

# Effects of sintering temperature and Si content on the purity of $Ti_3SiC_2$ synthesized from Ti/Si/TiC powders

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## Abstract

To improve the purity of titanium silicon carbide ( $Ti_3SiC_2$ ), Ti/Si/TiC powders with molar ratios of 1:1:2, 1:1.05:2, 1:1.1:2 and 1:1.15:2 were prepared by mixture method for 24 h in Ar atmosphere. The synthesis process was performed at 1200–1400 °C under a pressure of 50 MPa with the pulse discharge sintering (PDS) technique. The results showed that the purity of  $Ti_3SiC_2$  was always higher than 92 wt.% in all the samples; however, the excess Si did not play a distinct role in improving the purity of  $Ti_3SiC_2$ . It was found that  $Ti_3SiC_2$  with a purity of about 97 wt.% could be rapidly synthesized at 1250–1300 °C, which is 200–300 °C lower than those synthesized from Ti/Si/C and Ti/SiC/C powders. Meanwhile, the microstructure of  $Ti_3SiC_2$  could be controlled to possess various grain sizes, such as fine, coarse or duplex grains. It is suggested that the synthesis reaction of  $Ti_3SiC_2$  should occur between Ti–Si liquid phase and TiC, which could explain why the excess Si did not decrease the content of TiC in the synthesized products.

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**Keywords:** Titanium silicon carbide ( $Ti_3SiC_2$ ); Pulse discharge sintering; Synthesis; Microstructure

## 1. Introduction

Ternary compound  $Ti_3SiC_2$  is one of the most remarkable materials because of its unique characteristics, such as low density of 4.53 g/cm<sup>3</sup> and high melting point in excess of 3000 °C [1]. Meanwhile, this novel material has a number of exceptional properties: (1) electrical and thermal conductivity [2,3], which at room temperature exceed those of Ti metal; (2) excellent oxidation resistance [4] and resistance to thermal shock [5]; and (3) a moderately low coefficient of thermal expansion. In addition, it can be treated as a potential plastic ceramic, which manifests plastic behavior even at room temperature [6–8]. As far as we are aware, the combination of machinability, strength, and ductility at elevated temperatures, and non-susceptibility to thermal shock has never been observed in any other materials [9].

In the recent decade, the synthesis processes of bulk

$Ti_3SiC_2$  samples were widely performed by various sintering methods at high temperature. In summary, the synthesis processes available were mainly conducted by two reactions, i.e. (1)  $3Ti+Si+2C \rightarrow Ti_3SiC_2$  and (2)  $3Ti+SiC+C \rightarrow Ti_3SiC_2$ . Wherein, the first reaction has been frequently used through the mixture of powders of Ti/Si/C by many investigators, such as Racault et al. [10], Lis et al. [11,12], Li et al. [13,14], Radhakrishnan et al. [15], Gao et al. [16,17], Zhou and Sun [18–20]. Barsoum and El-Raghy [21,22], Gao et al. [17], employed the second reaction to fabricate  $Ti_3SiC_2$ , however, it is noted that the sintering processes above were often conducted at very high temperatures (higher than 1400 °C) for a long time. Recently, it was found that  $Ti_3SiC_2$  could also be synthesized by the powder mixture of Ti/Si/TiC at temperatures near 1400 °C through cold-isostatic-pressing (CIP) and reactive sintering method [23]. To decrease the sintering temperatures, recently, a pulse discharge sintering (PDS) or spark plasma sintering (SPS) technique has been reported to synthesize ceramics and metallic materials, for example: Ti–Al [24],  $Al_2O_3$  [25], nano-materials [26] in a short time. In our previous work, it has been confirmed that the PDS technique can effectively decrease the synthesis temperature of  $Ti_3SiC_2$  to about 1300 °C from powder mixtures of Ti/SiC/TiC [27] and Ti/TiSi<sub>2</sub>/TiC

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[28]. In the present work, Ti/Si/TiC powder mixtures with different content of Si will be employed for the synthesis of  $\text{Ti}_3\text{SiC}_2$  by the PDS technique and the effect of Si content on the purity of  $\text{Ti}_3\text{SiC}_2$  in the products will be further investigated.

## 2. Experimental procedure

Ti, Si and TiC were selected as starting powders and their sizes and purity are 10  $\mu\text{m}$  and 99.9% (Ti), 10  $\mu\text{m}$  and 99.9% (Si), 2–5  $\mu\text{m}$  and 99% (TiC), respectively. To compare the effect of Si content on the purity of  $\text{Ti}_3\text{SiC}_2$  in the synthesized samples, the excess Si was added into the mixture powders. The molar ratios of Ti:Si:TiC are 1:1:2, 1:1.05:2, 1:1.1:2 and 1:1.15:2, which are referred to as M1, M2, M3 and M4, respectively. The mixing process was conducted in a tubular mixer in an Ar atmosphere for 24 h. During mixing, some zirconia balls with the size of 3 mm in diameter were put into the container to ensure a better mixing effect. The powder mixtures were weighed and filled in a cylindrical graphite mold with an inner diameter of 20 mm and outer diameter of 50 mm and height of 40 mm, with two graphite punches of 20 mm in diameter and 25 mm in length pressed at two ends. The graphite dies and powder mixture set was 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  $\text{\AA}$  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 program. In the present experiment, the heating rate was controlled in the range of 50  $^\circ\text{C}/\text{min}$  and the applied pressure was maintained constant at 50 MPa during sintering. After sintering, the surface of samples was ground to remove the graphite layer and analyzed by X-ray diffractometry (XRD) with  $\text{CuK}\alpha$  radiation at 30 kV and 40 mA to determine the  $\text{Ti}_3\text{SiC}_2$  content by means of the standard additive method. Subsequently, the samples were mechanically polished and etched by a solution of  $\text{H}_2\text{O}:\text{HNO}_3:\text{HF}$  (2:1:1). The microstructures of the synthesized  $\text{Ti}_3\text{SiC}_2$  samples were observed by optical microscopy (OM) and scanning electron microscopy (SEM).

## 3. Results and discussion

### 3.1. XRD analysis of the synthesized samples

Fig. 1 shows the XRD patterns of the mixed Ti/Si/TiC powder and M1 samples sintered at various temperatures

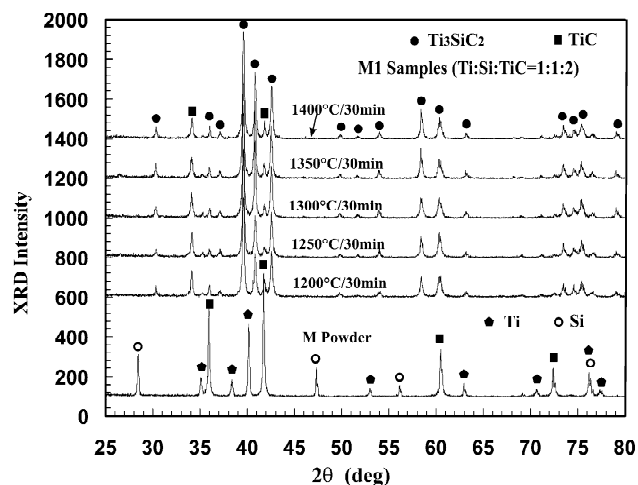


Fig. 1. XRD patterns of Ti/Si/TiC powder and M1 samples sintered at 1200–1400  $^\circ\text{C}$  for 30 min.

of 1200–1400  $^\circ\text{C}$  for 30 min. It can be seen that there are several  $\text{Ti}_3\text{SiC}_2$  peaks, including the main peak, in all the M1 samples. In addition, there are two TiC peaks with lower intensities, where the peak at  $2\theta=41.8^\circ$  is the main peak of TiC. It is apparent that, after sintering, all the Ti and Si peaks disappeared and the TiC peaks were decreased to very low intensity in the M1 samples. For the M2–M4 samples sintered at the same conditions, their XRD patterns displayed similar behavior to the M1 samples, for example as shown in Fig. 2. It was not found that the TiC peaks in the XRD results of the M2–M4 samples have lower intensity than those of M1 samples. From the results above, it can be concluded that there should be only two phases in all the samples, i.e. main phase of  $\text{Ti}_3\text{SiC}_2$  and impurity phase of TiC with low intensity. This indicates that, irrespective of Si content, all the Ti/Si/TiC powders in different compositions are suitable mixtures for the synthesis of  $\text{Ti}_3\text{SiC}_2$  with lower TiC content at the temperature range of 1200–1400  $^\circ\text{C}$  by

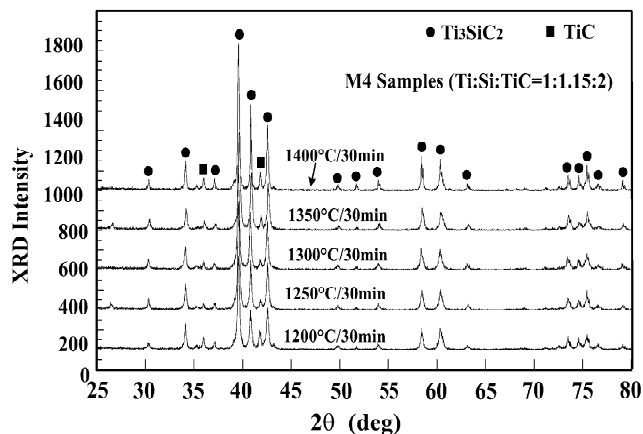


Fig. 2. XRD patterns of the M4 samples sintered at 1200–1400  $^\circ\text{C}$  for 30 min.

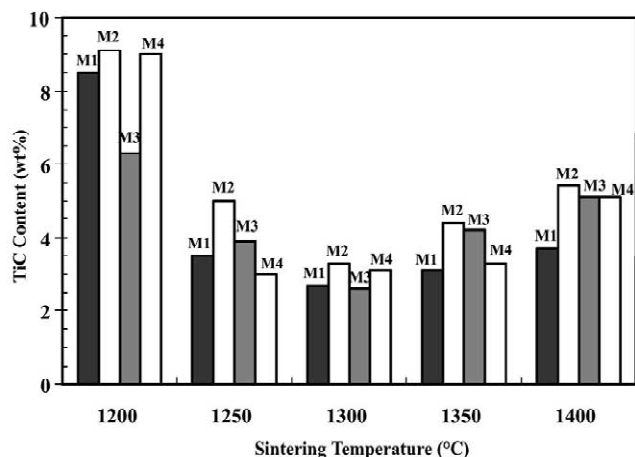


Fig. 3. TiC content in the M1–M4 samples sintered at 1200–1400 °C for 30 min.

short-time sintering through the PDS technique. However, the excess of Si seems not to play a notable role in decreasing the TiC content even in the M4 samples, which contains the highest Si in the composition.

### 3.2. Purity of $Ti_3SiC_2$ in the synthesized samples

To determine the TiC content in the synthesized samples, one bulk sample sintered at 1300 °C for 15 min was drilled to collect some  $Ti_3SiC_2$  powder. Then the powder was incorporated into some pure TiC powder to make the mixtures of ( $Ti_3SiC_2 + TiC$ ) with weight ratios of 90:10, 80:20, 70:30, 60:40 and 50:50. Then the mixed powders were examined by XRD respectively to establish the quantitative relationship between intensity ratios of TiC to  $Ti_3SiC_2$  peaks versus the amount of additive TiC. This procedure was often referred to as the standard additive method [23]. The calibrated results showed that the relationship between the weight percentage  $W_{TSC}$  of

$Ti_3SiC_2$  phase (or  $W_{TC}$  for TiC phase) and the integrated intensity ratio  $I_{TC}/I_{TSC}$  of TiC to  $Ti_3SiC_2$  main peak follows the equations below:

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

From the results in Figs. 1 and 2, it can be seen that there are only two phases, i.e.  $Ti_3SiC_2$  and TiC, in the synthesized samples, consequently the contents of TiC and  $Ti_3SiC_2$  can be calculated by the above equations. Fig. 3 shows the TiC content calculated from the XRD results in M1–M4 samples sintered in the temperature range of 1200–1400 °C for 30 min. It can be seen that at 1200 °C, the TiC content in all the M1–M4 samples are fairly high (about 6–10 wt.%). When the sintering temperature was in the range of 1250–1350 °C, the TiC content could be decreased to below 4 wt.% for almost all the samples. However, the excess Si content did not play an obvious role in improving the purity of  $Ti_3SiC_2$  in the M2–M4 samples. This result is not as expected prior to the experimentation and will be discussed in the following section. Since the purity of  $Ti_3SiC_2$  in all the samples nearly displayed a similar variation with sintering temperature, the M1 and M3 powders were selected and further sintered for different times so as to optimize the synthesis conditions of  $Ti_3SiC_2$  with high purity.

Fig. 4a demonstrates the quantitative results of TiC content in M1 and M3 samples sintered for 15 min. It was found that the TiC content in M3 samples is higher than that of M1 samples at temperatures below 1275 °C, and almost the same as M1 samples at higher sintering temperature. When the sintering was conducted for 30 min, as shown in Fig. 4b, the TiC content in M3 samples is still slightly higher than that of M1 samples at all the sintering temperatures. From the results above, it can be known that the optimum sintering should be conducted in the con-

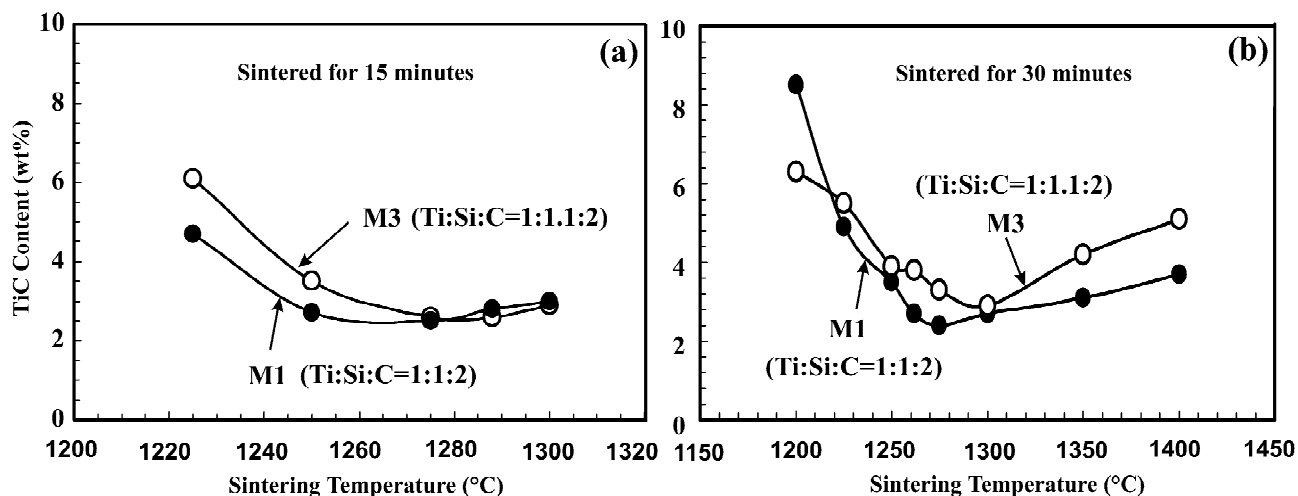


Fig. 4. TiC content in the M1 and M3 samples sintered at 1200–1400 °C for 15 and 30 min.

dition of 1250–1300 °C for shorter time (15–30 min), and the lowest TiC content can be reduced to 2.5 wt.% in the M1 samples. Recently, by using the same powder of Ti/Si/TiC, Li and Miyamoto [23] also synthesized  $\text{Ti}_3\text{SiC}_2$  at temperatures near 1400 °C through cold-isostatic-pressing (CIP) and reactive sintering technique for 2 h. It implies that the high purity  $\text{Ti}_3\text{SiC}_2$  could be synthesized at relatively low temperatures for short times through the PDS technique. However, it seems that the excess Si in the M2–M4 samples could not further improve the purity of  $\text{Ti}_3\text{SiC}_2$  if the starting powder is Ti/Si/TiC, which is quite different from that sintered from Ti/Si/C powder [13,16,17] and will be explained in the following section. Nevertheless, it can be concluded that, in addition to the powder mixtures of Ti/Si/C and Ti/SiC/C, Ti/Si/TiC powder is also a useful mixture for the synthesis of  $\text{Ti}_3\text{SiC}_2$  with high purity. When the PDS technique is utilized, the sintering temperature can be effectively decreased to below 1300 °C, which is about 200–300 °C lower than that used by the former powder mixtures, and particularly the sintering time could be shortened substantially to around 15 min.

### 3.3. Microstructures of $\text{Ti}_3\text{SiC}_2$

By observing all the M1–M4 samples, it was found that their microstructures sintered at the same temperatures and times are quite similar. Fig. 5 shows the microstructure of the samples sintered at different temperatures and times observed by OM and SEM. When the sintering temperature was 1200 °C, as shown in Fig. 5a, the microstructure consists of homogenous grains with 5–10  $\mu\text{m}$  in length and 2–5  $\mu\text{m}$  in width. When the sintering temperature was increased to 1250 °C, some grains became somewhat larger and appeared lath-like with more than 20  $\mu\text{m}$  in length, as shown in Fig. 5b, indicating that some  $\text{Ti}_3\text{SiC}_2$  grains could begin to grow at this sintering temperature. At an increased sintering temperature of 1300 °C, the lath-like grains could continue to grow with increased sintering time. As shown in Fig. 5c–e, the grain size can reach to about 50  $\mu\text{m}$  in length ( $t=8$  min), 60–80  $\mu\text{m}$  in length and 30–40  $\mu\text{m}$  in width ( $t=30$  min), and more than 100  $\mu\text{m}$  in length and 50  $\mu\text{m}$  in width ( $t=60$  min). At higher sintering temperatures of 1350 °C and 1400 °C, the lath-like grains were found to grow slowly, while, the volume fraction continued to increase (see Fig. 5f).

From the micrographs above, it can be concluded that the grain size and volume fraction of the coarse grains strongly depend on the sintering temperature, especially in the range of 1250–1300 °C. Meanwhile, the size and volume fraction of coarse grains can be dramatically affected by the sintering time at higher sintering temperatures. These observations clearly show that the microstructure of  $\text{Ti}_3\text{SiC}_2$  can be changed greatly in the lower sintering temperature range from 1250 to 1300 °C. By observing all the M1–M4 samples sintered at various

temperatures and times, the dependence of microstructure on the synthesis conditions was summarized and illustrated in Fig. 6. The microstructure of  $\text{Ti}_3\text{SiC}_2$  was classified into three types, i.e. fine ( $d \leq 10 \mu\text{m}$ ), coarse ( $d \geq 50 \mu\text{m}$ ) and duplex ( $10 \mu\text{m} \leq d \leq 50 \mu\text{m}$ ) grains, depending on the sintering temperature and time, which are similar to the results by Barsoum and El-Raghy [22]. Therefore, the  $\text{Ti}_3\text{SiC}_2$  samples with different microstructures could be controlled at relatively lower temperatures and shorter times through PDS Ti/Si/TiC powder. However, by using the Ti/SiC/C powders, the microstructure of  $\text{Ti}_3\text{SiC}_2$  had to be adjusted at very high temperature ranges of 1450–1600 °C and a long time of 4–24 h [21,22]. Obviously, the optimum sintering temperature (1250–1300 °C) and time (15–60 min) for the Ti/Si/TiC powder with the PDS technique are distinctly lower or shorter than those fabricated from Ti/SiC/C powders.

### 3.4. Effect of Si content on the purity of $\text{Ti}_3\text{SiC}_2$

From the synthesis processes used in the past, it is found that the synthesized  $\text{Ti}_3\text{SiC}_2$  could not achieve high purity (>90%) at temperatures lower than 1350 °C and short time no matter by using either Ti/Si/C or Ti/SiC/C mixture powders [10–22]. Radhakrishnan et al. [13] and Li et al. [16,17] found that the purity of  $\text{Ti}_3\text{SiC}_2$  could be further improved by adding excess Si to the starting powders of Ti/Si/C. In the present synthesis process for  $\text{Ti}_3\text{SiC}_2$ , however, it was not as expected that the increase in Si content would show significant effect on the purity of  $\text{Ti}_3\text{SiC}_2$ , which will be explained as follows.

Li and Miyamoto [23] proposed that the synthesis process for  $\text{Ti}_3\text{SiC}_2$  from the starting powder of Ti/Si/TiC should be as the following reaction at first:



Then, the released C in the reaction would react with Ti to form new TiC. In the end, all the TiC particles reacted with Ti and Si to completely form  $\text{Ti}_3\text{SiC}_2$ . Provided that the reaction above is right, it is possible to continuously decrease the TiC content with the addition of excess Si into the Ti/Si/TiC powders. However, the present experiment did not support this hypothesis since the TiC content was not reduced in the M2–M4 samples. Therefore, the synthesis reaction of  $\text{Ti}_3\text{SiC}_2$  suggested by Li and Miyamoto should be reconsidered. In addition, if we consider the lattice structures of TiC and  $\text{Ti}_3\text{SiC}_2$ , it seems impossible for the above reaction to form  $\text{Ti}_3\text{SiC}_2$  during sintering of Ti/Si/TiC powders. It is known that TiC has an octahedral structure; meanwhile,  $\text{Ti}_3\text{SiC}_2$  is a layered hexagonal structure, in which two TiC cells are separated by Ti and Si layers [29,30]. If one  $\text{Ti}_3\text{SiC}_2$  is synthesized by three TiC and one Si as in reaction (1), one of the Ti–C atomic bonds must be separated to form Ti and C atoms. Then the separated Ti atom will connect with the Si atom,

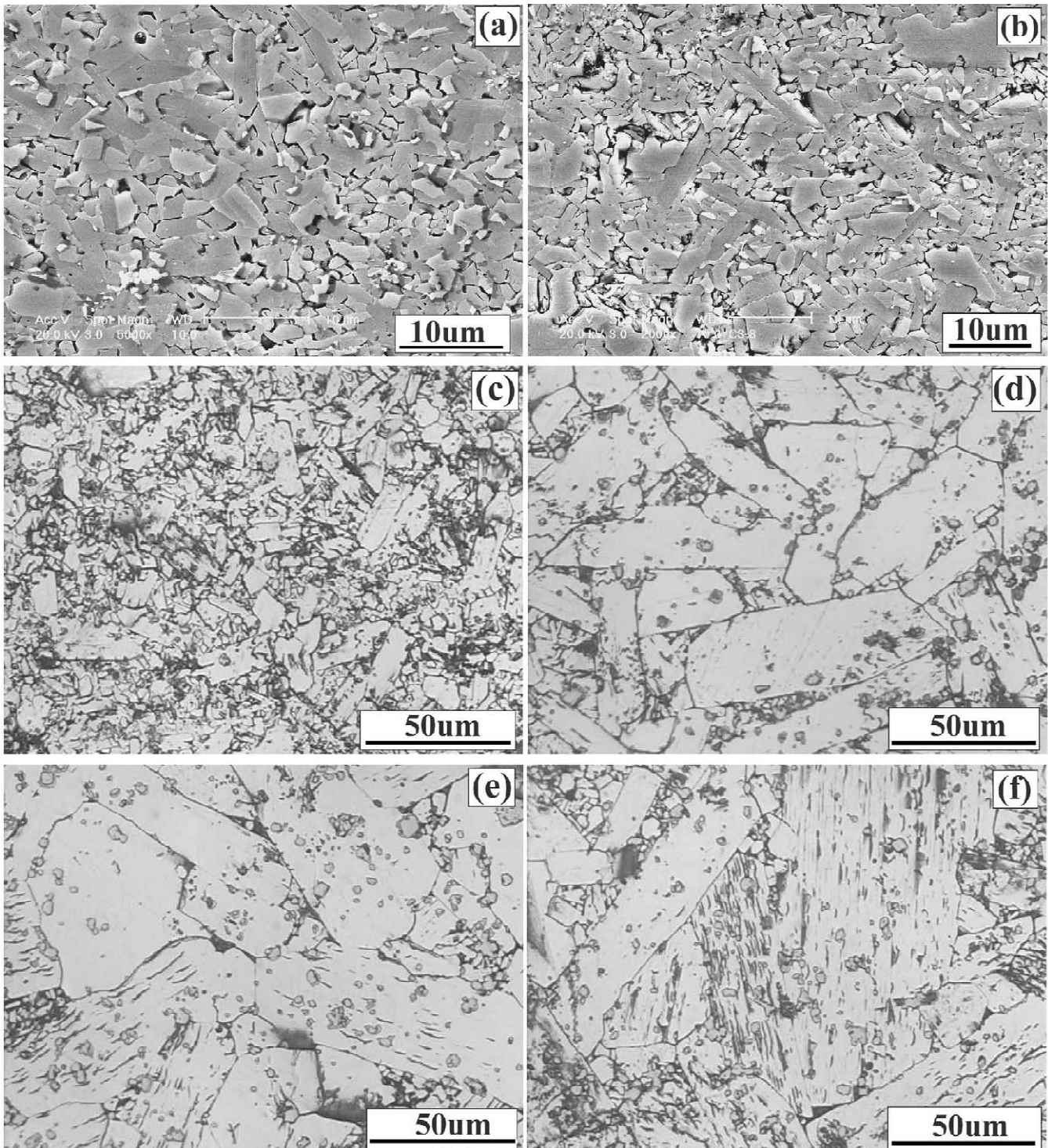


Fig. 5. Microstructure of the samples sintered at 1200–1400 °C observed by OM and SEM. (a)  $T=1200\text{ }^{\circ}\text{C}$ ,  $t=30\text{ min}$ ; (b)  $T=1250\text{ }^{\circ}\text{C}$ ,  $t=30\text{ min}$ ; (c)  $T=1300\text{ }^{\circ}\text{C}$ ,  $t=8\text{ min}$ ; (d)  $T=1300\text{ }^{\circ}\text{C}$ ,  $t=30\text{ min}$ ; (e)  $T=1300\text{ }^{\circ}\text{C}$ ,  $t=60\text{ min}$ ; (f)  $T=1400\text{ }^{\circ}\text{C}$ ,  $t=30\text{ min}$ .

and the C atom will be released. From the viewpoint of thermodynamics, it is difficult for such a reaction among Ti, Si and TiC powders to occur. Therefore, there must be some other reactions to form  $\text{Ti}_3\text{SiC}_2$  during sintering of Ti/Si/TiC powder.

As reported by Sato et al. [17], they assumed that the

TiC phase would form at first during sintering of  $\text{Ti}_3\text{SiC}_2$  by the elemental powders of Ti/Si/C as follows:



Since the Ti–Si system has two eutectic reactions for the

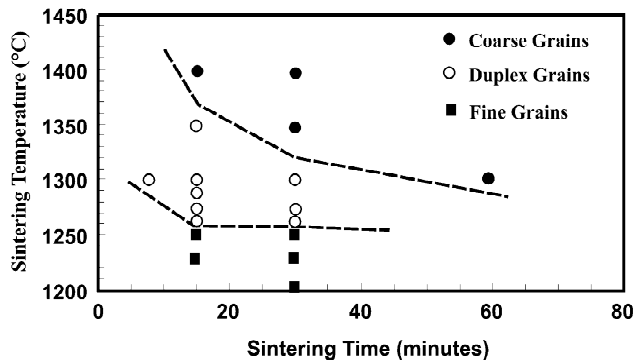
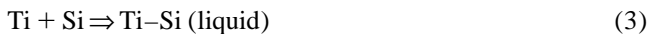
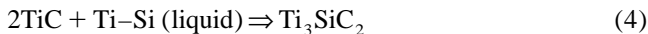


Fig. 6. Dependence of microstructure in the M1–M4 samples on sintering temperature and time.

Si–TiSi<sub>2</sub> and Ti–Ti<sub>5</sub>Si<sub>3</sub> compositions both at the temperature of 1333 °C, the eutectic liquid phase begins to appear between Ti and Si particles as follows:



Finally, Ti<sub>3</sub>SiC<sub>2</sub> will form at the interfaces between the Ti–Si liquid and TiC particles, i.e.



In the present synthesis process of Ti<sub>3</sub>SiC<sub>2</sub>, it is assumed that there should be only the reactions (3) and (4) which occurred during sintering because the TiC has existed in the starting powder of Ti/Si/TiC in advance. Therefore, the synthesis process would be simplified to reactions (3) and (4) and could be illustrated as in Fig. 7. It can be seen that Ti<sub>3</sub>SiC<sub>2</sub> would be easily synthesized by two TiC cells and Ti–Si liquid phase after the formation of Ti–Si liquid phase. In the PDS process, pulse electric field may activate the surfaces of the powder particles, which can enable an easy sintering process. Meanwhile, the plasma occurred between the particles, or the high electrical resistance at the contacts of neighboring particles may locally increase the temperature to a higher level than the

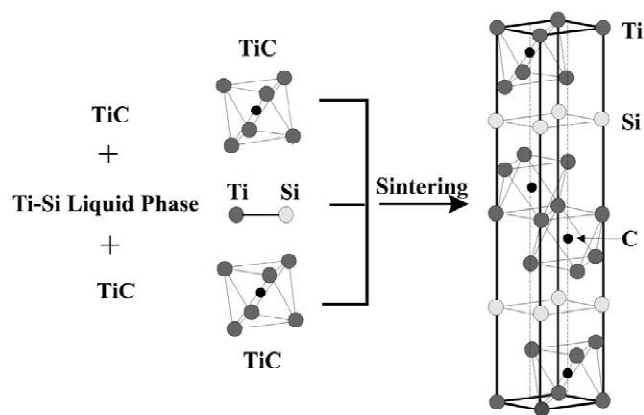


Fig. 7. Schematic illustration showing the synthesis process of Ti<sub>3</sub>SiC<sub>2</sub> from Ti–Si liquid phase and TiC.

controlled average temperature. This local high temperature contributes to the eutectic reaction between Ti and Si, which could effectively promote the synthesis reaction of Ti<sub>3</sub>SiC<sub>2</sub> [24–26]. This explains why both the optimum sintering temperature and time for Ti<sub>3</sub>SiC<sub>2</sub> were decreased to below 1300 °C and 15 min due to the application of the PDS technique.

On the other hand, since the formation of Ti<sub>3</sub>SiC<sub>2</sub> from Ti/Si/TiC powder resulted from the reaction of Ti–Si liquid phase with TiC, the purity of Ti<sub>3</sub>SiC<sub>2</sub> would be mainly affected by the following factors. One is whether the TiC particles are homogeneously mixed with Ti–Si particles or not. Another is whether the TiC particle could completely react with the Ti–Si liquid phase or not during sintering. From the aforementioned results, it is known that the purity of Ti<sub>3</sub>SiC<sub>2</sub> in the M1 samples could be achieved to higher than 97 wt.%. It is indicated that the distribution of Ti/Si/TiC powder mixture should be sufficiently homogenous after 24-h mixing. The 2–3 wt.% TiC impurity might be due to the incomplete reaction or the lack of Ti–Si liquid phase. When adding the excess of Si into Ti/Si/TiC mixture, one can only improve the concentration of Si in the Ti–Si liquid phase, but could not provide new Ti–Si liquid phase in the reactant products. Therefore, the excess of Si could not play a decisive role in the purity of Ti<sub>3</sub>SiC<sub>2</sub>. From the difference in the synthesis reactions above, it is suggested that Ti/Si/TiC powder can be regarded as a new favorable mixture to synthesize Ti<sub>3</sub>SiC<sub>2</sub> at relatively lower temperature and short time, especially by using the PDS technique.

#### 4. Conclusions

In a very wide temperature range from 1200 to 1400 °C, the TiC content in all the samples synthesized by the powders of Ti/*x*Si/2TiC (*x*=1, 1.05, 1.1 and 1.15) could be decreased to below 10 wt.%; when the sintering temperature was in the range from 1250 to 1300 °C, the TiC content was reduced to 2–3 wt.%. However, the excess of Si content did not play an obvious role in the purity of Ti<sub>3</sub>SiC<sub>2</sub> at applied temperature range. The grain size of Ti<sub>3</sub>SiC<sub>2</sub> is sensitive to the sintering temperature from 1250 to 1300 °C, which just corresponds to the optimum sintering temperature. By controlling the sintering temperature and time, different microstructures of Ti<sub>3</sub>SiC<sub>2</sub>, such as fine, coarse and duplex grains, could be obtained. Therefore, it is possible to synthesize high performance Ti<sub>3</sub>SiC<sub>2</sub> with high purity and various grain sizes through sintering the Ti/Si/TiC mixture powders at temperature ranges from 1250 to 1300 °C. In comparison with the reactive sintering technique [23], the PDS technique could decrease the sintering temperature by using the same powders of Ti/Si/TiC. Therefore, it is suggested that Ti/Si/TiC powder should be one of the favorable mixtures

for the synthesis of  $Ti_3SiC_2$  at relatively lower temperature and shorter time by using the PDS technique.

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