Mechanical properties of Ti₃AlX (X = C, N): Ab initio study

V. KANCHANA[(a)]

Defence Metallurgical Research Laboratory, Kanchanbagh - Hyderabad 500 058, India

Abstract – Elastic properties of the alloys Ti₃AlC and Ti₃AlN are derived from the first-principles total energy calculations based on the full-potential linear muffin-tin Orbital (FP-LMTO) method. From the computed elastic constants, theoretical values of Young's modulus, shear modulus, Poisson's ratio, sound velocities and Debye temperature are evaluated. By analysing the ratio between the bulk and shear moduli, it is found that Ti₃AlN is ductile in nature, whose ductility is expected to be greater than that of Ti₃Al, whereas Ti₃AlC is found to be brittle. The site-projected density of states and the charge density plots have been used to analyse the chemical bonding between the Ti₆N and Ti₆C cluster and the surrounding metallic lattice of Al atoms. This further reveals that the strong covalent nature of Ti-C bonds in Ti₃AlC, together with the high Young, shear and bulk moduli, make the compound more brittle than Ti₃AlN.

Introduction. – The early transition-metal nitrides have great technological potential as hard coatings and wide–band-gap semiconductors and possibly for application in magnetic recording and sensing. One of the most stable structures for ternary and multinary compound is the cubic perovskite structure. The family of the compounds with the perovskite crystal structure is of scientific interest due to their versatile physical properties such as high Young's modulus, high melting point, colossal magnetoresistance (CMR) and ferroelectricity. The cubic inverse perovskite or anti-perovskite nitrides consists of relatively unexplored branch of perovskite family with captivating electronic properties which can be tuned desirably [1].

This inverse perovskite is a cubic crystal structure with light metal atom (Al) at the cube corner sites, heavy atom (Ti) at the face-centered positions and the non-metal (N,C) in the body-centered position. This structure is nothing but an ordinary perovskite structure, where the heavy metal atoms have exchanged positions with the non-metal atoms in the unit cell as shown in fig. 1.

At present there exists only countable number of ternary early transition metal nitrides and carbides which possess the anti-perovskite structure, which can be summarised as Ti₃AlN [2], Ti₃AlC [3] and scandium-based cubic inverse perovskite nitrides such as Sc₃AlN, Sc₃InN [4–6]. Recently,
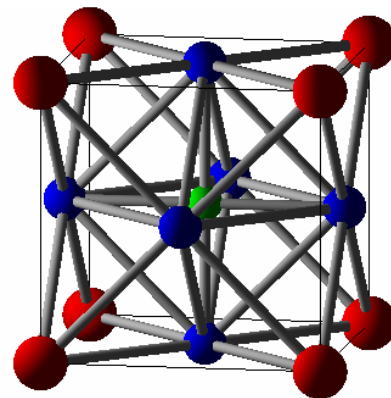

Fig. 1: (Colour on-line) Crystal structure of anti-perovskite Ti₃AlN. The Al atoms (red) are at the corner, Ti (blue) at the face-centered position and N (green) in the body centered position.

Sc₃GaN with the same structure is predicted theoretically [7]. The electronic structure and chemical bonding in these cubic inverse perovskite nitrides have not been investigated previously. The fundamental mechanism of chemical bonding in specific crystal directions leading to certain macroscopic phenomena such as high conductivity and elasticity or stiffness needs to be explored and understood further.

_____
[(a)]E-mail: `kanchana.vaithee@gmail.com`

The present study is to focuss mainly on the Ti-based alumino nitride and carbide with the anti-perovskite structure, which is less explored both experimentally and theoretically, with the motivation of finding a promising material with improved mechanical properties in comparison with TiAl and Ti_3Al.

The intermetallic compound TiAl has been studied as a high temperature material because of its low density and high melting temperature. However, it still suffers from insufficient ductility and fracture toughness at room temperature and poor elevated strength [8,9]. Alloying with third element and microstructural modifications through thermo-mechanical treatments are essential for further improvement of room temperature ductility and high temperature strength of TiAl. Among the alloying elements, carbon is important because it is known to be contained in TiAl as an impurity and it is expected to alter the ductility and strength of TiAl. It is also reported that, addition of carbon increases the hardness of binary TiAl alloys [10] and the hardness of Ti_3AlC is reported to be 11 GPa recently by Wilhelmsson *et al.* [11].

The ternary carbide precipitate phases that have received much attention are Ti_3AlC (cubic perovskite)and Ti_2AlC (hexagonal). A fundamental property of precipitates is their interface energy with respect to the host. Calculations of energies and atomic structures of the interfaces of the hexagonal and cubic ternary carbide phases in the tetragonal TiAl have been studied recently by Benedek *et al.* [12].

The perovskite type carbides and nitrides of Ti-Al system are worth exploring as there are earlier reports by Kawabata *et al.* [13] revealing the optimum additions of interstitial elements such as carbon, nitrogen and boron leading to the the improved mechanical properties of TiAl. Yuki *et al.* [14] investigated the effect of nitrogen addition on the mechanical properties of cast γ-TiAl alloys and reported that both the room temperature ductility and strength increases with increasing the nitrogen content up to 0.3 mass %. Hosoda *et al.* [15] carried out the synthesis and charecterisation of Ti_3AlC in which the authors adopted mechanical alloying and hot pressing methods using elemental powders of Ti, Al and C. By considering the superior high temperature strength and low density around $4.29\,g/cm^3$, the authors conclude Ti_3AlC to be a new high temperature light-weight structural material.

From the theoretical side, electronic structure calculations explaining the density of states and bonding features of Ti_3AlN and Ti_3AlC have been performed [16,17]. But no reports are available explaining the mechanical properties of Ti_3AlC and Ti_3AlN. The present paper is aimed to shed more light on the elastic properties of these alloys and to predict the nature of these compounds. The rest of the paper is organized in the following manner. The second section describes the computational details including the calculation of elastic constants. Results are elaborated in the third section and finally the last section concludes the paper.

Computational details. –

The electronic structure method. In this work, the all-electron full-potential linear muffin-tin orbital (FP-LMTO) method has been used to calculate the total energies as well as the basic ground-state properties [18]. Here the crystal is divided into two regions: non-overlapping muffin-tin spheres surrounding each atom and the interstitial region between the spheres. We used a double κ spdf LMTO basis (each radial function within the spheres is matched to a Hankel function in the interstitial region) for describing the valence bands. The following basis set Ti($3s$, $3p$, $4s$, $4p$, $3d$), C($2s$, $2p$), N($2s$, $2p$), Al($3s$, $3p$, $3d$) are used in the calculations. The exchange correlation potential was calculated within the generalized gradient approximation (GGA) scheme [19]. The charge density and potential inside the muffin-tin spheres are represented by spherical harmonics up to $l_{max} = 6$, while in the interstitial region, 28670 plane waves with energies up to 236.01 Ry were included in the calculation. Total energies were calculated as a function of volume, for a (26 26 26) k-mesh which corresponds to 560 k points in the IBZ and are fitted to the Birch equation of state [20] to obtain the ground-state properties.

The elastic constants. There are 21 independent elastic constants, C_{ij}, but the symmetry of the cubic crystal lattice reduces this number to only three independent elastic constants C_{11}, C_{12}, and C_{44}. The bulk modulus B of this system can be expressed as a linear combination of C_{11} and C_{12}.

The condition for elastic stability is that B, $C_{11} - C_{12}$, and C_{44} are positive [21]. The elastic constants can be obtained by calculating the total energy as a function of volume conserving strains that break the cubic symmetry. The details of the calculation can be found elsewhere [22].

Once the single-crystal elastic constants are computed, related properties of (poly-crystal) alloys may also be evaluated. It is to be noted that because of the elastic anisotropy, Youngs's modulus E, shear modulus G of a cubic single crystal may depend on the direction and to be treated accordingly. The shear modulus anisotropy is usually represented as the ratio between two elastic constants C_{44} and C':

$$A_G = \frac{2C_{44}}{C_{11} - C_{12}}. \tag{1}$$

There are no exact expressions for poly-crystal averaged shear moduli in terms of the C_{ij}, but one can evaluate approximate averages of the lower and upper bounds given by various theories. According to Hill [23], the arithmetic average of the Voigt [24] and Reuss [25] values can be used as an estimate to the average shear modulus which is represented as G_H and is shown in the following relations:

$$G_H = \frac{G_R + G_V}{2}, \tag{2}$$

$$G_V = \frac{3C_{44} + C_{11} - C_{12}}{5}, \tag{3}$$

Table 1: Calculated ground-state and elastic properties of Ti_3AlC and Ti_3AlN at the theoretical equilibrium volume. The available experimental values are given in parenthesis.

Property	Ti_3AlN	Ti_3AlC
Lattice constant (Å)	$4.11(4.11)^a$	$4.16 (4.16)^b$
Unit cell volume (Å)^3	69.426 (69.426)	71.991 (71.991)
Bulk modulus B (GPa)	194.62	185.14
Density (g/cm^3)	4.406	4.211
C_{11} (GPa)	249.94	380.52
C_{12} (GPa)	166.96	87.44
C_{44} (GPa)	60.502	88.711
Shear modulus G_H (GPa)	52.014	108.591
G_H/B	0.267	0.5865
Young's modulus E (GPa)	143.277	272.496
Poisson's ratio σ	0.3753	0.2546
Anisotropy factor A	1.4582	0.6053
v_s (km/s)	3.4359	5.0781
v_l (km/s)	7.7403	8.8515
v_m (km/s)	3.8740	5.6380
Debye temperature (K)	479.54	689.96
Cauchy's pressure ($C_{12} - C_{44}$)	106.458	-1.271

^{a} Ref. [2].

^{b} Ref. [26].

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})}, \qquad (4)$$

$$E = \frac{9BG}{3B + G}. \qquad (5)$$

Having calculated Young's modulus E, bulk modulus B, and shear modulus G, the Debye temperature can be calculated in a manner similar to our earlier work [23], which is an important fundamental parameter closely related to many physical properties such as specific heat and melting temperature.

Results and discussions. –

Ground-state properties and electronic density of states. The calculated ground-state properties such as equilibrium lattice constant and the elastic constants are tabulated in table 1. The calculated lattice constants for both the compounds are in close agreement with the experiments. The calculated bulk modulus at the theoretical equilibrium volume finds no experimental results for comparison.

The total and partial density of states (DOS and PDOS) as well as the charge density plots of Ti_3AlC and Ti_3AlN were calculated using the tight-binding linear muffin-tin orbital method [27] and are given as figs. 2–5. The overall electronic structure of both the compounds remains the same with slight changes which are discussed below. In the case of Ti_3AlN, the higher lying electronic states which extend from -8 eV to 0 eV includes both the metal-metal (Ti-Al) and metal–non-metal (Ti-N) interactions. The $3p$ states of Al lying close to the Fermi level hybridises strongly with the Ti p and d states, whereas, the interaction of Ti with N-$3p$ states is little
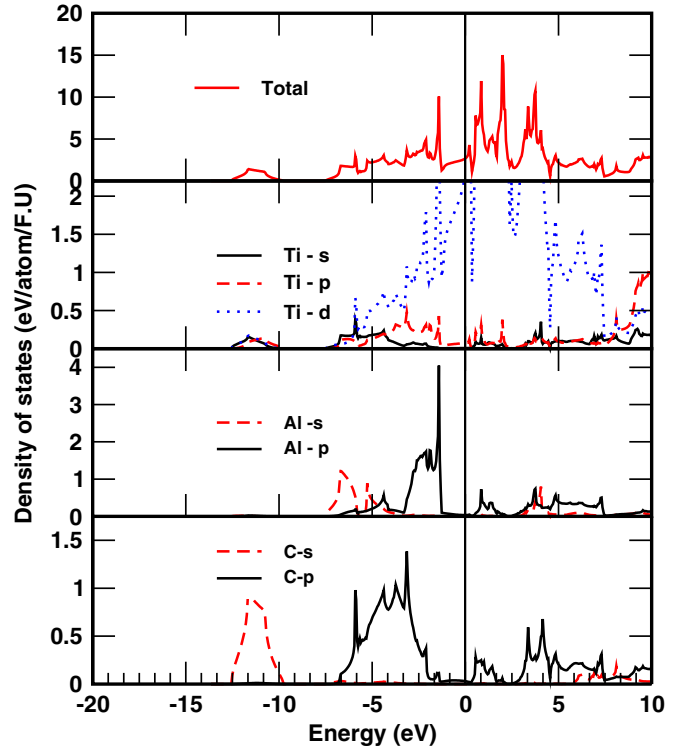

Fig. 2: (Colour on-line) Partial density of states of Ti_3AlC. The zero of the x-axis represents the Fermi level.

deeper in energy. The fine DOS structure present near the Fermi level deserves particular attention. The upper edge of the occupied sub band and the lower edge of the empty subband is determined by the distribution of the Ti-$3d$ states as seen from the DOS and the Fermi level lies in
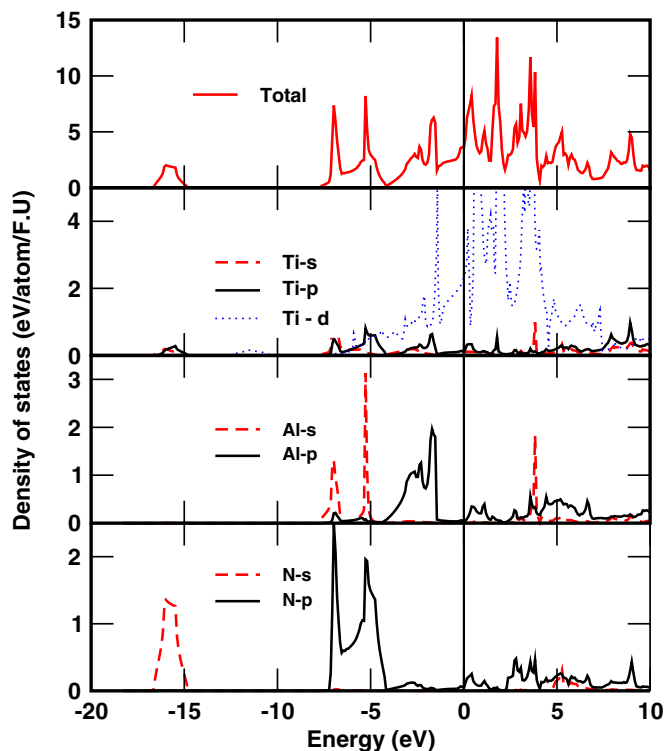
Fig. 3: (Colour on-line) Partial density of states of Ti$_3$AlN. The zero of the x-axis represents Fermi level.
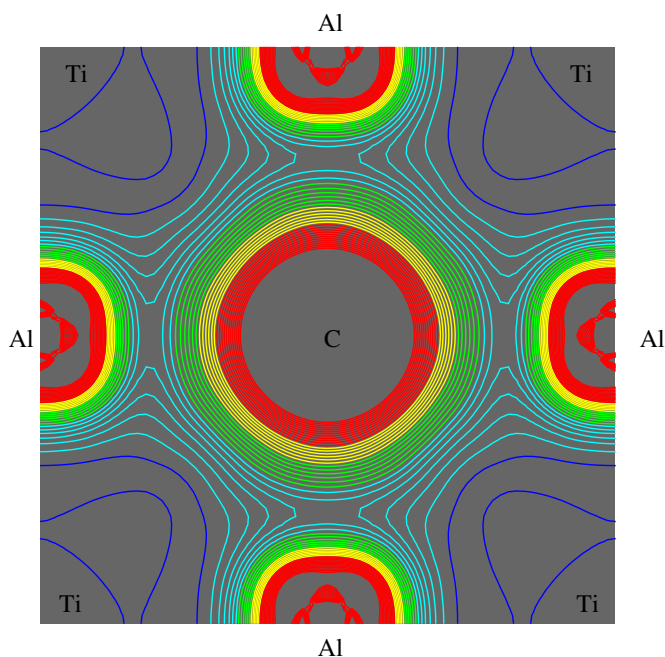

Fig. 4: (Colour on-line) Charge density plots of Ti$_3$AlC in the [100]-plane. Ti atoms are at the corners and the C atom is at the centre.

the local DOS minimum. This main feature evident from the electronic structure of Ti$_3$AlN, provides a qualitative explanation for the stability of this compound. Indeed the shift of E_F, towards lower binding energies, caused by Ti
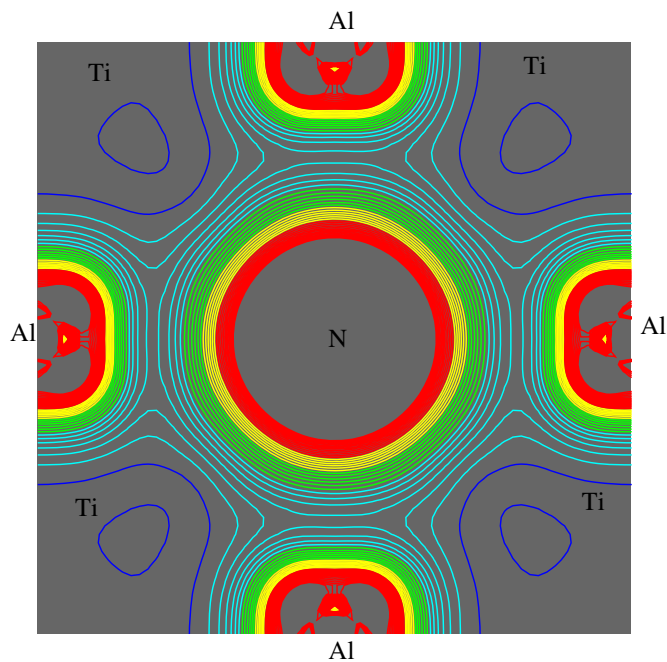

Fig. 5: (Colour on-line) Charge density plots of Ti$_3$AlN in the [100]-plane. Ti atoms are at the corner and the N atom at the centre.

being replaced by a transition metal of larger valence will eventually result in a sharp increase in the DOS at E_F, leading to the destabilisation of the structure. A similar effect can also be felt by decreasing the electron concentration in the system. When comparing the PDOSs of Ti$_3$AlN and Ti$_3$AlC, it could be noticed that the N-p states are little deeper in energy and also narrow compared to the C-p states. Hence the extent of overlap of Ti-p states with C-p states is more when compared with the N-p states. This spreading of the bond state in the case of Ti$_3$AlC could be taken as an indication of increased covalent character prevailing in Ti$_3$AlC, than in Ti$_3$AlN. At the Fermi level, the main contribution to the density of states arises from the Ti-d states with a small admixture from C-p and N-p states, which can be seen from the figures. To emphasis more on the bonding nature of Ti-N and Ti-C in these compounds, charge density plots were plotted in the [100]-plane for both the compounds and are given in fig. 4 and fig. 5, respectively. The spatial pattern of the electron density distribution clearly shows the electron density to concentrate along the Ti-C/N bonds and reveals a low density along the Ti-Al and C/N-Al bonds. Further it can be noticed that the covalency of Ti-X bond is more pronounced in Ti$_3$AlC than in Ti$_3$AlN, which renders the compound more covalent when compared to Ti$_3$AlN.

Elastic constants and mechanical properties determination. Elastic constants are fundamental and indispensable for describing the mechanical properties of materials. Elastic constants for pure metals are available in the literature. In contrast, the data available for alloys and intermetallic compounds are very limited. Hence

efforts have been taken to calculate the elastic constants of these compounds, which further lead to the calculation of Young's modulus, shear modulus, anisotropy factor, which can be derived using the standard relations based on the three independent elastic constants as mentioned in the above section. The complete set of elastic constants and the related properties are calculated and are tabulated in table 1. Having acquired the necessary data, we now try to elaborate more on the ductile or brittle nature of these compounds, which is the key point of the present paper.

Now we try to explain more on the calculated quantities and relate them to the mechanical behaviour of the materials under study. Young's modulus (E) which is calculated and given in table 1, defines the ratio between the linear stress and strain. The larger the value of E, the stiffer is the material. Young's modulus of Ti$_3$AlN is found to be 143.277 GPa, which is quite lower when compared to Young's modulus value of Ti$_3$AlC (272.496 GPa) and Sc$_3$AlN (211.33 GPa), respectively [28]. In general, it can be put forth that, as Young's modulus increases, the covalent nature of the compound also increases, which further has an impact on the ductility of the compounds, which is discussed from other aspects also. It is also evident from the density of states plot, showing more covalent nature of Ti-C bonding compared to Ti-N bonding in Ti$_3$AlN, which could account for the brittle nature of Ti$_3$AlC.

The elastic anisotropy is an important factor, as it is highly correlated with the possibility of inducing micro cracks in the materials. For a completly isotropic systems, the anisotropy factor A takes the value of unity and the deviation from unity measures the degree of elastic anisotropy. Here both the compounds Ti$_3$AlN and Ti$_3$AlC are found to be anisotropic and the anisotropy factors are given in the table.

The ductile-brittle nature of materials is often discussed in terms of elastic constants of the relevant material. The Cauchy's pressure, defined as the difference between the two particular elastic constants $C_{12} - C_{44}$ is considered to serve as an indication of ductility: if the pressure is positive (negative), the material is expected to be ductile (brittle) [29]. Here Cauchy's pressure of Ti$_3$AlN is positive, which is a clear indication for the compound to be ductile.

Another index of ductility is the G_H/B ratio reported in table 1. As mentioned previously, the system is anisotropic and we use Hill's shear modulus G_H to explain further the ductile or brittle nature of the compound. According to Pugh's ratio, the high (low) G_H/B ratio is associated with the brittle (ductile) nature of the materials [30]. The critical number which separates the ductile and brittle was found to be 0.57. This ratio is around 0.586 for Ti$_3$AlC and 0.267 for Ti$_3$AlN, which clearly highlights the ductile nature of Ti$_3$AlN. Comparing with Ti$_3$Al, which has a G_H/B ratio of 0.48 [31], we are lead to a conclusion that Ti$_3$AlN is more ductile than Ti$_3$Al.

In an alternate way, one can interpret the bulk modulus to represent the resistance to the volume change against external forces, inturn indicating the average bond strength, and the shear modulus on the other hand to represent the resistance to shear deformation against external forces, indicating the resistance to the change in bond angle. In such a case, G_H/B represents the relative directionality of bonding in the material. Hence the bonding is more covalent in Ti$_3$AlC, which has a G_H/B ratio of 0.586, which is higher than that in Ti$_3$AlN, having the G_H/B value of 0.267. This covalent nature was also evident in the charge density plots, which results in the conclusion that Ti$_3$AlN could be more ductile than Ti$_3$AlC.

It would be appropriate to conclude the elastic properties by analysing Poisson's ratio σ, which is defined using Hill's limit [23] with the following equation:

$$\sigma = \frac{3B - 2G_H}{2(3B + G_H)}. \tag{6}$$

Poisson's ratio generally quantifies the stability of the crystal against shear and takes the value between -1 and 0.5 which are the lower and the upper bounds. The lower bound is where the materials does not change its shape and the upper bound is where the volume remains unchanged. Poisson's ratio decreases, when the non-central effects becomes more important. Here the value of σ is around 0.25 for Ti$_3$AlC and 0.375 for Ti$_3$AlN, which shows the enhanced covalent character evident in Ti$_3$AlC, with respect to Ti$_3$AlN. The Poisson's ratio for TiAl and Ti$_3$Al are found to be 0.220 and 0.287, respectively [31,32]. The increase in the above value when going from TiAl and Ti$_3$Al to Ti$_3$AlN clearly shows that the ductility should be higher in Ti$_3$AlN.

As an extension, Debye temperature Θ_D, is also calculated, which determines the thermal charecteristics of the material. As a matter of fact, a higher Θ_D, would imply a higher thermal conductivity associated with the material. From the present calculations, the Θ_D is estimated, to be around 479.5 K and 689.96 K for Ti$_3$AlN and Ti$_3$AlC, respectively. The calculated Θ_D for the above compounds are of similar order when compared with that of TiAl and Ti$_3$Al, which are reported to be 590 K, 485 K, respectively [32]. This clearly indicates that these cubic inverse perovskite systems have a relatively high Θ_D, which is an indication of the stiff lattice and hence the good thermal conductivity which they possess.

Summary. – In summary, the elastic properties of Ti$_3$AlC and Ti$_3$AlN have been calculated using the FP-LMTO method with the intention of elaborating the mechanical properties of the system so as to bring out the ductile or brittle nature of the compound. The elastic constants are predicted for the first time and by analysing the ratio between the bulk and the shear moduli, it is concluded that Ti$_3$AlN could be more ductile, with a ductility greater than that of Ti$_3$Al, whereas Ti$_3$AlC is found to be brittle. This result is substantiated by the site-projected density of states and the charge density

plots. The strong covalent nature of the Ti-C bonds present in Ti_3AlC, further strengthens the above fact that Ti_3AlC could be brittle. In addition, the high shear, Young and bulk moduli and low Poisson's ratio associated with Ti_3AlC when compared with Ti_3AlN, clearly allows us to arrive at the solution that Ti_3AlC could be more brittle, which would probe further experimental investigations.

$* * *$

REFERENCES

[1] NIEWA R., SCHNELLE W. and WAGNER F. R., *Z. Anorg. Allg. Chem.*, **627** (2001) 365.

[2] SCHUSTER J. C. and BAUER J., *J. Solid State Chem.*, **53** (1984) 260.

[3] JEITSCHKO W., NOWOTNY H. and BENESOVSKY F., *Monatsh. Chem./Chem. Mon.*, **95** (1964) 319.

[4] KRICHNER M., SCHNELLER W., WAGNER F. R. and NIEWA R., *Solid State Sci.*, **5** (2003) 1247.

[5] HÖGLUND C., BIRCH JENS, BECKERS MANFRED, ALLING BJÖRN, CZIGÁNY ZSOLT, MÜCKLICH ARNDT and HULTMAN LARS, *Eur. J. Inorg. Chem.*, **2008**, issue No. 8 (2008) 1193.

[6] MAGNUSON M., MATTESINI M., HÖGULUND C., ABRIKOSOV I. A., BIRCH J. and HULTMAN L., *Phys. Rev. B*, **78** (2008) 235102.

[7] MIKHAYLUSHKIN A. S., HÖGULUND C., BIRCH J., CZIGÁNY ZS., HULTMAN L., SIMAK S. I., ALLING B., TASNÁDI F. and ABRIKOSOV I. A., *Phys. Rev. B*, **79** (2009) 134107.

[8] LIPSITT H. A., in *High Temperature Ordered Intermetallic Alloys*, edited by KOCH C. C., LIU C. T. and STOLOFF N. S., *MRS Symp. Proc.*, **39** (1985) 351.

[9] TIAN W. H. and NEMOTO M., *Intermetallics*, **5** (1997) 237.

[10] VAN-THYNE R. J. and KESSLER H., *Trans. AIME*, **196** (1954) 193.

[11] WILHELMSSON O., PALMQUIST J. P., LEWIN E., EMMERLICH J., EKALUND P., PERRSON P. O. A., HOGBERG H., LI S., AHUJA R., ERIKSSON O., HULTMAN L. and JANSSON U., *J. Cryst. Growth*, **291** (2006) 290.

[12] BENEDEK R., SEIDMAN D. N. and WOODWARD C., *Interface Sci.*, **12** (2004) 57.

[13] KAWABATA T., TADANO M. and IZUMI O., *ISIJ Int.*, **31** (1991) 1161.

[14] YUKI I., AMANO N., UOZUMI M., INUI H. and YAMAGUCHI Y., *J. Jpn. Inst. Met.*, **58** (1994) 564.

[15] HOSODA H., INAMURA T. and WAKASHIMA K., *MRS Symp. Proc.*, **980** (2007) 395.

[16] MATAR S. F., LE PETTICORPS YANN and ETOURNEAU JEAN, *J. Mater. Chem.*, **7** (1997) 99.

[17] IVANOVSKII A. L., MEDVEDEVA N. I. and NOVIKOV D. L., *Phys. Solid State*, **39** (1997) 929.

[18] SAVRASOV S. Y., *Phys. Rev. B*, **54** (1996) 16470.

[19] PERDEW J. P., BURKE K. and ERNZERHOF M., *Phys. Rev. Lett.*, **77** (1996) 3865.

[20] BIRCH F. J., *J. Appl. Phys.*, **9** (1938) 279.

[21] WALLACE D. C., *Thermodynamics of Crystals* (Wiley, New York) 1972.

[22] KANCHANA V., VAITHEESWARAN G. and SVANE A., *J. Alloys Compd.*, **455** (2008) 480.

[23] HILL R., *Proc. Phys. Soc. London*, **65** (1952) 350.

[24] VOIGT W., *Ann. Phys. (Leipzig)*, **38** (1889) 573.

[25] REUSS A., *Z. Angew. Math. Phys.*, **9** (1929) 49.

[26] TIAN W. H. and NEMOTO M., *Intermetallics*, **7** (1999) 1261.

[27] The Stuttgart TB-LMTO-ASA code version 4.7, see url http://www.fkf.mpg.de/andersen/.

[28] MATTESINI M., MAGNUSON MARTIN, TASNÁDI F., HÖGLUND C., ABRIKOSOV I. A. and HULTMAN L., *Phys. Rev. B*, **79** (2009) 125122.

[29] PETTIFOR D., *Mater. Sci. Technol.*, **8** (1992) 345.

[30] PUGH S. F., *Philos. Mag.*, **45** (1954) 823.

[31] TANAKA K., OKAMOTO K., INUI H., MINONISHI Y., YAMAGUCHI M. and KOIWA M., *Philos. Mag. A*, **73** (1996) 1475.

[32] TANAKA K., ICHITSUBO T., INUI H., YAMAGUCHI M. and KOIWA M., *Philos. Mag. Lett.*, **73** (1996) 71.