JOURNAL OF MATERIALS SCIENCE **34** (1999) 169–174

Bond lengths in the ternary compounds Ti_3SiC_2, Ti_3GeC_2 and Ti_2GeC

M. Y. GAMARNIK, M. W. BARSOUM
Department of Materials Engineering, Drexel University, Philadelphia, PA 19104, USA

The interatomic distances in the ternary compounds Ti_3SiC_2, Ti_3GeC_2 and Ti_2GeC have been determined precisely by comparing the lattice parameters of Ti_3GeC_2 and Ti_2GeC, on the one hand, and Ti_3GeC_2 and Ti_3SiC_2, on the other. The assumptions made were that the Ti–Ge and Ti–C distances in the Ge-containing phases were identical, and that the differences in the Ti–Si and Ti–Ge distances in Ti_3SiC_2 and Ti_3GeC_2 phases were equal to the differences in the covalent radii of Si and Ge. While the results clearly show that the TiC octahedra in the ternary phases are distorted, the extent of that distortion is smaller than previously reported. The extent of the distortion was found to depend on the type of atoms surrounding the TiC_6 octahedrons; the deformation is larger in the Ge-containing than in the Si-containing compounds. However, the Ti–C–Ti distances appear to be insensitive to the nature of the compound. © *1999 Kluwer Academic Publishers*

1. Introduction

Recently, researchers [1, 2] have reported on two related classes of ternary compounds, Ti_3SiC_2 and Ti_3GeC_2, henceforth referred to as the 312s and the H-phases (M_2BX, where M is a transition metal, and B is a B-group element and X is either C or N) that are characterized by having the B-group elements exist in close-packed planes that separate transition carbide or nitride octahedra (see Fig. 1). A preliminary characterization of the 312s, Ti_2AlC, Ti_2AlN and Ti_2GeC, indicated that all these phases are as readily machinable as graphite and possess hardnesses in the range of 3–5 GPa, rendering them much harder than graphite, but relatively soft for ceramics. Furthermore, with conductivities in the range $2–5 \times 10^6\ \Omega^{-1}\ m^{-1}$, they are roughly two orders of magnitude more conductive than graphite. They all exhibit remarkable plasticity at elevated temperatures with yield points that, for the most part, are substantially higher than the best superalloys available today. Post-deformation scanning electron micrographs of fractured surfaces and experiments on highly oriented polycrystals leave little doubt that deformation is dominated by basal slip, which is operative even at ambient temperatures. These results, together with microstructural evidence strongly indicate that the bonding between the B-group elements and the transition metal carbide or nitride layers is relatively weak.

The structure of Ti_3SiC_2 and its lattice parameter were first determined in the late 1960s [3]. A hexagonal structure was proposed (Fig. 1a) with $a = 0.309$ nm and $c = 1.766$ nm. The atomic positions of the Ti atoms correspond to the $2a$, Si to the $2b$ and C to the $4f$ Wyckoff positions of the space group $D_{6h}^4 - P6_3/mmc$ (space group number 194, [4]) Since that time the lattice parameters have been measured on chemical vapour deposition (CVD) samples [5], on single crystals [6], and by convergent beam electron diffraction in a transmission electron microscope [7], which independently confirmed the X-ray diffraction information. The result of these studies are summarized in Table I, and are in general agreement with the original values.

As far as we are aware, the only paper in the literature that deals with the structure of Ti_3GeC_2 is [8], which showed that it is isostructural with Ti_3SiC_2, with $a = 0.306$ nm and $c = 1.766$ nm. Similarly, to the best of our knowledge, the lattice parameters of Ti_2GeC, the structure of which is shown schematically in Fig. 1b, have only been determined once [9], and are listed in Table I.

In order to solve for the interatomic distances, the z-parameter, defined as the ratio of $d_{C,312}/c$ (see Fig. 1a), has to be known. Jeitschko and Nowotny [3] report a value of 0.1357 for Ti_3SiC_2. As far as we are aware z was never determined for Ti_3GeC_2. For Ti_2GeC, the reported z value is 0.086 (for the H-phases the z-parameter is defined as: $z = d_c/2c$, where d_c is defined in Fig. 1b, and c is the lattice parameter). The method used to arrive at these values was by a minimization, through trial and error, of the differences between the measured and calculated intensities of the X-ray reflections for various z-parameter values. Unfortunately, this technique is quite inaccurate and can result in significant errors because of preferred orientation and other systemic errors in measuring and quantifying the intensities of the X-ray reflections.

Therefore, the aim of this investigation is to determine the bond lengths in the 312 and the H-phase with higher accuracy, than previously reported.

0022–2461 © *1999 Kluwer Academic Publishers*

TABLE I Lattice parameters of the ternary compounds Ti_3SiC_2, Ti_3GeC_2 and Ti_2GeC determined in this work and those previously reported

Compound	a (nm)	c (nm)	c/a	Reference
Ti_3SiC_2	$0.306\,65 \pm 0.000\,05$	1.7671 ± 0.0003	5.7625	
	0.3068 ± 0.0002	1.7669 ± 0.0006	5.75	[3]
	0.3066	1.7646	5.755	[6]
	0.3064	1.765	5.76	[5]
	0.307	1.769	5.762	[7]
Ti_3GeC_2	$0.308\,74 \pm 0.000\,05$	1.7806 ± 0.0003	5.767	
	0.3077	1.776	5.772	[8]
Ti_2GeC	$0.308\,08 \pm 0.000\,06$	1.2929 ± 0.0003	4.197	
	0.3079	1.293	4.199	[9]

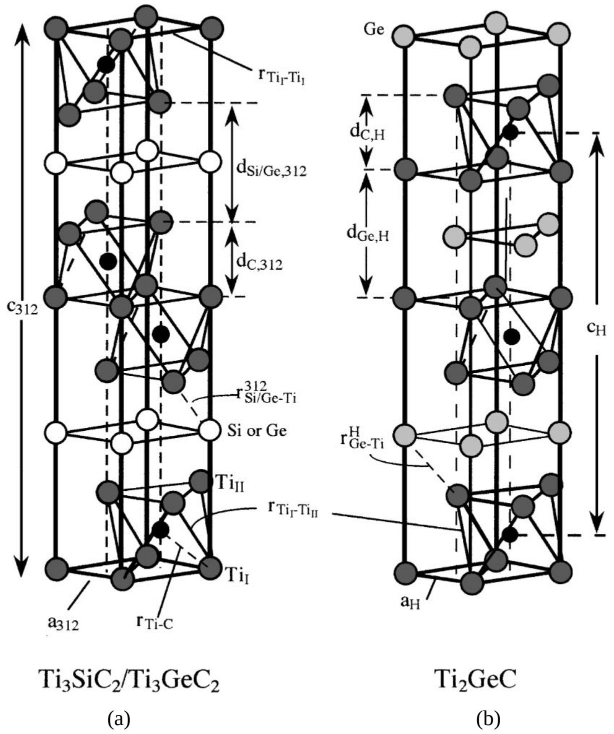

Figure 1 Unit cell of (a) the 312 phases and (b) the H-phases.

2. Experimental procedure

2.1. Method of determination of interatomic distances

As shown in Fig. 1a, b, the c-axis in the 312 and H-phases can be expressed by linear combinations of various distances along the c-axis. From the figure it is obvious that

$$
\begin{aligned}
c_{312} &= 4\,d_{C,312} + 2\,d_{Si/Ge,312} \\
c_H &= 2\,d_{C,H} + 2\,d_{Ge,H}
\end{aligned}
\tag{1}
$$

where $d_{C,312}$ is double the distance of the interplanar spacing between hexagonal nets of Ti and C atoms and $d_{Si/Ge,312}$ is double the interplanar spacing between the close-packed planes of Ti and Si or Ge in the 312 phases. $d_{C,H}$ and $d_{Ge,H}$ are the corresponding distances in the H-phase (Fig. 1b). Once these distances are known, together with the lattice parameters, all the interatomic distances can be determined.

The relationships between the interatomic distances and the lattice parameters in the 312 phases are

$$
\begin{aligned}
r_{Ti_I-Ti_I} &= a \\
r^{312}_{Ti-Si/Ge} &= \left(\frac{a^2_{312}}{3} + \frac{d^2_{Si/Ge,312}}{4}\right)^{1/2} \\
r^{312}_{Ti_I-Ti_{II}} &= \left(\frac{a^2_{312}}{3} + d^2_{C,312}\right)^{1/2} \\
r^{312}_{Ti-C-Ti} &= \left(\frac{4a^2_{312}}{3} + d^2_{C,312}\right)^{1/2}
\end{aligned}
\tag{2}
$$

where $r^{312}_{Ti-Si/Ge}$, $r^{312}_{Ti_I-Ti_I}$, $r^{312}_{Ti_I-Ti_{II}}$ and $r^{312}_{Ti-C-Ti}$ are, respectively, the interatomic distances between the Ti and Si or Ge atoms, the Ti atoms within the close-packed planes, the Ti atoms not in the close-packed planes and double the Ti–C distance. All distances are defined in Fig. 1a. Note that an identical set of equations applies to Ti_2GeC.

Focusing on Ti_3GeC_2 and Ti_2GeC and rearranging Equation 1, one obtains the following expressions

$$
\begin{aligned}
d_{C,312} &= \frac{c_{312} - c_H}{2} - (d_{C,312} - d_{C,H}) \\
&\quad - (d_{Ge,312} - d_{Ge,H}) \\
d_{Ge,312} &= c_H - \frac{c_{312}}{2} + 2(d_{C,312} - d_{C,H}) \\
&\quad + 2(d_{Ge,312} - d_{Ge,H})
\end{aligned}
\tag{3}
$$

where 312 in this case refers to Ti_3GeC_2.

The Ti–C and Ti–Ge clusters in the H and 312 phases are identical and thus it is not unreasonable to assume that the Ti–C and Ti–Ge interatomic distances would be almost identical. Consequently, the followings assumptions are made

$$
r^{312}_{Ti-Ge} = r^H_{Ti-Ge} \quad \text{and} \quad r^{312}_{Ti-C} = r^H_{Ti-C}
\tag{4}
$$

TABLE II Interatomic distances (nanometres) in the ternary compounds Ti_3SiC_2, Ti_3GeC_2 and Ti_2GeC determined in this work and those reported by [3] and [9]. For comparison's sake the lattice parameters of $TiC_{0.66}$ [3] are also included

		Ti_3SiC_2			Ti_2GeC	
	$TiC_{0.66}$ [13]	This work	[3]	Ti_3GeC_2	This work	[9]
$r_{Ti_I-Ti_I}$	0.3055	0.306 65	0.3068	0.308 74	0.308 08	0.3079
$r_{Ti_I-Ti_{II}}$	0.3055	0.304 54	0.2971	0.303 49	0.304 17	0.284 76
$r_{Ti-C-Ti}$	0.4320	0.432 18	0.427	0.432 93	0.432 93	0.4195
$r_{Ti-Si/Ge}$		0.262 63	0.2696	0.267 54	0.267 54	0.2768
d_C	0.2494	0.247 79	0.2385	0.245 63	0.246 74	0.222 37
$d_{Si/Ge}$		0.387 97	0.4065	0.399 03	0.399 71	0.4241
z-parameter		0.014 02	0.0135		0.009 53	0.0086

where r^{312}_{Ti-Ge} and r^{312}_{Ti-C} are, respectively, the Ti–Ge and Ti–C distances in the 312 phase and r^{H}_{Ti-Ge} and r^{H}_{Ti-C} the corresponding distances in the H phase. Combining Equations 2 and 4 and rearranging terms one obtains

$$\Delta d_C = d_{C,312} - d_{C,H} = \frac{4}{3(d_{C,312} + d_{C,H})}\left(a_H^2 - a_{312}^2\right)$$

$$\Delta d_{Ge} = d_{Ge,312} - d_{Ge,H} \qquad (5)$$

$$= \frac{4}{3(d_{Ge,312} + d_{Ge,H})}\left(a_H^2 - a_{312}^2\right)$$

Between Equations 3 and 5 there are four unknowns ($d_{C,312}$, $d_{C,H}$, $d_{Ge,H}$, $d_{Ge,312}$) and four equations. A closed form solution is easily arrived at by the method of successive approximations. The solution converges quite rapidly if the starting value for $d_{C,H}$ is taken to be $(c_{312} - c_H)/2$ while that for $d_{Ge,312} = c_H - 0.5c_{312}$. The results are listed in Table II.

Silicon does not form an H-phase; consequently, this technique cannot be used to solve for the interatomic distances in Ti_3SiC_2. Instead the interatomic distances are determined by comparing the two 312 structures. The basic assumption here is that the differences between the Ti–Si and Ti–Ge distances are due to the differences in atomic radii. In other words the following assumption is made

$$r_{Ti-Si} = r_{Ti-Ge} - (r_{Ge} - r_{Si}) \qquad (6)$$

where r_{Ge} and r_{Si} are the atomic radii of the Ge and Si atoms, respectively. These values in turn can be accurately determined from precise lattice parameter measurements on Si and Ge. The values used here are $r_{Ge} = 0.122\,49$ nm and $r_{Si} = 0.117\,58$ nm, and the difference is thus 0.004 91 nm. Using this value r_{Ti-Si} is calculated from Equation 6 and $d_{Si,312}$ is calculated from one of the expressions in Equation 2, namely

$$d_{Si,312} = 2\left(r^2_{Ti-Si} - \frac{a^2_{Si,312}}{3}\right)^{1/2}$$

Similarly $d_{C,312}$ can be calculated from

$$d_{C,312} = \frac{c_{Si,312} - 2d_{Si,312}}{4}$$

2.2. Materials and methods

The processing details are discussed elsewhere [1, 2]. In summary, −325 mesh Ti powders (99% purity) were mixed with either SiC and graphite, or Ge (−325 mesh, 99.99% purity, Johnson Matthey) in the proper molar ratios. The powders were then cold pressed to form a green body that was placed in a vacuum hot press and subjected to the following temperature–pressure cycles:

1. Ti_3SiC_2: heating to 1600 °C at 10 °C min^{-1} and held at that temperature for 4 h under a pressure of 40 MPa before furnace cooling.
2. Ti_3GeC_2: heating at 5 °C min^{-1} to 900 °C, soak at that temperature for 1 h, further heated at the same rate to 1200 °C for 4 h and then heated further to 1500 °C and held at that temperature for an additional 4 h before furnace cooling. The load was ramped at 22 kN h^{-1} up to a maximum load that corresponded to a pressure of 45 MPa. Both the temperature and pressure ramps were started simultaneously.
3. Ti_2GeC: heating at 5 °C min^{-1} to 900 °C, soak at that temperature for 1 h, further heated at the same rate to 1200 °C for 4 h and then slowly cooled. The pressure cycle was identical to that used for Ti_3GeC_2.

X-ray diffraction of powdered samples that were machined out of the centre of the densified body were X-rayed using CuK_α radiation and a Ni-filter. The lattice parameters were determined from the positions of the peaks using a precise, self-correcting method [10, 11]. This method accounts for goniometer aberrations, especially the shift, s, from the goniometer axis of the sample reflecting plane. Using this method the shift, s, is included as an unknown. Other aberrations, i.e. the zero position of the detector, the horizontal and vertical divergences of the X-ray beam, etc., are included in the free term of the Bragg equations and have been estimated by well known formulae, see for example [12]. The additional Bragg equation needed to determine s is provided by a correcting reflection in the X-ray patterns–the Bragg reflection used here is one that occurs at small angles (approximately 10–20°) to obtain higher accuracy in the determination of the s values, because the reflections at small Bragg angles are more sensitive to shifts in s than the reflections at higher angles. The latter were used for the determination of the lattice parameters.

The lattice parameters were determined from the positions of the maxima of the reflections. The positions of the 1 1 0 and 0 0 1 6 reflections were used to determine the lattice parameters for the 3 1 2 phases, while the 1 1 0 and 0 0 1 2 peaks were used for the H-phase. The 0 0 2 and 0 0 1 6 reflections were used as the correcting reflections for the 312s, while the 0 0 2 and 0 0 1 2 were used for the Ti_2GeC. The angles at which these reflections occurred were used to account for the shift in *s* [10, 11].

The results are listed in Table I, and compared with other reported values. With the exception of the lattice parameters of Ti_3GeC_2, which differ by about 0.3% from the only other reported value, they are in excellent agreement.

3. Results and discussion

Using the values of the lattice parameters measured here, and the procedure outlined above, the interatomic distances were solved for and the results are listed in Table II, together with values of the lattice parameters for $TiC_{0.66}$ taken from [13]. $TiC_{0.66}$ was used instead of TiC because the ratio of C to Ti in the 312 phase is 0.66. For comparison's sake the interatomic distances reported in [3] for Ti_3SiC_2 and in [9] for Ti_2GeC are also included.

Before discussing the results it is important to discuss briefly the assumptions made in Equations 4 and 6. In the first assumption, Equation 4, it is assumed that the Ti–C and Ti–Ge distances are identical in the Ti_3GeC_2 and Ti_2GeC structures. Given that both distances reflect the same cluster of atoms, this is not an unreasonable assumption. The second assumption is that the differences in the Ti–Si and Ti–Ge distances are equal to the differences in the radii of Si and Ge, which again is quite plausible. It is worth noting that we are not claiming that the radii in the ternaries are equal to those in the covalent crystal, but rather the much less egregious assumption that the differences in radii in the ternaries are due to the differences in radii in the covalent crystals. In other words, any distortion that is occurring to the atoms as a result of their being in the octahedral arrangement of the Ti atoms will occur equally or proportionally for both Si and Ge.

A perusal of Table II clearly indicates that the interatomic distances determined in this work and those reported earlier are quite different. The differences are traceable to the value of the *z*-parameter; in the previous work *z* is significantly smaller than the values determined here. As discussed below, one of the ramifications of choosing a smaller *z*-parameter is that the Ti–C–Ti distances one calculates for the ternary compounds become significantly shorter than the corresponding distances in TiC_x. The Ti–C–Ti distance in TiC_x is a weak function of x (it varies from 4.33 to 4.32, i.e. a 0.2% change, as x changes from 1 to 0.66 [13]), consequently it is unreasonable to assume that that distance should change that dramatically when going from TiC_x to the ternary compounds. The fact that the Ti–C–Ti distances calculated in this work and listed in Table II, are in such good agreement with the Ti–C–Ti distance in $TiC_{0.66}$ is indirect evidence for the soundness of our method and assumptions.

This distortion in the Ti–C–Ti distances can be further quantified as follows. The functional dependence of the changes in the $r_{\mathrm{Ti-C-Ti}}$ distances in the ternaries normalized with respect to $TiC_{0.66}$ on, $\varepsilon_{\mathrm{Ti_I-Ti_I}}$, defined as

$$\varepsilon_{\mathrm{Ti_I-Ti_I}}(\%) = \frac{r^{312}_{\mathrm{Ti_I-Ti_I}} - r^{\mathrm{TiC}}_{\mathrm{Ti_I-Ti_I}}}{r^{\mathrm{TiC}}_{\mathrm{Ti_I-Ti_I}}} \times 100$$

is plotted in Fig. 2a, together with the corresponding results of Nowotny and coworkers [3, 9]. The weak dependence of $r_{\mathrm{Ti-C-Ti}}$ on the $\mathrm{Ti_I}$–$\mathrm{Ti_I}$ distances, i.e. *a*

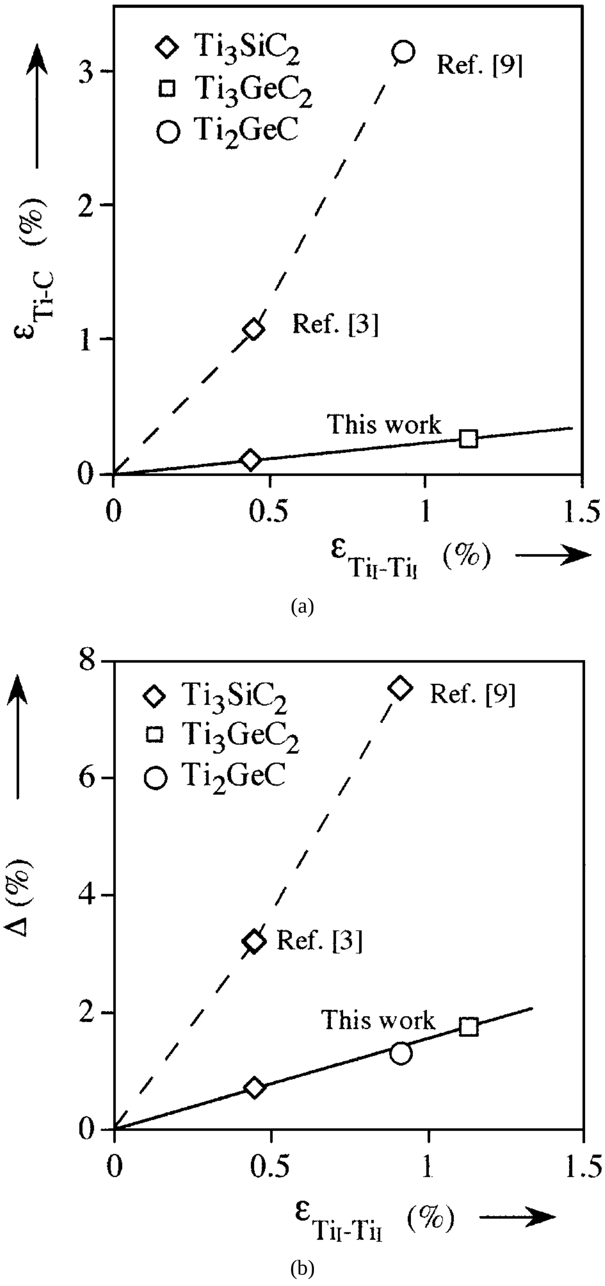

Figure 2 Dependence of (a) the relative change in the Ti–C–Ti interatomic distances on the relative changes in the $\mathrm{Ti_I}$–$\mathrm{Ti_I}$ distances in the ternary compounds normalized with respect to Ti–$C_{0.66}$ (see text for details), and (b) the distortion of the TiC octahedra in the ternary phases on the relative changes in the $\mathrm{Ti_I}$–$\mathrm{Ti_I}$ distances normalized with respect to $TiC_{0.66}$.

parameter, when compared with the previous results is apparent from the figure. Furthermore our results appear to extrapolate to the origin as they should. The largest distortion of about 0.2% occurs in Ti_3GeC_2, and is less for the other two phases, and significantly smaller than the previous results.

In addition to affecting the Ti–C–Ti distances in the ternaries slightly as compared with TiC, the existence of Si hexagonal layers in the Ti_3SiC_2 structure, and of Ge hexagonal layers in the Ti_3GeC_2 and the Ti_2GeC structures leads to the anisotropic deformation of the regular CTi_6 octahedrons that are present in TiC_x. This distortion occurs by expansion along the a-axis and contraction along the c-axis, and can be quantified by defining the following function

$$\Delta(\%) = \frac{r_{\mathrm{Ti_I-Ti_{II}}} - r_{\mathrm{Ti_I-Ti_I}}}{r_{\mathrm{Ti_I-Ti_I}}} \times 100$$

When plotted versus $\varepsilon_{\mathrm{Ti_I-Ti_I}}$ (Fig. 2b), and once again compared with previous results [3, 9] the differences become apparent. Based on our calculations the maximum distortion of less than 2% occurs in Ti_3GeC_2. The corresponding distortion in Ti_2GeC reported earlier is greater than 7% and extrapolates to a value greater than 9% for Ti_3GeC_2. In both cases, however, the deformation of the CTi_6 octahedrons in the Ge compounds Ti_3GeC_2 and Ti_2GeC is larger than in the Si compound Ti_3SiC_2.

Based on our calculations, the changes in Ti–C–Ti distances realized by the deformation of CTi_6 octahedrons, are smaller than the changes in the Ti–Ti distances. This implies that the distortion is realized mostly by bond rotations, which have to be energetically preferable to changing the equilibrium distances between the Ti and C. A significant increase in the interatomic distances would lead necessarily to an increase in the pair interaction potential, which in turn would result in a significant increase in the crystal energy. Bond rotations on the other hand should not lead to significant increases in the crystal energy because they would not greatly affect the pair interaction potential. Furthermore, the $\mathrm{Ti_I}$–$\mathrm{Ti_{II}}$ distances in the ternary compounds are still larger than the Ti–Ti distances in metallic Ti (0.291 nm).

It is worth mentioning that this tendency of the octahedra to distort has been observed in X-ray diffraction studies of annealed substoichiometric TiC_x. $TiC_{0.67}$ that was annealed for a month at 730 °C showed a slight rhombohedral distortion with a rhombohedral angle $\alpha = 90.2°$, with the lattice being compressed along the (1 1 1) directions [14]. The same group has also shown that ordering occurs in TiC when $x < 0.67$ and the temperature $T < 1000$ K. Two forms of order have been observed: a cubic $Fd3m$ type in which the (1 1 1) planes are alternately one-quarter and three-quarters filled, and the $R_3^- m$ or CuPt ordered structure where the close-packed planes are alternately full or empty. Theoretical calculations have shown that the CuPt structure had a slight energy advantage [15]. The similarity between the CuPt-type structure and Ti_2GeC would lend credence to that conclusion.

Finally, it is worth speculating on the origin of the observed distortion. At this time it is felt that the distortion could result from an electron transfer from in between the Si–Ti close-packed planes into the d–d bonds of the $\mathrm{Ti_I}$–$\mathrm{Ti_{II}}$ atoms. Such a charge transfer would result in the observed distortion as well as result in a weakening of the Ti–Si bonds. It is this weakening of the bonds that allows the planes to shear easily with respect to each other and which would account for most of their mechanical properties, such as relatively low hardnesses, machinability and a deformation mechanism that is dominated by basal slip [1, 2]. It is acknowledged here that the exact details of the electronic structure and electron density distributions cannot be answered without recourse to more sophisticated numerical models. However, the results obtained in this work should be accounted for in any successful model.

4. Conclusions

1. The bond lengths in the ternary compounds Ti_3SiC_2, Ti_3GeC_2 and Ti_2GeC were determined with precision using a method of comparison of the lattice parameters of the structures containing the same atomic layers.

2. The results obtained show while anisotropic deformation, i.e. expansion along the a-axis and contraction along the c-axis, of the CTi_6 octahedrons occurs in ternary compounds, it is significantly smaller than previously believed.

3. The Ti–C–Ti distances calculated for the ternary compounds are comparable with those in TiC_x. This indicates that the distortion is accommodated by rotation of Ti–C bonds in the CTi_6 octahedrons rather than their shrinking.

4. The results obtained indicate the difference in anisotropic deformation of the CTi_6 octahedrons depending on the types of atoms located outside the CTi_6 octahedrons. The deformation of the CTi_6 octahedrons is largest in Ti_3GeC_2 and smallest for Ti_3SiC_2.

Note added in proof

Since this paper was submitted, the following two papers on the structure of Ti_3SiC_2 determined by Reitveld analysis of neutron data, have been accepted for publication in J. Phys. Chem. Sol.; i) E. H. Kisi, J. A. A. Crossley, S. Kyhra and M. W. Barsoum, and ii) M. W. Barsoum, T. El-Raghy, C. J. Rawn, W. D. Porter, H. Wang, E. A. Payzant and C. R. Hubbard. Both papers confirm the distances calculated by Jeitchko and Nowotny for Ti_3SiC_2. For that structure, the difference between our data and the neutron diffraction data is of order of the estimated accuracy of the neutron diffraction data.

Acknowledgements

We would like to thank Mr T. El-Raghy and Dr D. Brodkin for fabricating the samples. We also would like to acknowledge the financial support of the National Science Foundation for this work under grant DMR-9634015.

References

1. M. BARSOUM and T. EL-RAGHY, *J. Amer. Ceram. Soc.* **79** (1996) 1953.
2. M. BARSOUM, D. BRODKIN and T. EL-RAGHY, *Scripta Metall Mater.* **36** (1997) 535.
3. W. JEITSCHKO and H. NOWOTNY, *Mh. Chem.* **98** (1967) 329.
4. T. HAHN (ed.), "International Tables for Crystallography," 3rd Edn (Kluwer, Dordrrecht, 1992).
5. T. GOTO and T. HIRAI, *Mater. Res. Bull.* **22** (1987) 2295.
6. J. J. NICKL, K. K. SCHWEITZER and P. LUXENBERG, *J. Less Common Metals* **26** (1972) 283.
7. S. ARUNAJATESAN and A. H. CARIM, *Mater. Lett.* **20** (1994) 319.
8. H. WOLFSGRUBER, H. NOWOTNY and F. BENESOVSKY, *Mh. Chem.* **98** (1967) 2401.
9. W. JEITSCHKO, H. NOWOTNY and F. BENESOVSKY, *ibid.* **94** (1963) 1201.
10. M. Y. GAMARNIK, *Dokladi Acad. Nauk. Ukr. SSR* **1** (1982) 7.
11. *Idem,* "Selfcorrecting Method for Precise Determination of Lattice Parameters" (Ed. of Institute of Geochemistry and Physics of Minerals, Academy of Science of Ukraine, Kiev 1984) p. 27.
12. D. M. KHEIKER and L. S. ZEVIN, "X-ray Diffractometry" (Fizmatgiz, Moscow, 1963) p. 380.
13. A. COTTRELL, "Chemical Bonding in Transition Metal Carbides" (Institute of Materials, London, 1995) p. 51.
14. V. MOISY-MAURICE, N. LORENZELLI, C. D. DE NOVION and P. CONVERT, *Acta Metall.* **30** (1982) 1769.
15. J. P. LANDESMANN, G. TREGLIA, P. TURCHI and F. DUCASTELLE, *J. Physique* **46** (1985) 1001.

Received 15 July 1997
and accepted 27 July 1998