

# Fabrication and Microstructure Characterization of $Ti_3SiC_2$ Synthesized from Ti/Si/2TiC Powders Using the Pulse Discharge Sintering (PDS) Technique

Zhe-Feng Zhang,<sup>†</sup> Zheng Ming Sun,<sup>‡</sup> Hitoshi Hashimoto, and Toshihiko Abe

AIST Tohoku, National Institute of Advanced Industrial Science and Technology, Sendai 983-8551, Japan

Ti/Si/2TiC powders were prepared using a mixture method (M) and a mechanical alloying (MA) method to fabricate  $Ti_3SiC_2$  at 1200°–1400°C using a pulse discharge sintering (PDS) technique. The results showed that the  $Ti_3SiC_2$  samples with <5 wt% TiC could be rapidly synthesized from the M powders; however, the TiC content was always >18 wt% in the MA samples. Further sintering of the M powder showed that the purity of  $Ti_3SiC_2$  could be improved to >97 wt% at 1250°–1300°C, which is ~200°–300°C lower than that of sintered Ti/Si/C and Ti/SiC/C powders using the hot isostatic pressing (HIPing) technique. The microstructure of  $Ti_3SiC_2$  also could be controlled using three types of powders, i.e., fine, coarse, or duplex-grained, within the sintering temperature range. In comparison with Ti/Si/C and Ti/SiC/C mixture powders, it has been suggested that high-purity  $Ti_3SiC_2$  could be rapidly synthesized by sintering the Ti/Si/TiC powder mixture at relatively lower temperature using the PDS technique.

## I. Introduction

RECENTLY, the ternary carbide  $Ti_3SiC_2$  has attracted many investigators, because it is a remarkable material that combines many of the best attributes of metals and ceramics. It has been determined that  $Ti_3SiC_2$  is a layered hexagonal structure in which almost close-packed planes of titanium are separated from each other by hexagonal nets of silicon; every fourth layers is a silicon layer. Carbon atoms occupy the octahedral sites between the titanium layers.<sup>1,2</sup> The melting point of  $Ti_3SiC_2$  has been reported to be >3000°C.<sup>3</sup> The Young's modulus and Vickers hardness of  $Ti_3SiC_2$  are 326 GPa and 4–6 GPa, respectively.<sup>4–6</sup>  $Ti_3SiC_2$  has many exceptional properties:<sup>1</sup> electrical and thermal conductivity,<sup>7</sup> which, at room temperature, exceed those of titanium-metal;<sup>2</sup> excellent oxidation resistance up to 1400°C,<sup>8</sup> resistance to thermal shock,<sup>9,10,3</sup> and moderately low coefficient of thermal expansion. In addition to these excellent physical properties,  $Ti_3SiC_2$  can maintain its strength to temperatures that render the best superalloys currently available.<sup>10</sup> When the large-grained  $Ti_3SiC_2$  polycrystalline samples are compressed at room temperature, they can display plastic behavior by a combination of sliding, delamination, kink band formation, and shear band formation.<sup>11,12</sup> Therefore,  $Ti_3SiC_2$  is damage tolerant at ambient temperatures and is capable of locally absorbing much energy at room temperature.<sup>4,5</sup> As far as we are aware, the combination of machinability, strength, and ductility at elevated temperatures,

nonsusceptibility to thermal shock, and good machinability never have been observed in other materials.<sup>13,14</sup>

$Ti_3SiC_2$  was first synthesized in 1967 by Jeitschko and Nowotny<sup>15</sup> via chemical reaction, and in 1987 by Goto and Hirai<sup>16</sup> via chemical vapor deposition (CVD). During the 1990s, various sintering processes were widely used to synthesize bulk  $Ti_3SiC_2$  polycrystals at high temperatures. In summary, the synthesis processes available were mainly conducted by two reactions, i.e.,  $3Ti + Si + 2C \rightarrow Ti_3SiC_2$  and  $3Ti + SiC + C \rightarrow Ti_3SiC_2$ . The former reaction has been frequently used by many investigators by mixing powders of titanium, silicon, and carbon: Racault *et al.*,<sup>17</sup> Lis and co-workers,<sup>18,19</sup> Radhakrishnan and co-workers,<sup>20,21</sup> Gao *et al.*,<sup>22</sup> Li *et al.*,<sup>23,24</sup> and Zhou, Sun, and co-workers.<sup>25–27</sup> Barsoum and El-Raghy,<sup>28,29</sup> Gao *et al.*,<sup>22</sup> and Tang *et al.*<sup>30</sup> used the latter reaction to fabricate  $Ti_3SiC_2$  polycrystals. However, the sintering processes above were often performed at high temperatures (>1400°C) for a long time. Recently, another powder mixture of Ti/Si/TiC was successfully used to synthesize  $Ti_3SiC_2$  samples that had high purity at temperature of ~1400°C using cold isolated-pressing (CIPing) and reactive sintering.<sup>31</sup> Some suitable powder bed has to be used during sintering; otherwise, the  $Ti_3SiC_2$  in the products could not have achieved high purity. To further decrease the sintering temperature and simplify the sintering procedure of  $Ti_3SiC_2$ , a new sintering technique, i.e., pulse discharge sintering (PDS), was used to synthesize  $Ti_3SiC_2$  in the present research. A characteristic of the PDS apparatus is the application of a pulse electric current and/or a direct current directly to the graphite mold and/or the powder compact to be sintered. Therefore, the parts prepared by the PDS technique often represent better mechanical properties than the parts prepared by existing sintering methods.<sup>32</sup> It has been shown that the PDS technique can sinter ceramic and metallic materials, e.g., Ti–Al<sup>33</sup> and Nb–Al<sup>34</sup> nanomaterials,<sup>35</sup> at relatively low temperature for shorter times. In our recent work,<sup>36–39</sup> we have used the PDS technique to synthesize  $Ti_3SiC_2$  from Ti/Si/C,<sup>36</sup> Ti/SiC/C,<sup>37</sup> Ti/SiC/TiC,<sup>38</sup> and Ti/TiSi<sub>2</sub>/TiC<sup>39</sup> powder mixtures. However, the purity of  $Ti_3SiC_2$  in the products was not high (93 wt%). However, the sintering temperature and time were obviously decreased in comparison with the HIPing technique.<sup>22–24,28–30</sup> In the present work, Ti/Si/TiC powder mixtures were further sintered using the PDS technique; meanwhile, some Ti/Si/TiC powders prepared by ball-milling were also sintered to compare the effect of mechanical alloying on the purity of  $Ti_3SiC_2$ .

## II. Experimental Procedure

Titanium, silicon, and TiC that had a stoichiometric molar ratio of 1:1:2 were selected as raw powders. The powder mixtures were prepared in two ways.

(1) *Mixing in a Turbula shaker mixer under argon atmosphere for 24 h (named M).* The sizes and purity of the M powders were (titanium) 10 μm and 99.9%, (silicon) 10 μm and 99.9%, and (TiC), 2–5 μm and 99%, respectively.

(2) *Mechanical alloying in a vibratory ball mill under argon atmosphere for 400 h (named MA).* The sizes were <150 μm,

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<sup>†</sup>JSPS Fellow, on leave from State Key Laboratory for Fatigue and Fracture of Materials, Institute of Metal Research, Chinese Academy of Sciences, P.R. China.

<sup>‡</sup>Author to whom correspondence should be addressed.

<300  $\mu\text{m}$ , and 2–5  $\mu\text{m}$ , respectively, for titanium, silicon, and TiC powders, and the purities were identical to those of the M powders. After 400 h of mechanical alloying, the powder was sieved to pass through a 75  $\mu\text{m}$  mesh.

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 diameter and 25 mm 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 served also as the pressing plates, compressed from upper and lower ends, respectively. The chamber was evacuated to a pressure of  $10^{-3}$  Pa before the sintering process was started. 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 program. The heating rate was controlled in the range of  $50^{\circ}\text{--}60^{\circ}\text{C}/\text{min}$ , and the applied pressure was maintained at a constant value of 50 MPa during sintering. The sintering temperatures were controlled in the range of  $1200^{\circ}\text{--}1400^{\circ}\text{C}$ , and the holding times were 15–60 min during the PDS technique. After they were sintered, the samples were  $\sim 6\text{--}7$  mm thick. Then, surfaces of samples were ground to remove the graphite layer and analyzed using X-ray diffractometry (XRD) with  $\text{CuK}\alpha$  radiation at 30 kV and 40 mA to determine the  $\text{Ti}_3\text{SiC}_2$  and impurity phases. The density of the synthesized samples was measured using the Archimedes method. The samples were then mechanically polished and etched using a solution of  $\text{H}_2\text{O}\text{--}\text{HNO}_3\text{--}\text{HF}$  (2:1:1) to expose the  $\text{Ti}_3\text{SiC}_2$  grains. With the help of optical microscopy (OM) and scanning electron microscopy (SEM), the etched samples were observed and analyzed.

### III. Results and Discussion

#### (1) XRD Analysis of the Synthesized Samples

Figure 1 shows the XRD results scanned at  $2\theta = 30^{\circ}\text{--}80^{\circ}$  in the MA powder and samples synthesized in the temperature range of  $1200^{\circ}\text{--}1400^{\circ}\text{C}$  for 30 min. For the MA powder, there were mainly three wide diffraction peaks marked as TiC; however, no titanium and silicon peaks appeared in the XRD result, which indicated a nonequilibrium structure of the ball-milled powder with TiC

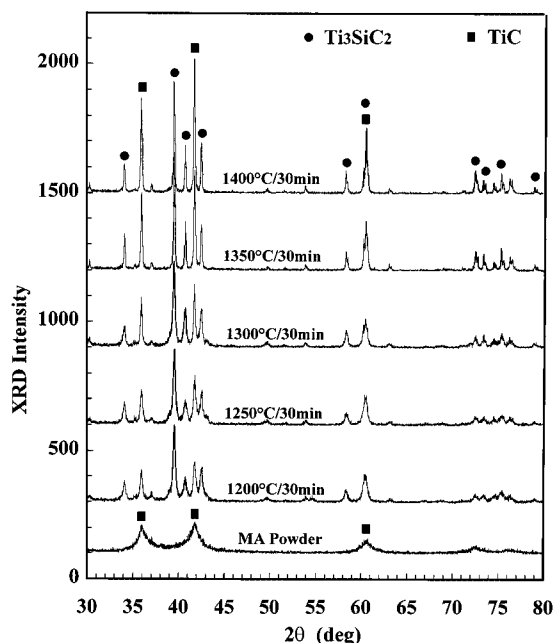


Fig. 1. XRD results of MA powder and samples sintered at  $1200^{\circ}\text{--}1400^{\circ}\text{C}$  for 30 min at  $2\theta = 30^{\circ}\text{--}80^{\circ}$ .

structure supersaturated with titanium and silicon. The sintered MA powder showed that there were at least eight peaks in the scanned range, of which  $\text{Ti}_3\text{SiC}_2$  was the main peak, except for the sample sintered at  $1400^{\circ}\text{C}$ . Therefore,  $\text{Ti}_3\text{SiC}_2$  had formed in these samples after sintering. Besides the  $\text{Ti}_3\text{SiC}_2$  peaks, there were three diffraction peaks marked as TiC at  $2\theta = 36^{\circ}$ ,  $41.8^{\circ}$ , and  $60.5^{\circ}$ . Meanwhile, the intensities of the TiC peaks in the MA samples increased with sintering temperature. Especially, when the sample was sintered at  $1400^{\circ}\text{C}$ , the TiC peak was higher than the  $\text{Ti}_3\text{SiC}_2$  peak and became the main peak. From the XRD results above, it seemed that the purity of  $\text{Ti}_3\text{SiC}_2$  in all the MA samples could not be very high.

Figure 2 shows the XRD results of the M powder and samples sintered at various temperatures of  $1200^{\circ}\text{--}1400^{\circ}\text{C}$  for 30 min. Figure 2 shows XRD peaks of M powder titanium, silicon, and TiC. Similar to the result of MA samples, the main peak also corresponded to  $\text{Ti}_3\text{SiC}_2$  in the M samples. However, the intensities of the TiC peaks in all the M samples were low and did not increase with sintering temperature. The mixed Ti/Si/TiC powder  $\text{Ti}_3\text{SiC}_2$  could be synthesized with less TiC using the PDS technique. To determine the purity of  $\text{Ti}_3\text{SiC}_2$  in all the synthesized samples, one bulk M sample sintered at  $1300^{\circ}\text{C}$  for 15 min was drilled to collect some  $\text{Ti}_3\text{SiC}_2$  powder. The drilled  $\text{Ti}_3\text{SiC}_2$  powder was incorporated into some pure-TiC powder to make various mixtures of  $\text{Ti}_3\text{SiC}_2\text{:TiC}$  (90:10, 80:20, 70:30, 60:40, and 50:50) by hand-mixing. The powders then were examined using XRD to establish the relationship of the intensity ratio of TiC: $\text{Ti}_3\text{SiC}_2$  peaks versus the content of TiC in these mixture powders. This procedure was often referred to as the standard additive method,<sup>31</sup> and the quantitative results are to be reported elsewhere.<sup>40</sup>

#### (2) Purity and Density of $\text{Ti}_3\text{SiC}_2$

Figure 3(a) shows the quantitative relationship of TiC content with sintering temperature in M and MA samples sintered at  $1200^{\circ}\text{--}1400^{\circ}\text{C}$  for 30 min. At a lower sintering temperature of  $1200^{\circ}\text{--}1300^{\circ}\text{C}$ , TiC content in MA samples nearly maintained constant values of 18–22 wt%, but reached higher values of 30–33 wt% at higher sintering temperatures of  $1350^{\circ}\text{--}1400^{\circ}\text{C}$ . It was apparent that the TiC content in all the MA samples was very high (>18 wt%) and increased with sintering temperature. This result implied the synthesized  $\text{Ti}_3\text{SiC}_2$  did not have a higher purity by sintering the mechanically alloyed Ti/Si/TiC powders when the present sintering process was used. One of the reasons might have been because of the difference in the starting sizes of the titanium and silicon powders in the MA and M mixtures. Another reason might have been that the powder prepared by ball-milling was

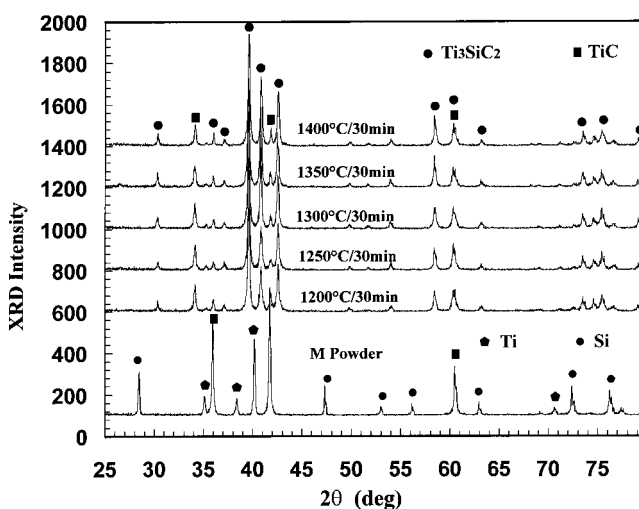


Fig. 2. XRD results of M powder and samples sintered at  $1200^{\circ}\text{--}1400^{\circ}\text{C}$  for 30 min at  $2\theta = 25^{\circ}\text{--}80^{\circ}$ .

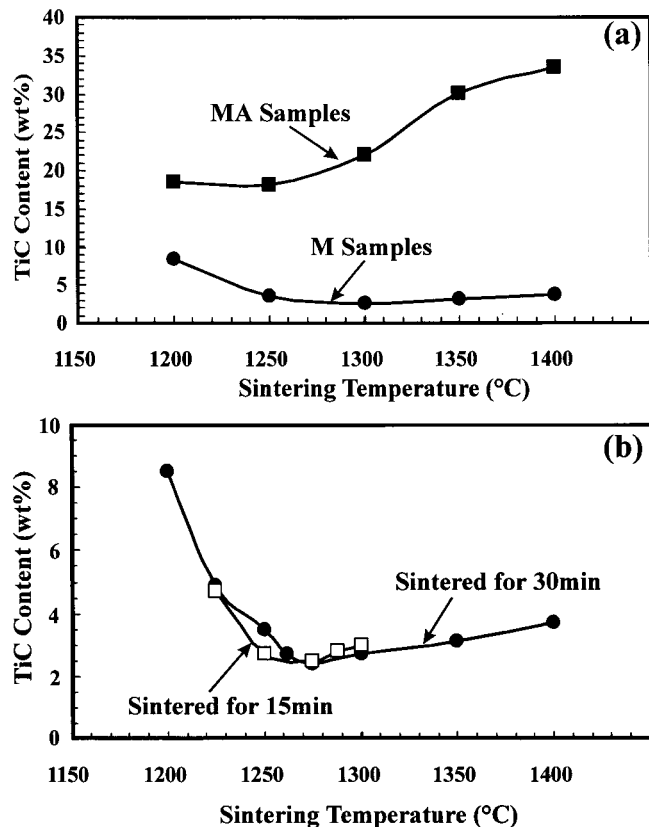


Fig. 3. Calculated TiC content in the synthesized products: (a) MA and M samples sintered at 1200°–1400°C for 30 min and (b) M samples sintered at 1200°–1400°C for 15 and 30 min.

sieved to pass through 75  $\mu\text{m}$  mesh, which might have caused off-stoichiometry of the MA powder to furthermore decrease the purity of the Ti<sub>3</sub>SiC<sub>2</sub>.

For the M samples shown in Fig. 3, the TiC content nearly maintained constant value at <5 wt% at a wide sintering temperature range of 1250°–1400°C. Apparently, the TiC content in the M samples was dramatically decreased in comparison with those in the MA samples. Therefore, the sintering process discussed below was mainly conducted on the M powders to synthesize Ti<sub>3</sub>SiC<sub>2</sub> with high purity. Figure 3(b) demonstrates the quantitative results of TiC content in the M samples sintered for 15 and 30 min. The TiC content was almost independent of the sintering time at applied sintering temperature. From the results above, it was found that the TiC content could reach the lowest value of ~3 wt% in the temperature range of 1250°–1300°C, which is ~200°–300°C lower than for those sintered from the Ti/Si/C and Ti/SiC/C powders.<sup>21–25,28–30</sup> The PDS technique could rapidly synthesize Ti<sub>3</sub>SiC<sub>2</sub> with high purity from the mixed Ti/Si/TiC powders at relatively low temperatures.

Figure 4 shows the dependence of density of the MA and M samples sintered for 30 min. The densities of the MA samples sintered at 1350° and 1400°C were ~4.60 g/cm<sup>3</sup>, as shown in Fig. 4(a). Even at a lower sintering temperature of 1200°–1300°C, their densities were higher than the theoretical density 4.53 g/cm<sup>3</sup> of the pure Ti<sub>3</sub>SiC<sub>2</sub>. The higher density of the MA samples could be attributed to the higher content of TiC impurity, whose density has been reported to be 4.9 g/cm<sup>3</sup>.<sup>17</sup> If the content and density of the TiC phase were taken into account, the theoretical density ( $\rho_T$ ) of the synthesized MA samples could be calculated, as shown in Fig. 4(a). It was apparent that the measured densities ( $\rho_M$ ) of the MA samples were lower than  $\rho_T$ . Furthermore, we could calculate the relative density of the MA samples from the ratio  $\rho_M/\rho_T$ . Figure 4(a) shows that the relative density ( $\rho_M/\rho_T$ ) of the MA samples synthesized at 1250°–1400°C was always >98%, which indicated a good densification process produced by the PDS technique.

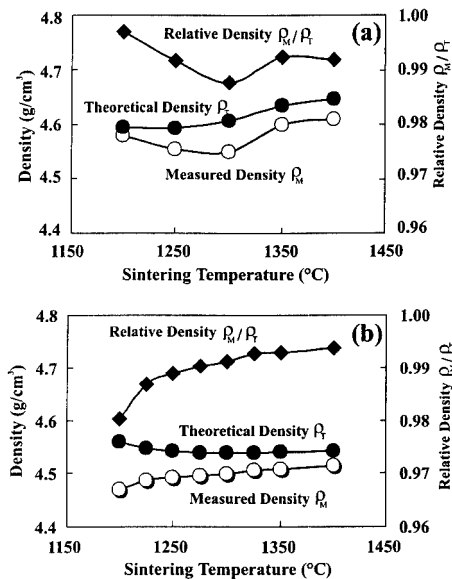


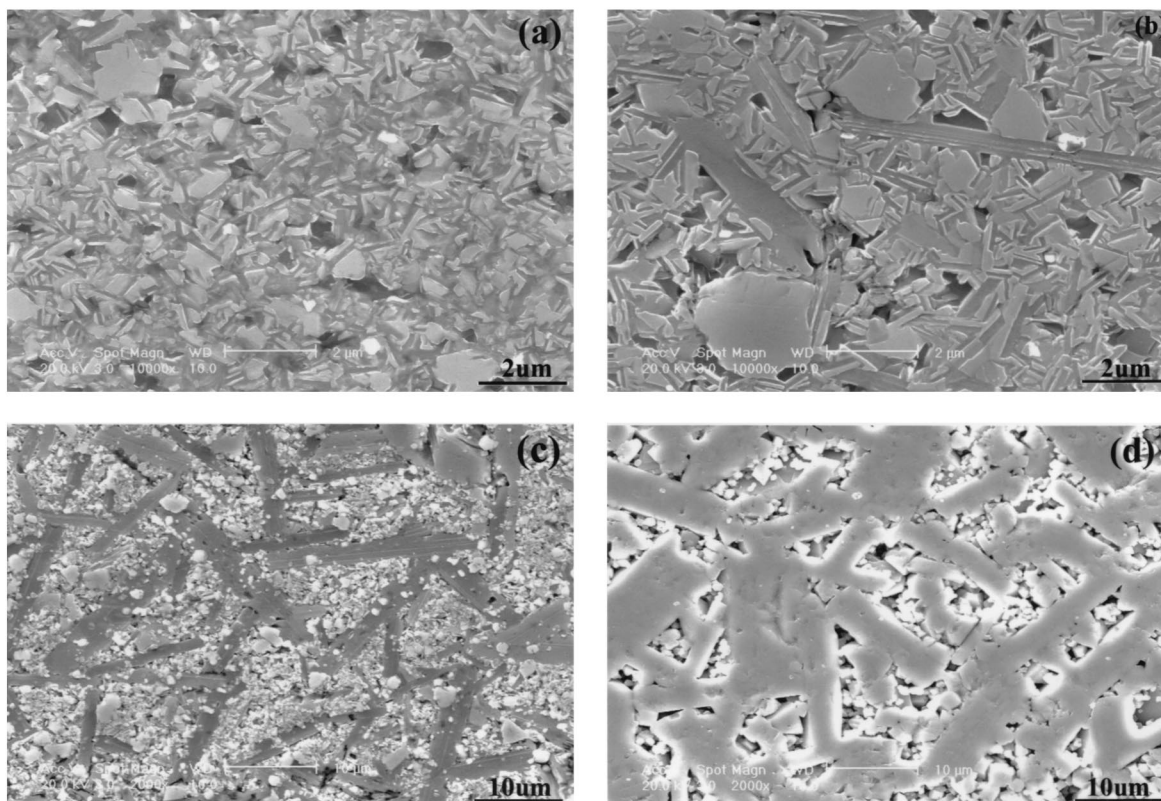
Fig. 4. Temperature dependence of measured, theoretical, and relative densities of samples sintered for 30 min: (a) MA and (b) M samples.

Similarly, the measured and theoretical densities of the M samples also could be obtained, as shown in Fig. 4(b). The measured density of Ti<sub>3</sub>SiC<sub>2</sub> was >4.50 g/cm<sup>3</sup> at the sintering temperature 1300°C. Similarly, the relative density of the M samples synthesized at 1300°–1400°C was always >99%. The two data sets in Fig. 4 indicated that the synthesized samples should be sufficiently condensed at a pressure of 50 MPa when the PDS technique was used.

Previously, Sato *et al.*<sup>24</sup> compared the mechanical-alloying effect of Ti/Si/C powders; they also found that the content of Ti<sub>3</sub>SiC<sub>2</sub> was, to some extent, higher in the hand-mixed samples than that in the mechanically alloyed samples. In combination with the present result, it was indicated that mechanical alloying of Ti/Si/C and Ti/Si/TiC powders could not improve the purity of synthesized Ti<sub>3</sub>SiC<sub>2</sub>, and was not a practicable method. Recently, by reactive sintering Ti/Si/TiC powder, Li and Miyamoto<sup>31</sup> also synthesized Ti<sub>3</sub>SiC<sub>2</sub> with purity >98 wt% at a temperature >1400°C for 2 h when a CIPing preprocess was used. The present synthesis process showed that the PDS technique could further decrease the sintering temperature to <1300°C, ~100°–150°C lower than the reactive sintering temperature and that it could shorten the sintering time substantially. Therefore, it could be concluded that, except for the Ti/Si/C and Ti/SiC/C powders, the Ti/Si/TiC powder was also a practicable mixture to synthesize Ti<sub>3</sub>SiC<sub>2</sub> with high purity. In particular, by using the PDS technique, the present optimized sintering temperature was ~200°–300°C lower than the previous temperatures.

### (3) Microstructures of Ti<sub>3</sub>SiC<sub>2</sub> Polycrystals

Figure 5 shows the micrographs of the MA samples observed using SEM. Figure 5 shows that most of the grains were very fine, ~1–2  $\mu\text{m}$  in diameter in the sample sintered at 1200°C, as shown in Fig. 5(a). At 1250°C, besides the fine grains, there were some coarse grains, ~5–10  $\mu\text{m}$  in length, as shown in Fig. 5(b). Ti<sub>3</sub>SiC<sub>2</sub> grains began to grow at this sintering temperature. When the sintering temperature increased to 1300° and 1400°C, the coarse grains grew to ~20–30  $\mu\text{m}$  in length and 5–10  $\mu\text{m}$  in width; accordingly, the volume fraction of the coarse grains had an obvious increase, as shown in Figs. 5(c) and (d). Meanwhile, there were many white fine grains or particles embedded in the lathlike coarse grains. EDX analysis showed that these white particles were a composition of TiC, which was consistent with the XRD results above.



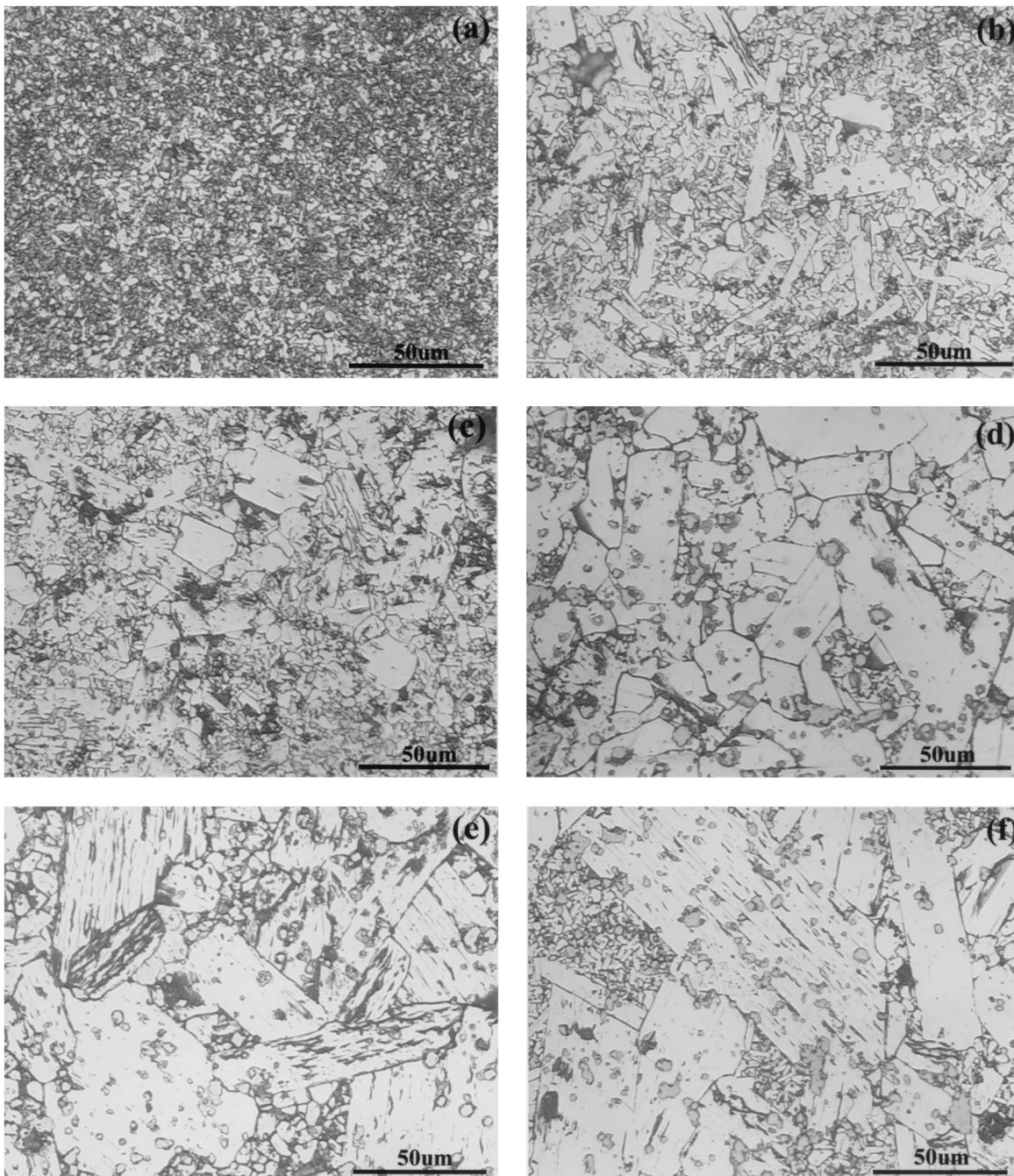
**Fig. 5.** Microstructure of the MA samples sintered at 1200°–1400°C for 30 min, observed using SEM: (a)  $T = 1200^{\circ}\text{C}$ , (b)  $T = 1250^{\circ}\text{C}$ , (c)  $T = 1300^{\circ}\text{C}$ , and (d)  $T = 1400^{\circ}\text{C}$ .

Figure 6 shows the OM micrographs of the M samples sintered at various temperatures and times. Figure 6(a) shows that the microstructure of the sample sintered at 1200°C for 3 min was very fine, and the grain size was  $\sim 5\ \mu\text{m}$  in diameter, which was somewhat larger than that of the MA samples in Fig. 5(a). When the sintering temperature was increased to 1250°C, the fine, equiaxed grains became somewhat larger; meanwhile, some lathlike grains appeared in the samples, as shown in Fig. 6(b). When the samples were sintered at 1300°C for various times, the lathlike grains could continuously grow to 50–60  $\mu\text{m}$  in length and 20–40  $\mu\text{m}$  in width, as shown in Figs. 6(c)–(e). Meanwhile, the volume fraction of lathlike grains was increased. At the higher sintering temperature of 1350° and 1400°C, the lathlike grains grew slowly, while their volume fraction continued to increase, as shown in Fig. 6(f). From the observations above, it was apparent that the size and volume fraction of the coarse grains in the M samples were distinctly larger than those in the MA samples. This meant that the growth of coarse grains in MA samples could be more difficult than that in M samples. The difference in grain size might have been due to the lower purity of  $\text{Ti}_3\text{SiC}_2$  in the MA samples, and, in turn, the TiC particles prevented the rapid growth of  $\text{Ti}_3\text{SiC}_2$  grains. Moreover, because the grain sizes and volume fraction of  $\text{Ti}_3\text{SiC}_2$  polycrystals strongly depended on the sintering temperature and time, by observing all the M samples, the microstructure distribution of  $\text{Ti}_3\text{SiC}_2$  was summarized and illustrated in Fig. 7. The microstructure of  $\text{Ti}_3\text{SiC}_2$  could be classified in three types, i.e., fine, coarse, and duplex-grained, in which the size of coarse grains was  $>10$  times that of the fine grains. For the duplex grains, the size and volume fraction of the coarse grains were a function of sintering temperature and time. Meanwhile, the purity of  $\text{Ti}_3\text{SiC}_2$  could be achieved at a very high value of 97 wt% in the sintering temperature range of the duplex grains. Therefore, it could be concluded that the microstructure of the M samples could be adjusted and optimized by controlling the sintering temperature and time. In turn, the performance of the synthesized  $\text{Ti}_3\text{SiC}_2$  products could be improved under the optimized sintering conditions. In comparison with the synthesis work using a HIPing

technique,<sup>28,29</sup> one of the advantages of the PDS technique was lower sintering temperature and shorter sintering time, by which the microstructure of  $\text{Ti}_3\text{SiC}_2$  also could be controlled to have various types.

#### (4) Comparison of Various Sintering Methods for $\text{Ti}_3\text{SiC}_2$

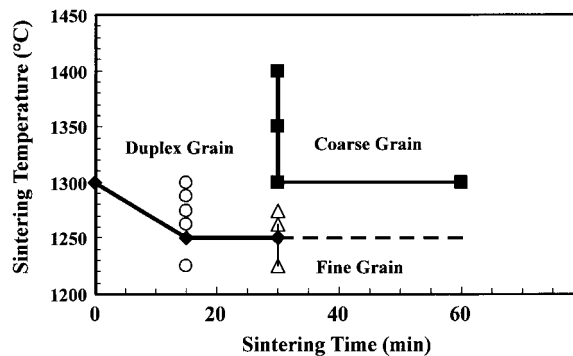
During the past decade,  $\text{Ti}_3\text{SiC}_2$  samples with various purities have been synthesized by many investigators using various methods. Lis and co-workers<sup>18,19</sup> sintered  $\text{Ti}_3\text{SiC}_2$  samples using HIPing or SHS-HIPing methods by using Ti/Si/C powders at 1200°–1800°C. They found that dense  $\text{Ti}_3\text{SiC}_2$  samples with purity  $>80\%$  could be synthesized at 1400°C for 3 h. By using the same mixture powders, Zhou, Sun, and co-workers<sup>25</sup> synthesized  $\text{Ti}_3\text{SiC}_2$  with purity of 87–93 wt% through *in situ* hot-pressing/solid-liquid reaction at a higher temperature range of 1450°–1600°C. To decrease the sintering temperature, they either added NaF additive into the mixture powders or used a fluctuant method for the synthesis of  $\text{Ti}_3\text{SiC}_2$  at a lower temperature range.<sup>26,27</sup> The purity in all the samples synthesized by the two methods was  $\leq 90\%$ . Radhakrishnan and co-workers<sup>20,21</sup> also prepared Ti/Si/C powders with excess silicon and then sintering them at 1350°C for 5 h; the purities of  $\text{Ti}_3\text{SiC}_2$  were 96 vol% and 98.7 vol%, respectively, for TSC1 (Ti:Si:C = 3:1.1:2) and TSC2 (Ti:Si:C = 3:1.2:2) products. Recently, Gao *et al.*,<sup>22</sup> Li *et al.*,<sup>23</sup> and Sato *et al.*<sup>24</sup> also found that  $\text{Ti}_3\text{SiC}_2$  with high purity could form only in a temperature range of 1400°–1500°C from the starting powder of Ti/Si/C using a HIPing technique. Barsoum and El-Raghy<sup>28,29</sup> synthesized  $\text{Ti}_3\text{SiC}_2$  from Ti/Si/C powder prepared by cold-pressing at 180 MPa and then by hot-pressing at 1450°–1700°C for 4–24 h. In their synthesized samples, there was  $<2$  vol% SiC and  $\text{TiC}_x$ , and the grain size varied with the sintering temperature and time. Recently, the third mixture powder of Ti/Si/TiC was used to fabricate  $\text{Ti}_3\text{SiC}_2$  with purity  $>98$  wt% at temperature  $>1400^{\circ}\text{C}$  for  $>2$  h.<sup>31</sup> From the synthesis processes available, it was suggested that  $\text{Ti}_3\text{SiC}_2$  should be sintered at temperatures  $>1350^{\circ}\text{C}$ , independent of the Ti/Si/C, Ti/SiC/C, or Ti/Si/TiC



**Fig. 6.** Microstructure of the M samples sintered at 1200°–1400°C, observed using OM: (a)  $T = 1200^{\circ}\text{C}$  and  $t = 30$  min, (b)  $T = 1250^{\circ}\text{C}$  and  $t = 30$  min, (c)  $T = 1300^{\circ}\text{C}$  and  $t = 15$  min, (d)  $T = 1300^{\circ}\text{C}$  and  $t = 30$  min, (e)  $T = 1300^{\circ}\text{C}$  and  $t = 60$  min, and (f)  $T = 1400^{\circ}\text{C}$  and  $t = 30$  min.

powder mixture used. In the present synthesis process of Ti<sub>3</sub>SiC<sub>2</sub>, the sintering temperature was decreased to <1300°C when the PDS technique was used. The difference in the synthesis processes of Ti<sub>3</sub>SiC<sub>2</sub> with different mixture powders was explained as follows.

In the PDS process, it was reported that a pulse electric field may produce and activate the surface of the powder particles, which can enable an easy sintering process. It has been identified that the temperature of the compacted powders, in general, was higher than the temperature of the graphite mold during the PDS process<sup>32</sup> because of the production of the plasma between the powder particles. Therefore, the plasma may have locally increased the temperature to a much higher level than the controlled average temperature, which could effectively promote the synthesis reaction of Ti<sub>3</sub>SiC<sub>2</sub>. On the other hand, Sato *et al.*,<sup>24</sup> for the synthesis of Ti<sub>3</sub>SiC<sub>2</sub> from Ti/Si/C powder, reported that they



**Fig. 7.** Microstructure distribution of Ti<sub>3</sub>SiC<sub>2</sub> in M samples sintered at various temperatures and times.

assumed that the TiC phase would form first, i.e.,  $\text{Ti} + \text{C} \rightarrow \text{TiC}$ , because, thermodynamically, the above reaction had the highest reactivity among all the reactions. Second, at a temperature near the eutectic point (1333°C), the eutectic liquid phase began to appear between titanium and silicon particles as follows:  $\text{Ti} + \text{Si} \rightarrow \text{Ti-Si}(l)$ . Third,  $\text{Ti}_3\text{SiC}_2$  formed at the interfaces between the Ti-Si liquid phase and TiC particles, i.e.,  $2\text{TiC} + \text{Ti-Si}(l) \rightarrow \text{Ti}_3\text{SiC}_2$ . Because TiC has an octahedral structure, whereas  $\text{Ti}_3\text{SiC}_2$  has a layered hexagonal structure in which almost close-packed planes of titanium are separated from each other by hexagonal nets of silicon, every fourth layers is a silicon layer.<sup>1,2</sup> In the present Ti/Si/TiC mixture, the TiC had existed in advance; therefore,  $\text{Ti}_3\text{SiC}_2$  could form by connecting the Ti-Si(l) and existing TiC, which was a more simple reaction process than for Ti/Si/C powder. Li and Miyamoto synthesized  $\text{Ti}_3\text{SiC}_2$  from the same Ti/Si/TiC powder at a temperature of  $\sim 1400^\circ\text{C}$ , which was higher than the eutectic point (1333°C) of the Ti-Si(l) phase. When the PDS technique was applied to the Ti/Si/TiC powder, the optimized sintering temperature and time were decreased to  $<1300^\circ\text{C}$  and 15 min, which should be mainly attributed to the effect of the activated plasma between powder particles during the PDS sintering. It is suggested that the PDS technique is a rapid method for the synthesis of  $\text{Ti}_3\text{SiC}_2$  at lower temperatures and shorter times. Meanwhile, Ti/Si/TiC powder is a favorable mixture to synthesize  $\text{Ti}_3\text{SiC}_2$  in comparison with Ti/SiC/C and Ti/Si/C powders,<sup>36–39</sup> especially by using the PDS technique. Furthermore, the Ti/Si/TiC powder should be considered as another new candidate mixture to synthesize  $\text{Ti}_3\text{SiC}_2$  samples or products in the future.

#### IV. Conclusions

(1) The mechanical alloying (MA) treatment of Ti/Si/TiC powders before sintering is not a practicable method to synthesize  $\text{Ti}_3\text{SiC}_2$  using the pulse discharge sintering (PDS) technique, because the content of TiC in the MA samples is always  $>18$  wt% at a wide temperature range of  $1200^\circ\text{C}$ – $1400^\circ\text{C}$ . However, at  $1250^\circ\text{C}$ – $1400^\circ\text{C}$ , the TiC content in the mixture method (M) samples synthesized from the Ti/Si/2TiC powder mixture can be decreased to  $<5$  wt%; when the sintering temperature is  $1250^\circ\text{C}$ – $1300^\circ\text{C}$ , the TiC content is further decreased to  $\sim 3$  wt%. The grain size of  $\text{Ti}_3\text{SiC}_2$  changes little in the temperature range of  $1200^\circ\text{C}$ – $1250^\circ\text{C}$ , and it is sensitive to the sintering temperature at  $1250^\circ\text{C}$ – $1300^\circ\text{C}$ .

(2) In the temperature range of  $1250^\circ\text{C}$ – $1400^\circ\text{C}$ , the microstructure of the M samples can be adjusted and optimized to have various types, such as fine, coarse, and duplex-grained, depending on the sintering temperature and time. Therefore, it is possible to synthesize  $\text{Ti}_3\text{SiC}_2$  polycrystals that have high performance through sintering Ti/Si/2TiC powder in the temperature range for a short time. It is suggested that the PDS technique is a rapid method for the synthesis of  $\text{Ti}_3\text{SiC}_2$  at lower temperatures and shorter times. Furthermore, Ti/Si/TiC powder can be considered as a new candidate mixture to fabricate  $\text{Ti}_3\text{SiC}_2$  products in the future.

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