accommodated by the $\gamma \rightarrow \alpha/\alpha_2$ phase transformation, underlined by the even higher total bulk modulus, fitted to the weighted atomic volume.

Accordingly, a Murnaghan-Birch type equation, based on solely attractive and repulsive atomic potentials, is insufficient to describe the present case: a term describing the phase transformations together with the above-mentioned ordering energies needs to be introduced.

The room-temperature transformation builds up a large amount of mechanically-stored energy, which eventually balances the disorder energy in the $\gamma$-phase. Upon heating under pressure, the system largely recovers between 750 K and 810 K, following the ambient-pressure phase fractions up to 1250 K.

Under high pressure, the solid-solid transition temperatures are shifted to higher values. The fraction of $\gamma$-phase increases to a maximum at 1420 K, while at ambient pressure, the maximum is reached at 1250 K. The sharp $\gamma$-phase dissolution temperature $T_{\gamma,\text{diss}}$ is increased, as well as the eutectoid temperature $T_{\text{eu}}$ for $\alpha_2 \rightarrow \alpha$ is expected at the minimum of the $\alpha$ fraction (see Table 2).

<table>
<thead>
<tr>
<th>Table 2. Transition and other distinct temperatures. Ambient pressure values after [29].</th>
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<tr>
<td>Max $\gamma$</td>
</tr>
<tr>
<td>---------------</td>
</tr>
<tr>
<td>$T_{\gamma,\text{max}} (0)$</td>
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<td>1250 K</td>
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Starting at \( \sim 1350 \, \text{K} \), approximately half of the \( \alpha-/\alpha_2 \)-phase transforms to the high-pressure \( \beta \)-phase, which plays an important role in the transformation kinetics. At \( T_{\text{ru}} \), the \( \alpha-/\alpha_2 \)-phase is at a minimum, and above \( T_{\gamma} \), it increases again, before the solid starts to melt above \( >1660 \, \text{K} \).

The ductile \( \beta \)-phase is present in three regions, namely \( (\alpha_2 + \beta + \gamma) \), \( (\alpha + \beta + \gamma) \) and \( (\alpha + \beta) \), while the highly anisotropic phases \( \alpha/\alpha_2 \) show a minimum of 2.9%, which potentially allows for the adjustment of processing parameters to property requirements and optimization.

The present study is the first of its kind in a two-phase titanium aluminate intermetallic, a composition of considerable technological importance for high-temperature applications and which has been the focus of fundamental research for over 25 years. Recently, titanium aluminides have been successfully implemented as high-temperature components in airplane jet engines. Regarding the development of giga-newton super presses, near-conventional forging of such material under high pressure becomes feasible. While the first fundamental results under high pressure and high temperature have been presented here, there remains a number of questions, such as more detailed studies of the pressurization process and an equation of state incorporating pressure, temperature, composition and atomic order.

The latter should lead to neutron scattering experiments, feasible at the PLANET beamline of the J-PARC facility \cite{83}, not only to investigate ordered \( \alpha_2 \), but also ordered \( \beta_0 \). Based on the pressure-temperature phase diagram of pure titanium, we predict that the high-temperature, high-pressure-induced \( \beta \)-phase is stabilized over a wide range of TiAl-based alloys, including binary \( (\alpha_2 + \gamma) \) titanium aluminides, which opens an extraordinary variety of alloy designs, processing and applications.

Note that essential to this study is the employment of a large volume pressure apparatus, which allows the evolution of a realistic microstructure in a realistic sample volume, rather than a micro- to nanometer-sized sample in a diamond anvil cell. Modern multi-anvil apparatuses, such as PLANET, also allow the addition of uni-axial stress components \cite{84}, enabling the study of in situ plastic deformation under high pressure. Similar complex high-pressure machines evolve at synchrotron sources \cite{42,43}, and the usage of two-dimensional detectors \cite{85} has also been realized, which then will allow the investigation of various deformation mechanisms and kinetics, by evaluation, such as in a materials oscilloscope \cite{38,39}.

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Author Contributions: The research was conceived of by K.-D.L., K.A., R.J.D. and H.S., who applied for the beam time. K.-I.F. and Y.H. designed the experimental setup and the pressure cell, which was manufactured by A.S., K.-I.F. and T.S., H.S. manufactured the samples. H.S., K.A., M.R. and K.-I.F. assembled the sample cells, while K.-I.F., M.R., Y.H. and K.-D.L. prepared the instrument. The diffraction experiments were run by all, but R.J.D., K.-D.L. undertook all post-experimental data analysis and wrote the first version of the manuscript. All authors checked and improved the manuscript. Figure 11 shows the investigators and support staff (Y.H. and R.J.D. are missing).

![Figure 11](image_url)

Figure 11. The experimentalists: support staff, Shuoyuan Zhang, and some of the authors, Koichi Akita, Mark Reid, Ayumi Shiro, Ken-ichi Funakoshi, Takahisa Shobu, Hiroshi Suzuki and Klaus-Dieter Liss.
Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

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<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<td>fcc</td>
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