Low temperature synthesis of Ti$_3$SiC$_2$ from Ti/SiC/C powders

Z. F. Zhang, Z. M. Sun and H. Hashimoto

Ternary carbide Ti$_3$SiC$_2$ was first synthesised through a pulse discharge sintering (PDS) technique from mixtures of Ti, SiC, and C with different molar ratios. Sintering processes were conducted at 1200–1400°C for 15–60 min at a pressure of 50 MPa. The phase constituents and microstructures of the synthesised samples were analysed by X-ray diffraction (XRD) technique and observed by scanning electron microscopy (SEM). The results showed that, for samples sintered from 3Ti/SiC/C powder at 1200–1400°C, TiC is always the main phase and only little Ti$_3$SiC$_2$ phase is formed. When the molar ratios Ti : SiC : C were adjusted to 3 : 1·1 : 2 and 5 : 2 : 1, the purity of Ti$_3$SiC$_2$ in the synthesised samples was improved to about 93 wt-%. The optimum sintering temperature for Ti$_3$SiC$_2$ samples was found to be in the range 1250–1300°C and all the synthesised samples contain platelike grains. The relative density of Ti$_3$SiC$_2$ samples was measured to be higher than 99% at sintering temperatures above 1300°C. It is suggested that the PDS technique can rapidly synthesise ternary carbide Ti$_3$SiC$_2$ with good densification at lower sintering temperature. MST/5647

Introduction

Ternary carbide Ti$_3$SiC$_2$ has been found to possess many of the best attributes of both metals and ceramics, for example low density (4·53 g cm^{-3}), high melting point (~3000°C),[1] good electric and thermal conductivity,[2,3] and excellent resistance to thermal shock.[4] This material has good damage tolerance and is capable of locally absorbing a lot of energy at room temperature.[5] Therefore, Ti$_3$SiC$_2$ or Ti$_3$SiC$_2$ based materials have been suggested to be promising potential candidates for many applications, for example structural materials for high temperature application; kiln furniture; wear and corrosion protection; and heat exchangers.[6]

To fabricate bulk Ti$_3$SiC$_2$ samples, various processes, including (1) chemical reaction,[7] (2) arc melting,[8] (3) HIP or SHS-HIP,[9–15] and (4) reactive sintering,[16–18] have been employed or developed. Most investigators,[9–12,16–18] preferred to consider elemental Ti/Si/C mixtures as starting powders. However, according to the literature,[9–12,16–18] the purity of the Ti$_3$SiC$_2$ synthesised from elemental powders is not sufficiently high in most cases. Barsoum and El-Raghy[13,14] successfully synthesised bulk Ti$_3$SiC$_2$ samples with high purity (more than 98 vol.-%) using Ti/SiC/C mixture powders through the HIP technique in the temperature range 1450–1600°C for 4–16 h. They found that the as sintered Ti$_3$SiC$_2$ samples displayed superior mechanical and physical properties.[6] Recently, an innovative technique for rapid sintering, i.e. pulse discharge sintering (PDS) or spark plasma sintering (SPS), has been developed to sinter ceramics and metallic materials, for example Ti–Al,[19] Nb–Al,[20] and nanomaterials.[21] The PDS apparatus originated from an electric discharge sintering machine and is similat to a conventional hot press (HP) apparatus. It is assumed that metals and ceramics with fine grains and high performances can be sintered at relatively low temperature and in a short time.[19–21]

In previous work[22,23] it has been confirmed that Ti$_3$SiC$_2$ samples can be rapidly synthesised through the PDS technique from Ti/SiC/TiC and Ti/Si/TiC powders at relatively low temperatures of 1250–1300°C. Application of the PDS technique to the synthesis of Ti$_3SiC_2$ from Ti/SiC/C powder has not previously been reported. The main purpose of the present work is to fabricate Ti$_3$SiC$_2$ compound from Ti/SiC/C powders with different molar ratios using the PDS technique so as to decrease the sintering temperature and to shorten the sintering time in comparison with the other available synthesis processes.[13–15]

Experimental procedure

Commercially available Ti, SiC, and C with mean particle sizes and purities of, respectively, 10 μm and 99·9%, 2–3 μm and 99%, 5 μm and 99·7% were used as the starting powders in the present study. The molar ratios of Ti/SiC/C were selected to be 3 : 1 : 1, 3 : 1·1 : 0·9, 5 : 2 : 1 and 3 : 1·5 : 0·5, respectively, referred to as M1, M2, M3, and M4, as shown in Table 1. The mixture process was conducted in a Turbula shaker mixer in Ar atmosphere for 24 h. These powder mixtures were weighed and filled in a cylindrical graphite mould with an inner diameter of 20 mm and outer diameter of 50 mm and height 40 mm, with two graphite punches 20 mm in diameter and 25 mm in length pressed at two ends. The graphite dies and powder mixture set were fixed in a pulse discharge sintering (PDS) apparatus, with two water cooled copper electrodes, which serve also as the pressing plates, compressed from upper and lower ends, respectively. The chamber was evacuated to a pressure of 10^{-3} Pa before starting the sintering process. At the beginning of sintering, a rectangular pulse current with an intensity of 800 A and a pulse length of 30 ms was applied for 30 s, followed by a direct current superimposed with a pulse current wave; the current intensity was automatically controlled according to a temperature

Table 1 Molar ratios of Ti : SiC : C in selected mixture powders M1–M4

|	M1	M2	M3	M4
Ti/SiC/C (molar ratio)	3 : 1 : 1	3 : 1·1 : 0·9	5 : 2 : 1	3 : 1·5 : 0·5
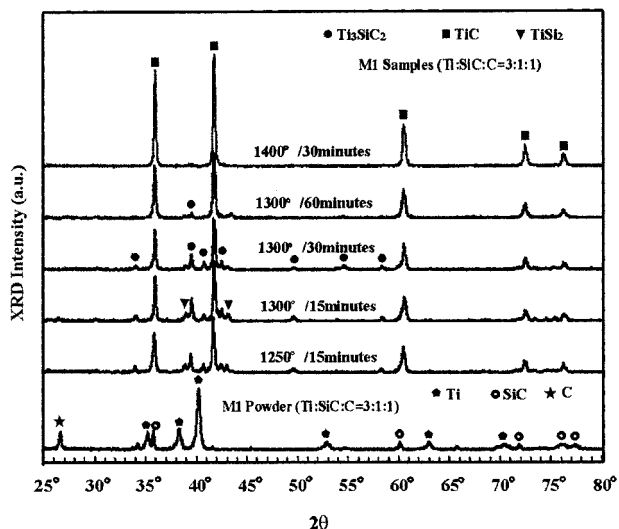
1 XRD profiles of 3Ti/SiC/C powder and M1 samples sintered at different temperatures and times

programme. The sintering temperatures were controlled in the range 1200–1400°C at a heating rate of 50–60 K min^{-1} and the holding time was in the range 15–60 min. The applied pressure was maintained constant at 50 MPa.

After sintering, the samples were ground to remove the graphite layer and analysed by X-ray diffractometry (XRD) with Cu K_{α} radiation at 30 kV and 40 mA to show the constituent phases. The purity of Ti₃SiC₂ in the synthesised samples was calculated by means of standard additive method.[23] After polishing, the sample surfaces were etched in a solution of $H_2O:HNO_3:HF$ (2:1:1) for 5–10 s to expose the Ti₃SiC₂ grains. The microstructures of the samples were observed by scanning electron microscopy (SEM); densities were measured by means of the Archimedes principle to show the degree of densification.

Results and discussion

Figure 1 shows the X-ray diffraction (XRD) profiles of the 3Ti/SiC/C powder and the M1 samples sintered in the temperature range 1250–1400°C for different times. For the 3Ti/SiC/C powder, Ti, SiC, and C peaks can clearly be seen in the XRD pattern. When the powder was sintered at different temperatures, it was found that all the Ti, SiC, and C peaks disappeared in the XRD patterns, indicating that the starting powders had reacted with each other to form new phases after sintering. It can also be seen that TiC is always the major phase in all samples; in particular, TiC becomes the unique phase in samples at the highest sintering temperature of 1400°C. When decreasing sintering temperature or sintering time, both Ti₃SiC₂ and TiSi₂ peaks began to appear in the XRD patterns, however, Ti₃SiC₂ and TiSi₂ peaks have much lower intensity in comparison with the TiC peaks. This indicates that Ti/SiC/C powder with stoichiometric molar ratio 3:1:1 cannot be synthesised to high purity Ti₃SiC₂ compounds over the relatively wide sintering temperature range 1250–1400°C. Ti₃SiC₂ phase preferred to form at relatively low sintering temperatures and short times using the PDS technique. Similar results were observed by Sato *et al.*[12] who synthesised Ti₃SiC₂ samples through the HIP technique from Ti/Si/C powder. They found that the purity of Ti₃SiC₂ decreased remarkably when the holding time at high sintering temperatures was extended. By using the HIP technique, however, Barsoum and El-Raghy[13,14] found that Ti₃SiC₂ phase tended to form
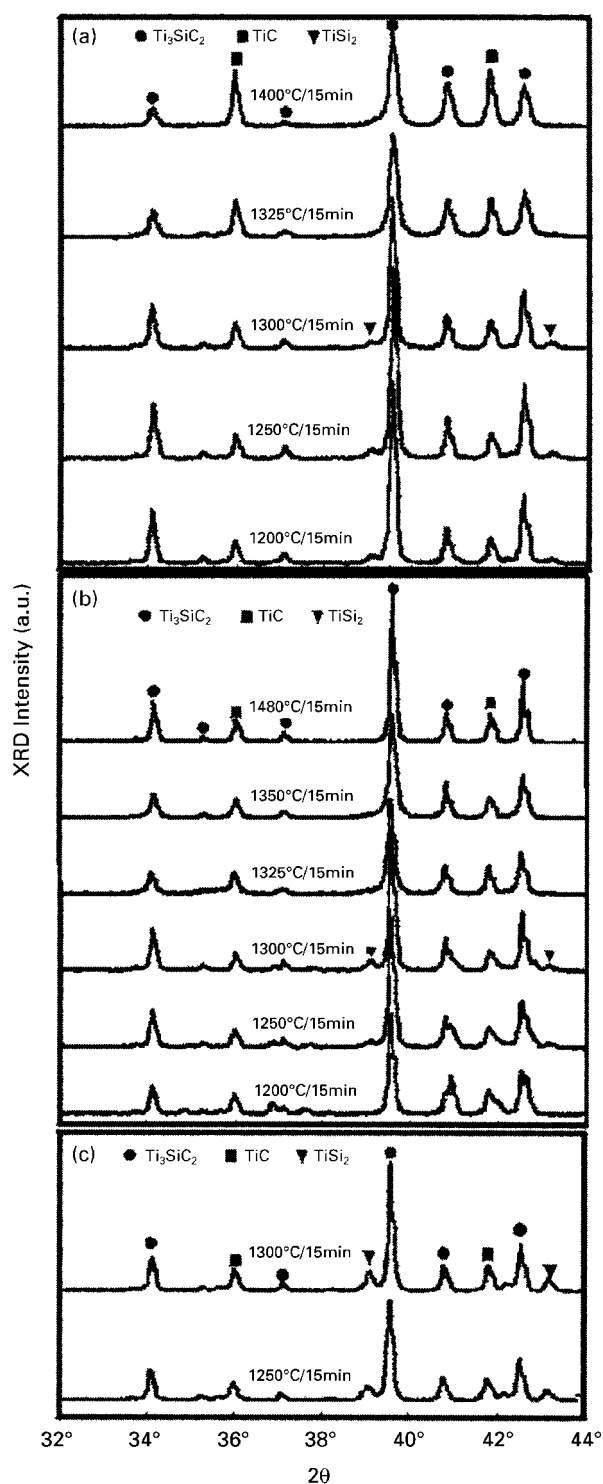

2 XRD profiles of synthesised samples sintered at 1200–1400°C for 15 min: *a* M2 samples from mixture 3Ti/1·1SiC/0·9C; *b* M3 samples from mixture 5Ti/2SiC/1C; *c* M4 samples from mixture 3Ti/1·5SiC/0·5C

at relatively high sintering temperature (1600°C) and long sintering times (4 h or more) from Ti/SiC/C powder.

The present results and the findings by Sato *et al.*[12] and Barsoum and El-Raghy,[13,14] suggest that both sintering techniques (PDS or HIP) and starting powders (Ti/Si/C or Ti/SiC/C) can enable the formation of Ti₃SiC₂ phase.

Figure 2a shows the XRD pattern of M2 samples synthesised from 3Ti/1·1SiC/0·9C powder in the temperature range 1200–1400°C for 15 min. It can be seen that the main peak in all the samples corresponds to Ti₃SiC₂ phase, and
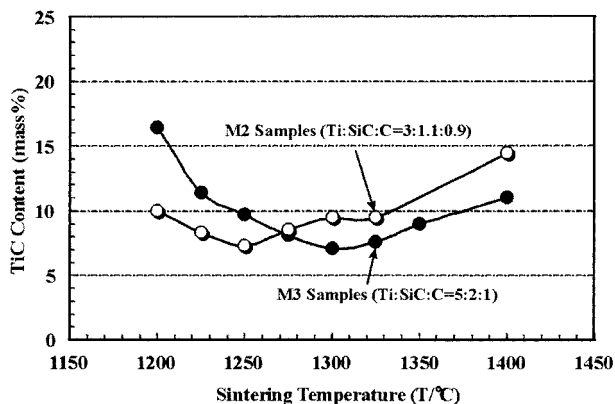
3 TiC content in M2 and M3 samples sintered at 1200–1400°C for 15 min

the second phase is TiC with relatively low intensity. Also, TiSi$_2$ peaks with lower intensity can be seen at $2\theta = 39°$ and $43.2°$ in samples sintered at $1200-1300°$C. For M3 samples synthesised from 5Ti/2SiC/C powder over the same temperature range (as shown in Fig. 2b) their XRD patterns exhibits similar features to those of the M2 samples. It is apparent that the purity of Ti$_3$SiC$_2$ phase in the synthesised M2 and M3 samples can be improved by adjusting the composition of the Ti/SiC/C starting powders. Increasing the content of SiC in the starting powder does not significantly decrease the intensities of TiC peaks, as shown in Fig. 2c. In contrast, the intensities of both TiC and TiSi$_2$ peaks in Fig. 2c are enhanced in comparison with those in the M2 and M3 samples. This means that increasing the content of SiC cannot monotonically improve the purity of Ti$_3$SiC$_2$ phase in products synthesised through the PDS technique from Ti/SiC/C powders.

In previous work,[23] the standard addition method was calibrated to calculate the content of Ti$_3$SiC$_2$ and TiC in a Ti$_3$SiC$_2$–TiC two phase mixture using the following two equations:

$$W_{TSC} = \frac{1.80}{1.80 + I_{TC}/I_{TSC}}$$

and

$$W_{TC} = \frac{I_{TC}/I_{TSC}}{1.80 + I_{TC}/I_{TSC}}$$

where W_{TSC} and W_{TC} are the weight percentages of Ti$_3$SiC$_2$ and TiC phases, respectively. I_{TC}/I_{TSC} is the integrated intensity ratio of TiC to Ti$_3$SiC$_2$ main peak and can be obtained from the XRD results.

Figure 3 shows the TiC content in M2 and M3 samples sintered at $1200-1400°$C for 15 min. It can be seen that with increasing sintering temperature, TiC content in M2 and M3 samples decreased, and reached a lowest value of about 7 wt-% at temperatures $1250°$C and $1300°$C, respectively. With further increase of sintering temperature, TiC content increased again. Therefore, the optimum sintering temperature for Ti$_3$SiC$_2$ from the Ti/SiC/C powder mixtures is in the range $1250-1300°$C, which is a relatively low temperature in comparison with other techniques.

Another interesting phenomenon is that the sintering time is very short, which was also found when sintering Ti/Si/TiC, Ti/SiC/TiC, and Ti/TiSi$_2$/TiC powder mixtures[22,23,28] by the PDS technique. It is thus apparent that the PDS technique can rapidly sinter Ti$_3$SiC$_2$ samples from several powder mixtures. Although the purity of Ti$_3$SiC$_2$ was not improved to a high value due to the application of the PDS technique, from Figs. 1–3, it is noted that the formation of Ti$_3$SiC$_2$ was controlled by the composition of the powder mixtures. It is thus possible to further purify the compound
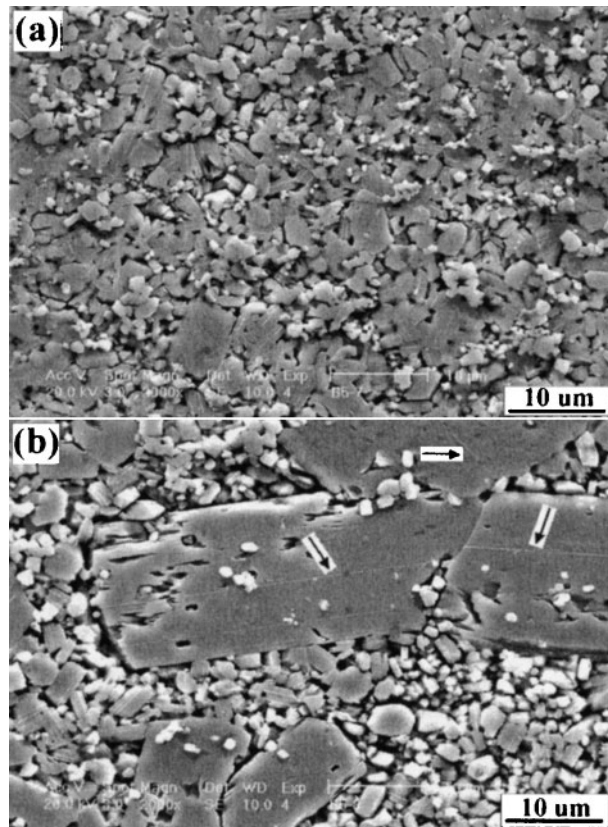

a M2 sample sintered at 1200°C for 15 min; *b* M3 sample sintered at 1350°C for 15 min

4 Microstructure of M2 and M3 samples sintered at various temperatures observed by SEM

by adjusting the composition of the Ti/SiC/C starting powder.

Figure 4 shows the typical microstructure of M2 and M3 samples sintered at different temperatures, observed by SEM. For sintering conducted at 1200°C, the microstructure of the samples consists of homogenous fine grains, as shown in Fig. 4a. These grains do not display an equiaxial feature and have platelike shape with average size about 5 μm in length and 2–3 μm in width. At 1350°C, as shown in Fig. 4b, some Ti$_3$SiC$_2$ grains can grow to a large size (30–50 μm in length and 20 μm in width), but they still have platelike features identical with the platelike Ti$_3$SiC$_2$ grains observed by many investigators.[7,8,12–14,18] It is interesting to find that the coarse Ti$_3$SiC$_2$ grains have plastically deformed in local regions, probably due to thermal stress during cooling or stress caused by the mechanical polishing. As indicated by the arrows in Fig. 4b, slipping within the coarse Ti$_3$SiC$_2$ grains only took place along one plane, which is also identical with the deformation mechanism of Ti$_3$SiC$_2$.[5,6]

Figure 5 shows the dependence of density of M2 and M3 samples on sintering temperature. It can be seen that when the sintering temperature is below 1225°C, the measured density ρ_M of M2 samples is lower than 4.50 g cm^{-3}. When the sintering temperature was increased to above 1250°C, the measured density improved to 4.50–4.52 g cm^{-3}, which is quite close to the theoretical density 4.53 g cm^{-3} of pure Ti$_3$SiC$_2$, as shown in Fig. 5a. For the M3 samples, as shown in Fig. 5b, density is slightly lower than that of M2 samples, but still reaches 4.50 g cm^{-3} at temperatures above 1300°C. Since the theoretical density of TiC is 4.90 g cm^{-3}, the theoretical densities ρ_T of the synthesised M2 and M3 samples were calculated by taking the purity of Ti$_3$SiC$_2$ in Fig. 3 into account, and the results are also shown in Fig. 5.
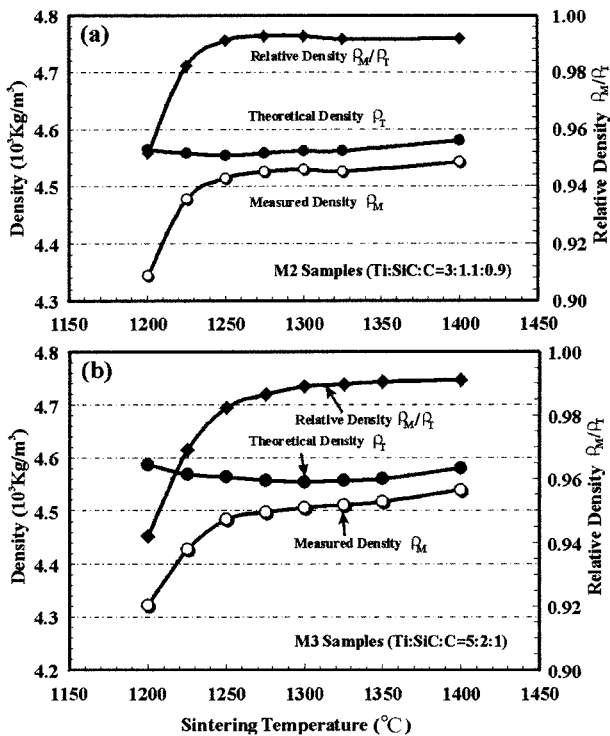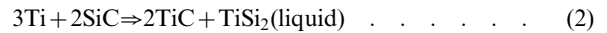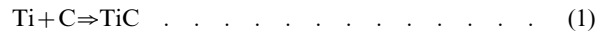
a M2 samples; *b* M3 samples

5 Dependence of measured density, theoretical density, and relative density on sintering temperature

It is apparent that the relative densities ρ_M/ρ_T of M2 and M3 samples are sufficiently high (over 98%) at sintering temperature above 1250°C. Thus, samples synthesised at relatively low temperature and for only a short time achieve good densification when using the PDS technique at a pressure of 50 MPa.

Recently, there have been several investigations of the reaction mechanisms between SiC and Ti. In one of them, an existing controversy about the presence or absence of Ti$_3$SiC$_2$ in the reactive SiC/Ti system was clarified by Kooi et al.,[24] who found that the Si released during the reaction SiC + Ti → TiC + Si, resulted in the formation of Ti$_5$Si$_3$. Naka et al.,[25] investigated the total diffusion path between SiC and Ti foil with a thickness of 50 μm in detail at temperature of 1400°C. The complete diffusion path was observed to be: β-Ti/Ti + TiC/Ti$_5$Si$_3$C$_x$ + TiC/Ti$_5$Si$_3$C$_x$/Ti$_3$SiC$_2$/SiC, and the diffusion path between Ti and SiC would be completed upon the appearance of Ti$_3$SiC$_2$. Barsoum and El-Raghy[14] proposed that there were several reaction phases, and the reaction path to form Ti$_3$SiC$_2$ during sintering powder mixture was as follows: Ti/Ti$_5$Si$_3$C$_x$/Ti$_5$Si$_3$C$_x$ + ‖ TiC$_x$/Ti$_3$SiC$_2$/SiC. They suggested that the nucleation and growth of Ti$_3$SiC$_2$ mainly took place within Ti$_5$Si$_3$C$_x$ phase. From the reaction paths of Ti$_3$SiC$_2$ available,[14,23,24] first of all, it can be determined that TiC must be one of the important intermediate phases during the formation of Ti$_3$SiC$_2$. Besides, Naka et al.[25] also observed the formation of TiSi$_2$ phase in the interface region of Ti/SiC at a bonding temperature of 1400°C for 10 h. From the microstructure features, they identified that the TiSi$_2$ phase had been formed from a liquid phase instead of a solid state reaction. From the present results in Fig. 1 and Fig. 2, except for the TiC phase, it can be seen that there is another intermediate phase, i.e. TiSi$_2$, which, however, was not observed by Barsoum and El-Raghy.[14] The reason might be that the present sintering temperature is relatively low and is very close to the eutectic point (1333°C) of the Si – TiSi$_2$ system. Therefore, it can be considered that the eutectic reaction should occur during the sintering of Ti/SiC/C powders

through the PDS technique in the present study. On the other hand, as we know, TiC has an octahedral structure and Ti$_3$SiC$_2$ is a layered hexagonal structure, in which two TiC are connected by Ti and Si layers.[26,27] Therefore, the octahedral TiC can be regarded as a unit cell of Ti$_3$SiC$_2$ in structure. Once the eutectic liquid phase TiSi$_2$ occurs, Ti$_3$SiC$_2$ would easily be formed at the interfaces between the Ti – TiSi$_2$ liquid and the formed TiC particles.

From the assumptions above, we can conclude that there should be mainly three reactions to form Ti$_3$SiC$_2$ during the sintering of Ti/SiC/C powders, i.e.

$$\text{Ti} + \text{C} \Rightarrow \text{TiC} \quad \dots \dots \dots \dots \dots \quad (1)$$

$$3\text{Ti} + 2\text{SiC} \Rightarrow 2\text{TiC} + \text{TiSi}_2(\text{liquid}) \quad \dots \dots \quad (2)$$

and

$$\text{Ti} + \text{TiSi}_2(\text{liquid}) + 4\text{TiC} \Rightarrow 2\text{Ti}_3\text{SiC}_2 \quad \dots \dots \quad (3)$$

The first reaction can be confirmed by all the synthesis work of Ti$_3$SiC$_2$ since TiC is always an important impurity phase in synthesised Ti$_3$SiC$_2$ products. The second reaction can be proved by the formation of TiSi$_2$ in Fig. 1 and Fig. 2, and from the literature.[24] Recently, Li et al.[11] and Sato et al.[12] proposed that the formation of Ti$_3$SiC$_2$ phase was caused by the solid – liquid reaction among Ti and TiC solid phases and TiSi$_2$ liquid phase. Therefore, we attempted to sinter the Ti/TiS$_2$/4TiC powder mixture by the PDS technique, and a relatively high purity of Ti$_3$SiC$_2$ (about 95 wt-%) was obtained at a sintering temperature of 1300°C for 15 min.[28] Since the PDS technique can effectually accelerate the synthesis processes in comparison with the HIP technique, the reaction mechanism in the PDS processes should be different from those in HIP processes. One reason might be that the pulse electric filed may activate the surface of the powder particles, to enhance the sintering process; possibly a plasma occurred between the particles to locally increase the temperature to a higher level than the controlled average temperature, which could effectively promote the synthesis reaction of Ti$_3$SiC$_2$.[19–21] Because the sintering processes were very short, it is possible for the third reaction proposed above to proceed during sintering of the Ti/SiC/C powder mixture.

Conclusions

Using pulse discharge sintering (PDS), Ti/SiC/C powders can be used to rapidly (15 min) synthesise Ti$_3$SiC$_2$ samples at the relatively low temperature of 1250 – 1300°C, which is much lower than that necessary when using the HIP technique. The synthesis products in such conditions were sufficiently well densified, for example, relative density was greater than 99% at sintering temperatures above 1300°C.

The composition of Ti/SiC/C played an important role in the synthesis of Ti$_3$SiC$_2$ samples using the PDS technique. For Ti/SiC/C powder with a molar ratio 3 : 1 : 1, only Ti$_3$SiC$_2$ samples of poor purity were obtained over the relatively wide sintering temperature range 1250 – 1400°C. When the molar ratio T : SiC : C was adjusted to 3 : 1·1 : 2 or 5 : 2 : 1, the purity of Ti$_3$SiC$_2$ in the synthesised samples was improved to about 93 wt-%. It is expected that the purity of Ti$_3$SiC$_2$ can be further improved by adjusting the composition of the starting Ti/SiC/C powders.

Acknowledgements

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