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Crystallographic relations between Ti_3SiC_2 and TiC

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Abstract Ti_3SiC_2 is a so-called not-so-brittle ceramic that combines the merits of both metals and ceramics. However, many previous works demonstrated that its bonding nature and properties were strongly related to TiC. In this paper the crystallographic relations between Ti_3SiC_2 and TiC were established and described based on the transmission electron microscopy investigation on the $\text{Ti}_3\text{SiC}_2/\text{TiC}$ interface in Ti_3SiC_2 based material. At $\text{Ti}_3\text{SiC}_2/\text{TiC}$ interface, the following crystallographic relationships were identified: $(111)\text{TiC} // (001)\text{Ti}_3\text{SiC}_2$, $(002)\text{TiC} // (104)\text{Ti}_3\text{SiC}_2$, and $[1\bar{1}0]\text{TiC} // [110]\text{Ti}_3\text{SiC}_2$. Based on the above interfacial relations an interfacial structure model was established. The structure of Ti_3SiC_2 could be considered as two-dimensional closed packed layers of Si periodically intercalated into the (111) twin boundary of $\text{TiC}_{0.67}$ (Ti_3C_2). The intercalation resulted in the transformation from cubic $\text{TiC}_{0.67}$ to hexagonal Ti_3SiC_2 . In the opposite case, de-intercalation of Si from Ti_3SiC_2 caused the transformation from hexagonal Ti_3SiC_2 to cubic $\text{TiC}_{0.67}$. Understanding the crystallographic relations between Ti_3SiC_2 and TiC is of vital importance in both understanding the properties and optimizing the processing route for preparing pure Ti_3SiC_2 .

Key words Titanium silicon carbide · Titanium carbide · Crystal structure · Interface

1 Introduction

Recent success in the synthesis and densification of Ti_3SiC_2 has disclosed the unusual properties of this promising material [1, 2, 3, 4]. The properties reported so far, which are the merits of both metals and ceramics, include: high melting point, low density, high modulus,

damage tolerance at room temperature, good thermal and electrical conductivity, excellent thermal shock and high-temperature-oxidation resistance. Such a unique combination of the properties embodied in one material is unexpected and is attractive to material scientists as well as physicists and chemists. These properties are believed to be strongly related to crystal and electronic structure and we are intrigued to establish the relations between them.

In reviewing the published papers concerning the processing and microstructure of Ti_3SiC_2 in literature, one will be amused by the following phenomena. (1) On one hand, in Ti_3SiC_2 synthesized using Ti, Si (or SiC) and C as initial materials, no matter what method was used, TiC always existed as the main impurity [5, 6, 7, 8]. (2) On the other hand, TiC could be used as one of the starting material to synthesize Ti_3SiC_2 , i.e. TiC could transform to Ti_3SiC_2 in the presence of Si [9, 10]. (3) Immersion of Ti_3SiC_2 samples in molten cryolite at 960°C resulted in the topotaxial de-intercalation of Si atoms from the basal planes of Ti_3SiC_2 to form a partially ordered cubic phase with approximate chemistry of $\text{Ti}(\text{C}_{0.67}, \text{Si}_{0.06})$ [11]. (4) The ab initio calculations on Ti_3SiC_2 and TiC revealed that the bond length of Ti-C in Ti_3SiC_2 was the same as that in TiC [12]. The facts listed above indicated that Ti_3SiC_2 is strongly related to TiC. Understanding the relations between them is vital in both understanding the properties of Ti_3SiC_2 and optimizing the processing route for Ti_3SiC_2 . In this paper, details on the crystallographic relations between Ti_3SiC_2 and TiC were established and described based on the observation of the $\text{Ti}_3\text{SiC}_2/\text{TiC}$ interface by transmission electron microscopy.

2 Relation to previous works

The crystal structure of Ti_3SiC_2 was first determined by Jeitschko and Nowotny [14] by means of single crystal photographs. The lattice parameters of the hexagonal cell were $a=3.06_8$, $c=17.66_9$ Å, respectively. The Ti atoms occupy the positions 2a and 4f ($Z_{\text{Ti}}=0.135$), the Si atoms

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occupy 2b and the C atoms occupy 4f ($Z_C=0.567_5$) of the space group $P6_3/mmc$. Arunajatesan and Carim [15] examined the symmetry, crystal structure and lattice parameters of Ti_3SiC_2 by convergent beam electron diffraction (CBED) and the X-ray diffractometry (XRD). Sun and Zhou [3] investigated the electronic structure and bonding properties in Ti_3SiC_2 . That the crystal structure and properties between Ti_3SiC_2 and TiC are related was known since the identification of Ti_3SiC_2 . Jeitschko and Nowotny [14] described the crystal structure of Ti_3SiC_2 as two edge-shared layers of Ti_6C octahedral groups which were linked together by a two-dimensional closed-packed layer of Si. They also found the similar bond length of Ti-C-Ti for Ti_3SiC_2 (which was 4.27 Å) and that for TiC_{1-x} ($x=1/3$, which was 4.32 Å). Although the co-existence of Ti_3SiC_2 and TiC was observed in Ti_3SiC_2 based materials by many of researchers [5,6,7,8], the crystal structure relations between them were seldom discussed. Recently, Barsoum et al [11] observed the transformation of hexagonal Ti_3SiC_2 to partially ordered cubic phase of $Ti(C_{0.67}, Si_{0.06})$ due to the de-intercalation of Si. The facts that Ti_3SiC_2 could be synthesized using TiC and Si as starting material were also attractive to the present authors to investigate the crystallographic relations between Ti_3SiC_2 and TiC. In this work we discussed in detail the crystallographic relations between Ti_3SiC_2 and TiC based on transmission electron microscopy investigation on the interfacial structure of Ti_3SiC_2/TiC . This work is of vital importance in both understanding the properties and optimizing the processing route for preparing pure Ti_3SiC_2 .

3 Experimental

The material used in this work was Ti_3SiC_2 , TSC^{ZS510}, which was prepared by the in-situ hot pressing/solid-liquid reaction method. Briefly, the material was made in the following procedure. Ti, Si, and graphite powders with near stoichiometrical compositions

were mixed and milled in a polypropylene jar for 10 h. After ball milling, the powders were cold-pressed into discs of 50 mm in diameter and then put in a graphite die. The in-situ hot pressing/solid-liquid reaction was conducted under a flowing argon atmosphere in a furnace using graphite as heating element. The material TSC^{ZS510} was hot pressed at 1550°C under a pressure of 40 MPa for 60 min. Details for the in-situ hot pressing / solid-liquid reaction process has been described elsewhere [5]. The Ti_3SiC_2 content in TSC^{ZS510} is 93 wt%, which was calculated using the Rietveld method [13], and the main impurity was TiC.

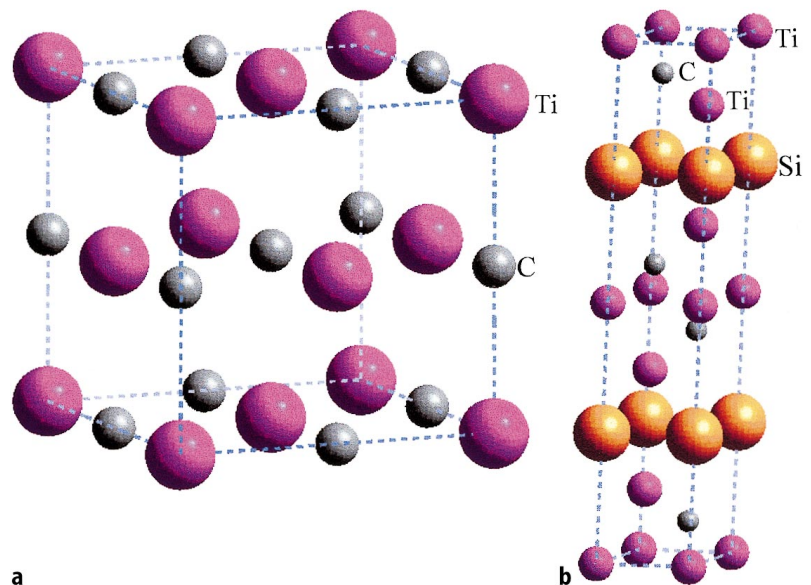
To understand the crystallographic relations between Ti_3SiC_2 and TiC, the Ti_3SiC_2/TiC interface was observed by transmission electron microscopy. Samples for TEM observation were made in the following procedure. Thin discs of 0.5 mm in thickness and 3 mm in diameter were cut by electrical discharge method followed by mechanical thinning and polishing by Dimple Grinder. Thin foils were made by ion beam milling at 5 kV using an incident angle of 15°. Microstructure observation was performed in a Philips EM-420 transmission electron microscope equipped with an energy dispersive spectroscopy (EDS) system. Selected area diffraction (SAD) and micro-diffraction (MD) techniques were used to determine the crystallographic relationship and interfacial structure between Ti_3SiC_2 and TiC.

4 Results

Before describing the interfacial structure and crystallographic relations between Ti_3SiC_2 and TiC, it is relevant to give details of the crystal structure of both Ti_3SiC_2 and TiC. When considering the crystal structure of TiC, the binary carbide is modeled in a 1:1 composition in the present work for the simplicity although it is known to be sub-stoichiometric in carbon, i.e. TiC_x with $0.56 < x < 0.98$. TiC crystallizes in the NaCl-type structure (space group $Fm\bar{3}m$) with four formula per unit cell, as shown in Fig. 1 (a). The lattice constant is $a=0.4327$ nm. Ti and C are at the origin and $(1/2, 1/2, 1/2)$ positions, respectively. Ti and C are octahedrally coordinated with each other, consequently, Ti_6C octahedra share edges.

Ti_3SiC_2 has a hexagonal crystal structure with a space group of $P6_3/mmc$, as shown in Fig. 1 (b) [14]. The lat-

Fig. 1 (a) Crystal structure of TiC; (b) Crystal structure of Ti_3SiC_2



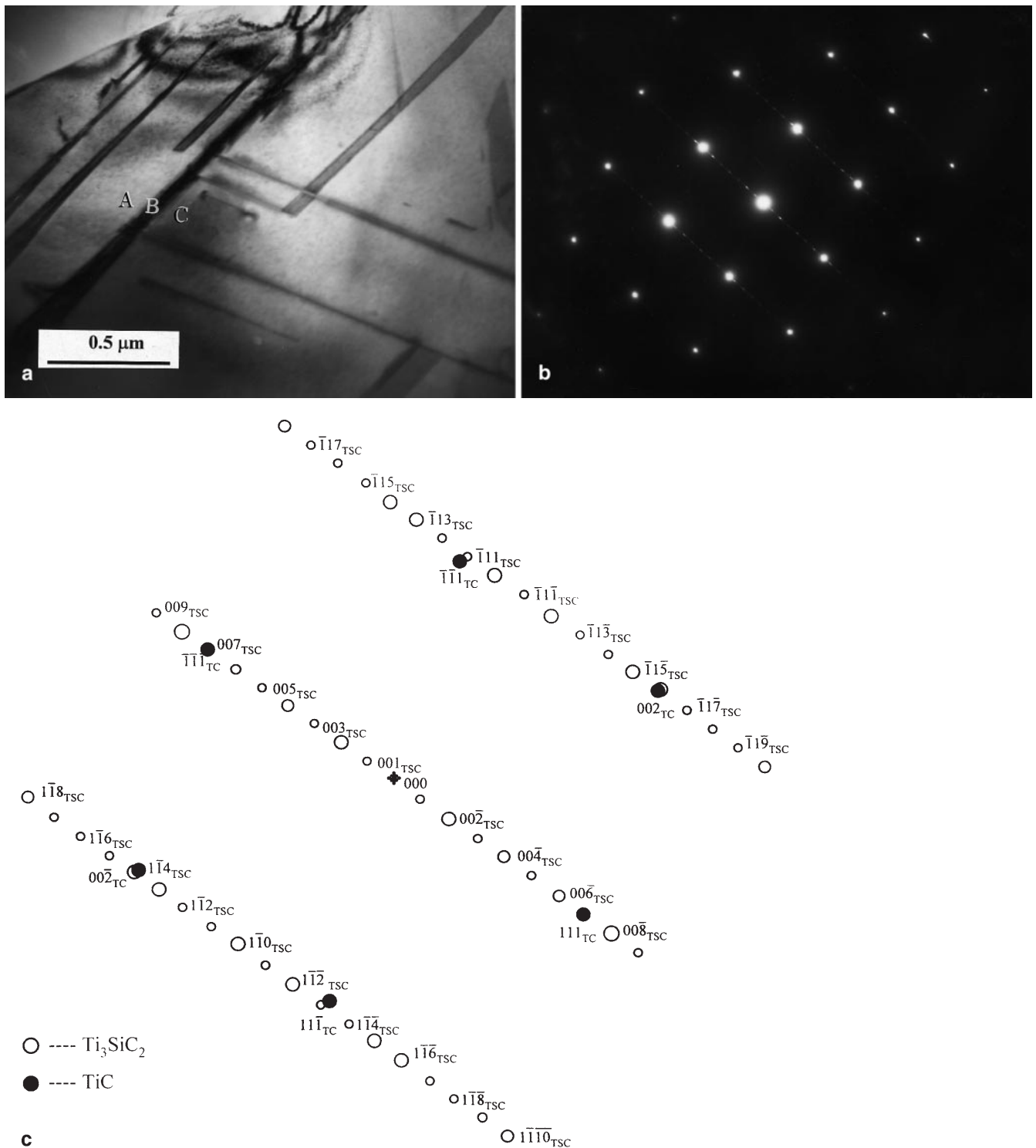


Fig. 2 (a) Bright field image of a TiC grain containing thin bands of Ti₃SiC₂, the thin band looked like twins in TiC; (b) Selected area diffraction patterns from the region near Ti₃SiC₂ bands, the electron beam was parallel to [110] zone axis of TiC and [110] zone axis of Ti₃SiC₂; (c) Indexed diffraction patterns of Fig. 2 (b)

tice parameters are $a=0.3068$ nm and $c=1.7669$ nm with two formula per unit cell. The atomic positions of Ti corresponds to the 2a and 4f ($Z_{\text{Ti}}=0.135$), Si to 2b, and C to the 4f ($Z_{\text{C}}=0.567$) [15]. The structure of Ti₃SiC₂ can be described as two edge-shared Ti₆C octahedron layers linked together by a two-dimensional closed packed Si layer.

To understand the crystallographic relationship between Ti₃SiC₂ and TiC, microstructure and interface of

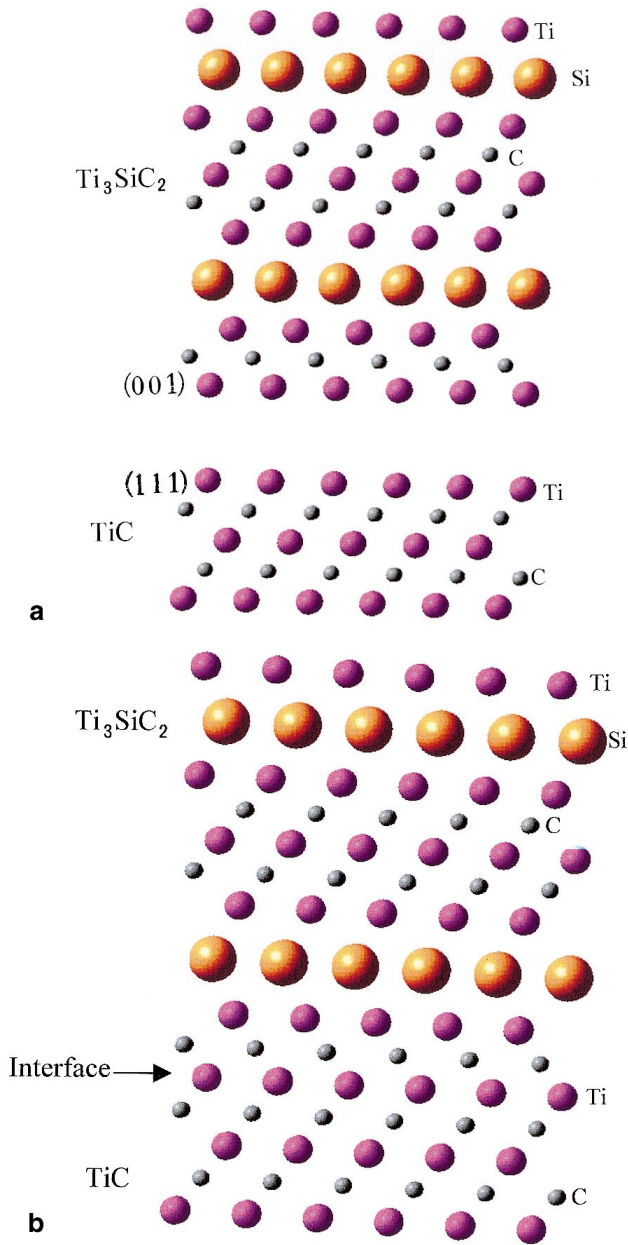


Fig. 3 (a) Projection of atoms on (110) plane of Ti_3SiC_2 (upper part) and on (110) plane of TiC (lower part); (b) The interfacial structure model based on the experimental observed crystallographic relations

Ti_3SiC_2 containing TiC (TSCZS⁵¹⁰) was investigated. In Ti_3SiC_2 containing TiC, inclusions of either TiC imbedded in Ti_3SiC_2 or Ti_3SiC_2 imbedded in TiC were identified in previous work [16]. In this work we examined the $\text{Ti}_3\text{SiC}_2/\text{TiC}$ interface in TiC grains containing Ti_3SiC_2 . Figure 2 (a) shows a bright field image of a TiC in which contrast (thin bands) from second phase is seen. The thin bands looked like the {111} twins in TiC. Tilting the foil, however, we did not find extra spots from {111} twins. We thus assume the contrast of the bands in Fig. 2(a) was from the second phase. To confirm this assumption, EDS analysis and dark field image technique was used.

When the probe beam of EDS X-ray was scanned from A to C as shown in Fig. 2 (a), an abrupt increase in Si content was observed at B. So we suppose that the bands in Fig. 2 (a) were thin layers of Ti_3SiC_2 . Then we tilted the foil laterally until the electron beam was precisely aligned along the $[1\bar{1}0]$ orientation of TiC. The resulting diffraction patterns from the region near the thin Ti_3SiC_2 layers are shown in Fig. 2 (b). The figure shows that aside from the $[1\bar{1}0]$ net pattern of TiC, there is a set of weak reflections. Analysis by using the dark field image technique revealed that the weak reflections in Fig. 2 (b) were from thin layers of Ti_3SiC_2 imbedded in TiC. Figure 2 (c) shows the indexed diffraction pattern of Fig. 2 (b). The zone axis of Ti_3SiC_2 is $[110]$. Examining the diffraction patterns shown in Fig. 2 (b), we found that the (007) reflection of Ti_3SiC_2 coincided with the (111) reflection of TiC, and the (104) spot of Ti_3SiC_2 coincided with the (002) spot of TiC. In other words, (001) plane of Ti_3SiC_2 grew epitaxially on {111} facets of TiC following the crystallographic relationships of

$$(111) \text{ TiC} // (001) \text{ Ti}_3\text{SiC}_2 \quad (1)$$

$$(002) \text{ TiC} // (104) \text{ Ti}_3\text{SiC}_2 \quad (2)$$

and

$$[1\bar{1}0] \text{ TiC} // [110] \text{ Ti}_3\text{SiC}_2 \quad (3)$$

Because of the similar interplanar spacings of d_{007} for Ti_3SiC_2 of 0.2521 nm and d_{111} for TiC of 0.2499 nm (the mismatch is only 0.8%), and the similar interplanar spacings of d_{104} for Ti_3SiC_2 of 0.2278 nm and d_{002} for TiC of 0.2164 nm, the interface between TiC and Ti_3SiC_2 is a coherent boundary.

5 Discussion

The above experimental results allowed an insight investigation on the interfacial structure and crystallographic relations between Ti_3SiC_2 and TiC. The crystal structures of TiC and Ti_3SiC_2 have been described in the previous section and are shown in Fig. 1(a) and Fig. 1(b). In understanding the interfacial structure and crystallographic relations between Ti_3SiC_2 and TiC, a model of the interfacial structure between TiC and Ti_3SiC_2 was established based on the experimental results and was shown in Fig. 3. In Fig. 3(a) projection of atoms on (110) plane of Ti_3SiC_2 is shown in the upper part and that on $(1\bar{1}0)$ plane of TiC is shown in the lower part. The interfacial structure between Ti_3SiC_2 and TiC is coherent and is illustrated in Fig. 3 (b). Looking at the distribution of atoms on the (110) plane of Ti_3SiC_2 , we can see that two adjacent covalent bond chains of Ti-C-Ti-C-Ti (Ti_3C_2 or $\text{TiC}_{0.67}$) in Ti_3SiC_2 share one Si atom, which is a characteristic structure feature for Ti_3SiC_2 and Ti_3GeC_2 [12, 17]. The other feature is that the angle between the two adjacent bond chains is $\sim 130^\circ$, which is very close to the angle of the {111} twin boundary in face centered cubic crystals like TiC. From this point of view we can consider the

structure of Ti_3SiC_2 as one Si atom intercalated between the two adjacent Ti-C-Ti-C-Ti bond chains. Or in other words, we can consider the structure of Ti_3SiC_2 as two-dimensional close packed layer of Si periodically intercalated into the twin boundary of TiC, which is clearly seen from the interfacial structure model shown in Fig. 3 (b). The intercalation of Si into Ti_3C_2 ($\text{TiC}_{0.67}$) changed the cubic $\text{TiC}_{0.67}$ to hexagonal Ti_3SiC_2 ($\text{TiSi}_{0.33}\text{C}_{0.67}$) as in the case observed in our transmission electron microscopy. The presence of thin layers of Ti_3SiC_2 as was shown in Fig. 2 can be attributed to the transformation from cubic TiC to Ti_3SiC_2 due to intercalation Si into TiC. In the opposite condition, de-intercalation of Si from Ti_3SiC_2 resulted in the transformation from hexagonal Ti_3SiC_2 to cubic $\text{TiC}_{0.67}$ [11]. Based on the above experimental results, we may conclude that transformation between hexagonal Ti_3SiC_2 and cubic TiC (actually $\text{TiC}_{0.67}$) is reversible depending on the local chemistry and other experimental conditions. The interfacial structure and the less mismatch especially between (111) of TiC and (001) of Ti_3SiC_2 makes us believe that the transformation between hexagonal Ti_3SiC_2 and cubic TiC (actually $\text{TiC}_{0.67}$) is possible. If we describe the cubic TiC using the notation

$$\text{ABCABCABC...} \quad (4)$$

then the structure of Ti_3SiC_2 can be described as

$$\text{ABCSiCBASiABCSiCBA...} \quad (5)$$

In other words, the structure of Ti_3SiC_2 can be described as Si periodically intercalated at (111) twin boundary of TiC. The bond length of Ti-C is 2.13 Å and that of Ti-Si is 2.67 Å [12], so that the bonding between Si and the Ti-C-Ti-C-Ti bond chain is relatively weak. The weak bonding might allow the de-intercalation of Si from Ti_3SiC_2 and form cubic phase TiC. Understanding the above crystal structure relationship, it is not surprising that the thin layers of Ti_3SiC_2 imbedded in TiC (Fig. 2 (a)) looked just like the twins in TiC. The angle between the adjacent thin layers of Ti_3SiC_2 is $\sim 71^\circ$, which is the same as the angle between {111} twins of TiC.

Knowing the crystal structure relationship between Ti_3SiC_2 is useful in both understanding the microstructure features and optimizing the parameters for the processing of Ti_3SiC_2 . Previous work demonstrated that in most of the Ti_3SiC_2 samples (bulk or powders) prepared using Ti, Si and C as initial materials, TiC was observed as the main impurity [5, 6, 7, 8]. The presence of TiC in Ti_3SiC_2 can be attributed to the facts that Si evaporated at high temperatures so that the local chemical composition changed during the synthesis of Ti_3SiC_2 . The lack of Si then resulted in the formation of TiC, which was detected by X-ray diffraction analysis as the main impurity in Ti_3SiC_2 [5, 6, 7, 8]. Thus it is difficult to prepare pure Ti_3SiC_2 using the conventional methods. Aside from the formation of TiC during the high temperature synthesis of Ti_3SiC_2 , transformation from Ti_3SiC_2 to TiC was also observed [6, 11]. Feng et al [6] annealed bulk Ti_3SiC_2 samples at temperatures of 1600–2000°C for 2 h in vacuum. They found that the surface layer was totally trans-

formed to TiC after annealing. The transformation from Ti_3SiC_2 to TiC at high temperatures in vacuum was probably due to the de-intercalation and evaporation of Si. Barsoum et al [11] immersed Ti_3SiC_2 samples in molten cryolite at 960°C and they observed the topotactic de-intercalation of Si atoms from the basal planes of Ti_3SiC_2 which resulted in the transformation of hexagonal Ti_3SiC_2 into a partially ordered cubic phase with approximate chemistry of $\text{Ti}(\text{C}_{0.67}, \text{Si}_{0.06})$. The de-intercalation of Si from Ti_3SiC_2 and the resulted transformation from hexagonal to cubic phase indicated that Ti_3SiC_2 was not stable at high temperatures in vacuum or in chemical environment where Si was possibly diffused out.

Although de-intercalation of Si from Ti_3SiC_2 makes Ti_3SiC_2 unstable, the reverse transformation from cubic $\text{TiC}_{0.67}$ to Ti_3SiC_2 by intercalating of Si into $\text{TiC}_{0.67}$ can be used as an important route for the preparation of Ti_3SiC_2 . Li and Miyamoto [9] and Radhakrishnan et al [10] had used TiC and Si to synthesize Ti_3SiC_2 and its composites. This process could be considered as the intercalation of Si into $\text{TiC}_{0.67}$ and transferred the cubic phase to hexagonal Ti_3SiC_2 . If this hypothesis is correct, it might be possible to prepare pure Ti_3SiC_2 by first preparing a Ti_3SiC_2 based material and then intercalating Si into the TiC inclusions and transforming the impurity phase of TiC to Ti_3SiC_2 . And novel techniques need to be developed to achieve this.

6 Conclusions

$\text{Ti}_3\text{SiC}_2/\text{TiC}$ interface in Ti_3SiC_2 based material was investigated using transmission electron microscopy. The following crystallographic relationships were identified in TiC grains containing thin layers of Ti_3SiC_2 : (111) TiC // (001) Ti_3SiC_2 , (002) TiC // (104) Ti_3SiC_2 , and $[1\bar{1}0]$ TiC // $[110]$ Ti_3SiC_2 . Based on the observed interfacial relations between Ti_3SiC_2 and TiC, an interfacial structure model was established and the crystallographic relations between Ti_3SiC_2 and TiC were discussed. The structure of Ti_3SiC_2 could be considered as two-dimensional closed packed layers of Si periodically intercalated into the (111) twin boundary of $\text{TiC}_{0.67}$ (Ti_3C_2). The intercalation resulted in the transformation from cubic $\text{TiC}_{0.67}$ to hexagonal Ti_3SiC_2 . In the opposite case, de-intercalation of Si from Ti_3SiC_2 caused the transformation from hexagonal Ti_3SiC_2 to cubic $\text{TiC}_{0.67}$. Understanding the crystallographic relations between Ti_3SiC_2 and TiC is of vital importance in both understanding the properties and optimizing the processing route for preparing pure Ti_3SiC_2 .

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