X-ray high-pressure study of Ti_2AlN and Ti_2AlC

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Abstract

The lattice parameters of Ti_2AlN and Ti_2AlC powders were measured as a function of pressure up to $\approx 50\,GPa$, using a synchrotron radiation source and a diamond anvil cell. No phase transformations were observed. As for most related layered carbides and nitrides, such as Ti_4AlN_3 and Ti_3SiC_2, the compressibilities of Ti_2AlN and Ti_2AlC along the c-axes are larger than those along the a-axes. The bulk modulus of Ti_2AlC at $186 \pm 2\,GPa$, is $\approx 10\%$ higher than that of Ti_2AlN at $169 \pm 3\,GPa$.
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1. Introduction

By now it is fairly well established that the layered, hexagonal ternary carbides and nitrides with the general formula $M_{n+1}AX_n$ (MAX)—where $n = 1-3$, M is an early transition metal, A is an A-group (mostly IIIA and IVA) element and X is either C and/or N—combine some of the best attributes of metals and ceramics. Like metals, they are electrically and thermally conductive, not susceptible to thermal shock, plastic at high temperatures and exceptionally damage tolerant, and most *readily machinable* (manual hack saw will suffice). Like ceramics, they are elastically rigid, lightweight, creep and fatigue resistant and maintain their strengths to high temperatures [1–7]. More recently Barsoum et al. have shown that the MAX phases are but a subset of much larger family of solids they termed kinking nonlinear elastic. These solids are characterized by a large c/a ratio (greater than about 1.5), which consequently ensures that the only deformation mode available is the formation of fully reversible, dislocation-based kink bands, KBs [8–10].

There are over 50 M_2AX or 2 1 1 phases [11]; three M_3AX_2 or 3 1 2, and two M_4AX_3 or 4 1 3. Of special interest to this work are Ti_2AlC and Ti_2AlN. These phases were first synthesized in powder form by Jeitchko and Nowotny in the early 1960s [12,13]. More recently, Barsoum et al. reported on the fabrication and characterization of predominantly single-phase samples as well as the mid-range composition, $Ti_2AlC_{0.5}N_{0.5}$ [14]. Like other MAX phases, all samples were readily machinable and excellent thermal and electric conductors. In the 25–1300 °C temperature range, the thermal expansion coefficient of Ti_2AlN ($8.8 \times 10^{-6}\,°C^{-1}$) and Ti_2AlC ($8.2 \times 10^{-6}\,°C^{-1}$) are quite similar.

In this paper, we will report on the compressibilities of Ti_2AlN and Ti_2AlC and compare the results with Ti_4AlN_3. We also explore the stability of these phases to pressures as high as 54 GPa.

2. Experimental details

Fully dense, predominantly single-phase samples of Ti_2AlN and Ti_2AlC (3-ONE-2, Voorhees, NJ) were fabricated by pressureless sintering of pre-reacted Ti_2AlC

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and Ti$_2$AlN powders in argon. The powders were commercially available (3-ONE-2, Voorhees, NJ).

Powdered samples were pressurized using a gasketed Diamond Anvil Cell (DAC) with 300–400 μm culets. A 250 μm initial thickness rhenium gasket was indented to about 50 μm. Since high-purity Al does not undergo structural phase transition at high pressure, has a low shear strength, it was the pressure-transmitting medium of choice [15–20]. Since its pressure–volume relation is well established, it also acted as a pressure marker [21]. Powdered samples were placed between two pieces of Al foil (≈ 15 μm thickness) and packed in the 100–125 μm diameter hole.

X-ray diffraction measurements for Ti$_2$AlC were conducted at room temperature using an angle-dispersive synchrotron radiation at the High Pressure Collaborative Access Team (HPCAT) beam line at the Advanced Photon Source (Argonne National Laboratory). A monochromatic beam, with a wavelength, $\lambda = 0.3678$ Å, was focused to a 10 μm spot size on the sample. For Ti$_2$AlN, the X-ray beam, with $\lambda = 0.496$ Å, was focused down to a 35 μm spot size. The spectra were collected at CHESS (Cornell University, Ithaca, NY). An image plate collected the X-ray diffraction patterns. Diffraction rings were recorded between $2\theta = 1°$ and $35°$. The FIT2D program [22,23] was employed to convert the image plate records into 2θs and intensities.

3. Results and discussion

The X-ray powder diffraction patterns for Ti$_2$AlN and Ti$_2$AlC are shown in Fig. 1. Apart from a few minor impurity peaks, all major peaks are assigned to the hexagonal structure with the space group P6$_3$/mmc. The cell parameters were determined using least-squares refinement on individually fitted peaks. The a and c parameters of Ti$_2$AlC were 3.06 and 13.71 Å, respectively; those for Ti$_2$AlN were 2.986 and 13.60 Å. In both cases, the measured cell parameters reported herein lie at the extrema of those, measured previously (Table 1) [11,14,24–27].

A summary of the relative changes of the lattice parameters and unit cell volumes with pressure are listed in Table 2. Fig. 2 plots the variations in lattice parameters versus applied quasi-hydrostatic pressure, P. Second-order polynomial least-square fits resulted in the coefficients listed in Table 3. In both cases, the contraction with pressure along the c-direction is greater than along the a-direction. The main difference between the two compounds, however, is clearly in the relative changes in the a-direction; the relative changes in the c-direction are almost indistinguishable. Along the a-direction Ti$_2$AlC is less compressible than Ti$_2$AlN, consequently, the anisotropy is greater for the former than for the latter. This conclusion is in accord with thermal expansion anisotropy results. For Ti$_2$AlC, the thermal expansion along the a-and c-directions are 7.1 ± 0.3 and $10.5 \pm 0.5 \times 10^{-6}$ K^{-1}, respectively. At 8.6 ± 0.2 and $7.0 \pm 0.5 \times 10^{-6}$ K^{-1}, the respective values for Ti$_2$AlN are closer to each other [14].

Another consequence is that the bulk modulus of Ti$_2$AlN is slightly lower than that of Ti$_2$AlC (Fig. 3).
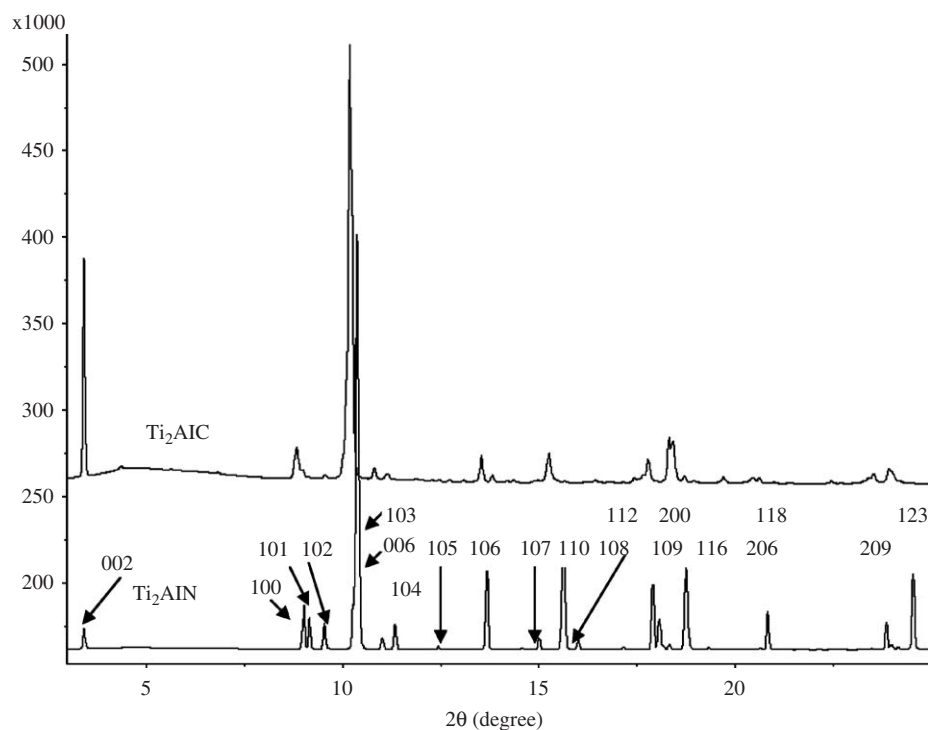

Fig. 1. X-ray powder diffraction patterns for Ti$_2$AlN (bottom) and Ti$_2$AlC (upper) phases studied in this work, both spectra were taken, at HPCAT, out of DAC. All major peaks were assigned to the hexagonal structure (P6$_3$/mmc), $\lambda = 0.4066$ Å.

Table 1
Ambient pressure lattice parameters and unit cell volumes of Ti_2AlX (X = C, N) compounds measured herein

Ti_2AlX	Ti_2AlC	Ti_2AlN
a (Å)	3.065 ± 0.004	2.986 ± 0.003
	3.058 [24]	3.029 [26]
	3.052 [25]	2.989 [14]
	3.062 [27]	2.991 [26]
	3.040 [11]	2.989 [11]
	3.051 [14]	2.991 [24]
c (Å)	13.71 ± 0.03	13.60 ± 0.02
	13.624 [24]	13.62 [26]
	13.64 [25]	13.61 [14]
	13.673 [27]	13.62 [26]
	13.60 [11]	13.614 [11]
	13.637 [14]	13.619 [24]
V_o (Å)^3	111.6 ± 0.6	105.0 ± 0.5

Previous results are also listed. Note the results of Ref. 27 are ab initio results.

Table 2
Relative unit-cell parameters and volume changes of Ti_2AlN and Ti_2AlC at various pressures

| Ti_2AlN				Ti_2AlC			
P (GPa)	V/V_o	a/a_o	c/c_o	P (GPa)	V/V_o	a/a_o	c/c_o
0	1	1	1	0	1	1	1
4.17	0.9740	0.9934	0.9870	8.46	0.9653	0.9892	0.9865
16.50	0.9187	0.9732	0.9699	10.27	0.9539	0.9862	0.9808
18.48	0.9072	0.9699	0.9643	12.14	0.9448	0.9859	0.9720
22.41	0.8992	0.9666	0.9624	21.26	0.9140	0.9778	0.9559
27.12	0.8790	0.9606	0.9525	28.24	0.8903	0.9685	0.9492
33.86	0.8566	0.9523	0.9445	37.63	0.8623	0.9582	0.9392
36.94	0.8476	0.9474	0.9444	49.6	0.8330	0.9467	0.9294
43.84	0.8263	0.9431	0.9289	53.95	0.8234	0.9417	0.9286
45.22	0.8263	0.9417	0.9317				
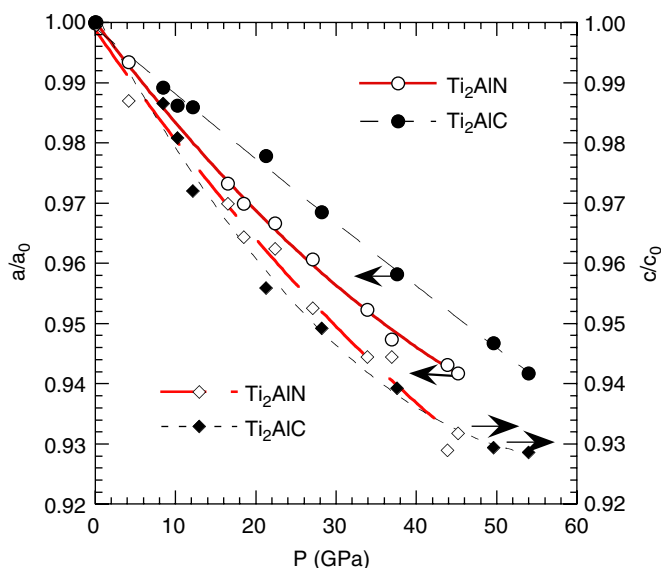
Fig. 2. Pressure dependencies of a/a_o (left axis) and c/c_o (right axis) for Ti_2AlX (X = C, N). Note that the lines are least-square fits of the data points.

Fitting the same results to the Birch-Murnaghan equation [28]

$$P = 3/2K_o[(V/V_o)^{-7/3} - (V/V_o)^{-5/3}]$$
$$\times \{1 + 3/4(K'_o - 4)[(V/V_o)^{-2/3} - 1]\}, \quad (1)$$

where K_o is the bulk modulus and K'_o its pressure derivative, yields a K_o of 169 ± 3 GPa for Ti_2AlN and 186 ± 2 GPa for Ti_2AlC (Table 3).

At this point, it is instructive to place the values of K_o measured here in perspective. As the compressibilities along both directions in Ti_4AlN_3 are lower than Ti_2AlN, it follows that K_o of Ti_2AlN is lower than the 216 GPa of Ti_4AlN_3 (Fig. 3). Similar to Ti_4AlN_3, however, the compressibility along the a- is less than along the c-direction. The main reason Ti_4AlN_3 is stiffer is that it is comprised of a larger fraction of strong M–X bonds compared to the M–A bonds that tend to be relatively weaker. Consistent with this notion is the fact that the bulk modulus of Ti_4AlN_3 (216 GPa) is lower than the corresponding value for TiN (300 GPa) [29]. The agreement between our results and those deduced from recent ab initio calculations is excellent: within 4% for Ti_2AlN [30] and within 10% for Ti_2AlC [31].

Based on the fact that the compressibilities along the c-direction for both Ti_2AlC and Ti_2AlN are quite similar (Fig. 2), it is reasonable to assume that the compressibility along the c-direction is dominated by the Ti–Al bonds that are identical in both compounds. Along the a-axis, on the otherhand, the main difference between the two compounds must thus be traced to the M–X bonds and/or vacancies. Given that the a-lattice parameters of Ti_2AlN are shorter than those in Ti_2AlC (Table 1) it is unlikely that the Ti–N bonds are weaker. We thus conclude that vacancies on the N-sublattice is responsible for the lower value of K_o for Ti_2AlN. A more detailed exposition of this notion will be published elsewhere [32].

4. Summary and conclusions

Using a synchrotron radiation source and a DAC, we measured the pressure dependencies of the lattice parameters of polycrystalline Ti_2AlN and Ti_2AlC samples up to pressures ≈ 50 GPa; no phase transformations were observed. Like what was observed in most of the MAX phases, the compressibility of Ti_2AlN and Ti_2AlC along the c-axis is larger than that along the a-axis. The bulk modulus for Ti_2AlC is 186 ± 2 GPa, which is 10% higher than that for Ti_2AlN, (169 ± 3 GPa).

Acknowledgments

Table 3
Fitting of relative lattice parameter and volume changes with pressure, P

Ti_2AlX	Ti_2AlC		Ti_2AlN	
$A/a_o = 1 + \beta P/P_o + \gamma(P/P_o)^2$	$\beta = -0.0011$	$\gamma = 7 \times 10^{-7}$	$\beta = -0.0018$	$\gamma = 10^{-5}$
$C/c_o = 1 + \beta P/P_o + \gamma(P/P_o)^2$	$\beta = -0.0024$	$\gamma = 2 \times 10^{-5}$	$\beta = -0.0019$	$\gamma = 9 \times 10^{-6}$
$V/V_o = \alpha + \beta P/P_o + \gamma(P/P_o)^2$	$\beta = -0.0045$	$\gamma = 2 \times 10^{-5}$	$\beta = -0.0054$	$\gamma = 3 \times 10^{-5}$
K_o (GPa)	186 ± 2		169 ± 3	
K'_o	4.0 ± 0.1		3.5 ± 0.2	
K_o (GPa) from ab initio	166 [31], 164 [24]		175 [24]	

P_o defines the units used and is equal to 1 GPa. The correlation coefficients values were all greater than 0.99. Also included are experimental bulk moduli and ab initio total energy calculation results.
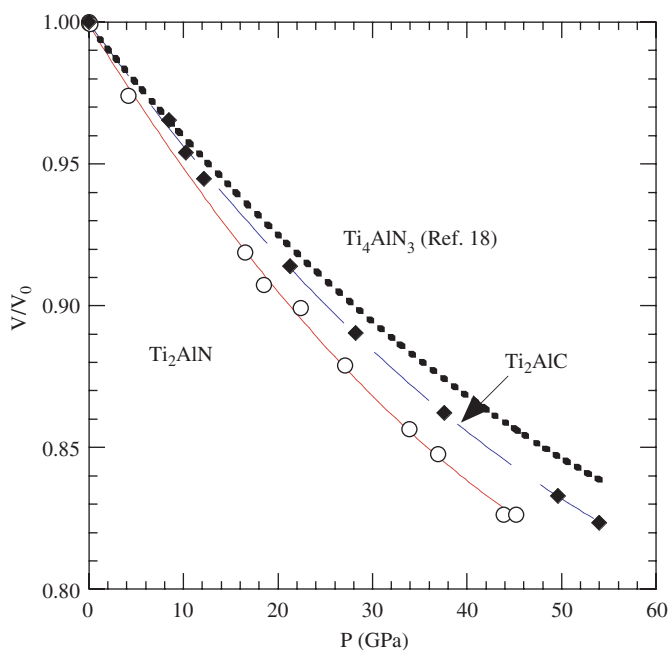

Fig. 3. Relative unit-cell volumes of Ti_2AlX (X = C, N) as a function of pressure. Also shown are the results for Ti_4AlN_3 taken from Ref. [18]. Note that the lines are least-square fits of the data points.

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