Rapid Synthesis of Ternary Carbide Ti$_3$SiC$_2$ through Pulse-Discharge Sintering Technique from Ti/Si/TiC Powders

Z.F. ZHANG, Z.M. SUN, and H. HASHIMOTO

Ti/Si/TiC powders with molar ratios of 1:1:2 (M1) and 2:2:3 (M2) were prepared for the synthesis of a ternary carbide Ti$_3$SiC$_2$ by using the mixture method for 24 hours in an Ar atmosphere. The synthesis process was conducted at 1200 °C to 1400 °C under a pressure of 50 MPa, using the pulse-discharge sintering (PDS) technique. After sintering, the phase constituents and microstructures of the samples were analyzed by X-ray diffraction (XRD) technique and observed by optical microscopy and scanning electron microscopy. The results showed that the phases in all the samples consisted of Ti$_3$SiC$_2$ and small amounts of TiC, and the optimum sintering temperature was found to be in the relatively low range of 1250 °C to 1300 °C. By the standard additive method, the relative content of Ti$_3$SiC$_2$ was calculated. For the M1 samples, the lowest TiC content can be only decreased to about 3 to 4 wt pct, whereas the content of Ti$_3$SiC$_2$ in the M2 samples is always lower than that in the M1 samples. When the M2 powder was sintered at 1300 °C for 8 to 240 minutes, the TiC peaks were found to show a very low intensity, and the corresponding content of Ti$_3$SiC$_2$ was calculated to be higher than 99 wt pct. The grain size of Ti$_3$SiC$_2$ increased from 5 to 10 μm to 80 to 100 μm in the entire applied sintering temperature range. The relative density of the M2 samples was measured to be higher than 99 pct at sintering temperatures above 1275 °C. It indicates that the PDS technique can rapidly synthesize high-content Ti$_3$SiC$_2$ from the Ti/Si/TiC powders in a relatively low temperature range.

I. INTRODUCTION

To improve the properties of products or structures, especially for those employed at high temperatures, many efforts have been made to fabricate high-performance materials, including metals and ceramics. Recently, ternary carbide Ti$_3$SiC$_2$ was found to be a novel material which combines many of the best attributes of both metals and ceramics, such as a low density (4.53 g/cm$^3$) and high melting point (~3000 °C). Besides, this ternary compound is elastically stiff, electrically and thermally conductive, machinable, relatively soft, and resistant to thermal shock. Also, it can deform by a combination of delamination and kink-band formation in individual grain, as well as by the formation of shear bands. Therefore, this material is very damage tolerant of different deformation modes before fracture. The combination of strength, ductility at elevated temperatures, non-susceptibility to thermal shock, and good machinability is seldom observed in other materials. Therefore, it is desirable to fabricate high-content Ti$_3$SiC$_2$ samples and to develop new synthesis techniques for a broad application of this novel material.

Ti$_3$SiC$_2$ was first synthesized by Jeitschko and Nowotny using a chemical reaction in 1967, followed by Goto and Hirao using the CVD (chemical vapor deposition) method in 1987. In the past decade, various processes, including (1) are melting, (2) chemical reaction, (3) hot isothermal pressing (HIP) or self-propagating high-temperature synthesis (SHS)-HIP, and (4) reactive sintering were employed and developed to synthesize Ti$_3$SiC$_2$ samples. Among these synthesis methods, the sintering process is a common way to fabricate bulk Ti$_3$SiC$_2$ samples, mainly by the following three reactions: (1) $3Ti + Si + 2C \rightarrow Ti_3SiC_2$, (2) $2Ti + SiC + C \rightarrow Ti_3SiC_2$, and (3) $Ti + Si + 2TiC \rightarrow Ti_3SiC_2$. Among the three reactions, the first reaction was frequently employed for the synthesis of Ti$_3$SiC$_2$ by many researchers, such as Pamplie et al., Li et al., Gao et al., Li and co-workers, Racu et al., Radhakrishnan et al., and Zhou and co-workers. However, Barsoum and El-Raghy synthesized high-content Ti$_3$SiC$_2$ samples through the second reaction in the temperature range from 1450 °C to 1600 °C. Li and Miyamoto synthesized Ti$_3$SiC$_2$ samples through cold isostatic pressing and reactive sintering a Ti/Si/TiC mixture at temperatures near 1400 °C. Recently, we developed two new reactions to synthesize Ti$_3$SiC$_2$ samples through mixtures of Ti/Si/TiC and Ti/TiSi$_2$/TiC powders by using a pulse discharge sintering (PDS) technique. This showed that the sintering processes could be rapidly completed at the relatively low temperature of 1300 °C. The PDS technique is a recently developed densification method which consists of a pulse electrical discharge process when plasma is generated between powder particles, followed by resistance heating while a uniaxial pressure is applied. It is assumed that densification is achieved by the contribution of three factors: plasma generation, resistance sintering, and pressure application. Therefore, the metals and ceramics can be sintered rapidly under relatively low temperatures, with fine grains and high performances due to the application of the PDS technique. In the present research, we further synthesized Ti$_3$SiC$_2$ samples from Ti/Si/TiC powder through the PDS technique at a relatively low temperature range.
Table I. Collected Molar Ratio of Ti:Si:C in TiSiC<sub>2</sub> Monolithic Phase Region from Isothermal Sections at 1200 °C and 1400 °C of Ti-Si-C Ternary Phase Diagrams Provided by Different Authors

<table>
<thead>
<tr>
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<tr>
<td>T = 1200 °C</td>
<td>Low</td>
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<td>Low</td>
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<tr>
<td>Ti (at. pct)</td>
<td>49.3</td>
<td>51.4</td>
<td>45.8</td>
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<tr>
<td>Si (at. pct)</td>
<td>18.8</td>
<td>20.8</td>
<td>16.7</td>
</tr>
<tr>
<td>C (at. pct)</td>
<td>29.2</td>
<td>31.3</td>
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II. EXPERIMENTAL PROCEDURE

Commercially available Ti, Si, and TiC powders with sizes and purities of 10 μm and 99.9 pct (Ti), 10 μm and 99.9 pct (Si), and 2 to 5 μm and 99 pct (TiC), respectively, were employed. First, several isothermal sections of the Ti-Si-C ternary-phase diagram at 1200 °C and 1400 °C, obtained from different investigators, were compared.<sup>[17,26]</sup> The atomic percentages of Ti, Si, and C in the TiSiC<sub>2</sub> monolithic-phase region were calculated from three ternary-phase diagrams of Ti-Si-C, and the quantitative results are listed in Table I. It is found that the monolithic-phase region of TiSiC<sub>2</sub> has a relatively wide composition range. For instance, the atomic percentage of Ti ranges from 45 to 52 pct, and the atomic percentages of Si and C are in the range of 16.7 to 22 pct and 29 to 38 pct, respectively. In the present sintering process, the stoichiometric ratio (Ti/Si:TiC = 1:1:2) of the TiSi/TiC powder (M1) was selected. Another molar ratio of TiSi:TiC was selected as 2:2:3 and referred to as M2. Whereas the atomic percentages of Ti, Si, and C in the stoichiometric M1 powder are, respectively, 50, 17, and 33 pct, the percentages in M2 powder will be equal to 50, 20, and 30 pct in the monolithic-phase region of TiSiC<sub>2</sub> from the Ti-Si-C ternary-phase diagrams. In addition, another TiSi/TiC powder (M3) with a molar ratio of 2:3:4 was prepared for comparing the effect of excess Si. Before sintering, the M1, M2, and M3 powders were mixed in a turbular shaker mixer in an Ar atmosphere for 24 hours. During mixing, some zirconia balls, measuring 3 mm in diameter, were put into the container to ensure better mixing. The powder mixtures were filled in a cylindrical graphite mold with an i.d. of 20 mm, o.d. 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 were fixed in a PDS apparatus, with two water-cooled copper electrodes, which serve also as the pressing plates, compressed from the upper and lower ends, respectively. Before initiating the sintering, the chamber was evacuated to a pressure of 10<sup>−3</sup> Pa.

During sintering, the heating rate was controlled in the range from 50 °C to 60 °C/min, and the applied pressure was maintained at 50 MPa. The sintering process was controlled at 1200 °C to 1400 °C for 8 to 240 minutes. After sintering, each side of the sample surface was ground to remove the graphite layer and the affected zone of carbon (more than 0.3 mm in depth). The phase analysis of the samples was conducted by X-ray diffraction (XRD) with Cu Kα radiation at 30 kV and 40 mA. The samples were mechanically polished and etched by a solution of H<sub>2</sub>O-HNO<sub>3</sub>-HF (2:1:1) to expose the TiSiC<sub>2</sub> grains. The microstructures of the samples were observed by scanning electron microscopy (SEM) and optical microscopy (OM). The density of the synthesized samples was measured by means of the Archimedes method.

III. RESULTS AND DISCUSSION

A. The XRD Analysis of the Synthesized Samples

Figure 1 shows the XRD patterns of the mixed TiSi/2TiC powder prior to sintering and of the M1 samples sintered at 1200 °C to 1400 °C for 30 minutes. For the powder, Ti, Si, and TiC peaks can be clearly seen in its XRD pattern. When the M1 powder was sintered at different temperatures, all the Ti and Si peaks disappeared, and TiSiC<sub>2</sub> peaks with high intensities appeared in the XRD patterns. Meanwhile, the TiC peak intensities were substantially decreased at all the sintering temperatures. This indicates that the M1 samples mainly consist of TiSiC<sub>2</sub> phase and a small amount of TiC. When the M1 powder was sintered for 15 minutes in this temperature range, their XRD patterns nearly showed the same features as those sintered for 30 minutes.

Figure 2 summarizes the XRD patterns of the 2Ti/2Si/3TiC powder and the M2 samples sintered at 1225 °C to 1325 °C for 15 minutes. The XRD pattern of the 2Ti/2Si/3TiC powder is similar to that of the TiSi/TiC powder in Figure 1. It is interesting that the two TiC peaks at 2θ = 36 and 41.8 deg TiC(111) and TiC(200, respectively) were decreased to very low intensity in the M2 samples sintered at 1275 °C to 1325 °C. In particular, the TiC peaks became too weak to be identified in the XRD patterns when the M2 sample was sintered at 1300 °C, and the primary diffraction peaks corresponded to TiSiC<sub>2</sub> phase. To further compare the effect of sintering time on the content of TiSiC<sub>2</sub>, the M2 powder was sintered at 1300 °C for different times, and their XRD patterns are shown in Figure 3.
Fig. 2—XRD patterns of 2Ti/2Si/3TiC powder and the M2 samples sintered at 1225 °C to 1325 °C for 15 min.

Fig. 3—XRD patterns of the M2 samples sintered at 1300 °C for 8 to 240 min.

Ti3SiC2 powder. This procedure is often referred to as the standard additive method. Figure 4 shows the XRD patterns of the five groups of mixture powders, along with the collected Ti3SiC2 powder. It can be seen that the intensity of TiC peaks (I_{TC}) monotonically increases with the added TiC amount. Meanwhile, the intensity of Ti3SiC2 peaks (I_{TSC}) decreased gradually with the addition of TiC. Besides, it is noted that the lower content of TiC can result in a higher peak intensity in comparison with the Ti3SiC2. It indicates that the diffraction intensity is quite different for the two phases of Ti3SiC2 and TiC. For a two-phase material, for example, Ti3SiC2 and TiC, their diffraction peak intensities can be expressed as follows:

\[ I_{TSC} = \frac{K_{TSC}W_{TSC}}{2\rho_{TSC}(\mu_{mTSC} + W_{TC}(\mu_{mTC}))} \]  
\[ I_{TC} = \frac{K_{TC}W_{TC}}{2\rho_{TC}(\mu_{mTC} + W_{TC}(\mu_{mTC}))} \]

where \( \rho_{TC} \) and \( \rho_{TSC} \) are the densities of the TiC and Ti3SiC2 phases, respectively; \( W_{TC} \) and \( W_{TSC} \) are the weight percentages of TiC and Ti3SiC2 phases, respectively; \( K_{TC} \) and \( K_{TSC} \) are the diffraction constants of the TiC and Ti3SiC2 phases, respectively; and \( (\mu_{m})_{TC} \) and \( (\mu_{m})_{TSC} \) are the absorption coefficients of the TiC and Ti3SiC2 phases. Therefore, the relative intensity of the TiC to Ti3SiC2 peaks (\( I_{TC}/I_{TSC} \)) will be

\[ \frac{I_{TC}}{I_{TSC}} = \frac{\rho_{TC}K_{TC}W_{TC}}{\rho_{TSC}K_{TSC}W_{TSC}} = K \frac{W_{TC}}{1 - W_{TC}} \]

Here, \( K \) is the ratio of \( \rho_{TC}K_{TC} \) to \( \rho_{TSC}K_{TSC} \) as a constant.

From the XRD results in Figure 4, the integrated intensity ratios of the TiC(200) and TiC(111) peaks to Ti3SiC2(104) were calculated, and the quantitative relationship between \( I_{TC}/I_{TSC} \) and the added TiC amount is shown in Figure 5. From the figure, a noticeable feature is that the intensity ratios do not show linear relations with the added TiC amount, which is consistent with Eq. [3]. However, in a similar method, the intensity ratio \( I_{TC}/I_{TSC} \) clearly showed a linear relation with the added TiC amount. As we know, when adding TiC into the (Ti3SiC2 + TiC) mixture, the content ratio of TiC to Ti3SiC2 in the mixture will not be
proportional to the added TiC amount. Since the intensity ratio $I_{TC}/I_{TSC}$ represents the content ratio of TiC to Ti$_3$SiC$_2$, it is natural that there should not be a linear relation between the intensity ratio and added TiC amount. From the present results, the constant $K$ was calculated to be 1.80 and 1.20, respectively, when calculated from TiC(200)/Ti$_3$SiC$_2$(104) and TiC(111)/Ti$_3$SiC$_2$(104), as shown in Figure 5. When knowing the integrated intensity ratio of a two-phase mixture of (Ti$_3$SiC$_2$ + TiC), by rearranging Eq. [3], the relative weight percentages of Ti$_3$SiC$_2$ and TiC can be expressed as follows:

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

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

If the volume fractions of Ti$_3$SiC$_2$ and TiC are used, the constant $K$ will be equal to 1.95 and 1.30, calculated from the TiC main and second peaks of (200) and (111), respectively.

C. The TiC Content of the Synthesized Samples

By using the calibrated Eqs. [4] and [5], the relative weight percentages of Ti$_3$SiC$_2$ and TiC in all the M1 and M2 samples were calculated from the XRD patterns of Figures 1 through 3. For the M1 samples, the TiC content was calculated from its main and secondary peak intensities of TiC(200) and TiC(111) at $2\theta = 41.8$ and 36 deg, respectively. It is found that the TiC contents calculated by the two peak intensities are identical. For the M2 samples, the TiC content was only calculated from its main peak intensity of TiC(200) at $2\theta = 41.8$ deg, because the XRD intensity at the secondary peak (TiC(111)) at $2\theta = 36$ deg is very low or negligible. Figure 6(a) shows the TiC content in the M1 and M2 samples sintered at 1225 °C to 1325 °C for 15 min. It can be seen that the TiC content in the M1 samples is approximately constant (about 3 to 4 wt pct) at 1250 °C to 1300 °C. However, the TiC content in the M2 samples is less than that in the M1 samples sintered in this temperature range. At 1300 °C, the TiC content in the M2 sample is reduced to a very low value of 0.8 wt pct. When the sintering process was conducted for 30 minutes, as shown in Figure 6(b), the M2 samples also had a lower TiC content than the M1 samples at the sintering temperature range. Figure 6(c) shows the effect of sintering time on the TiC content in the M2 samples sintered at 1300 °C. It is apparent that the TiC content in the M2 samples is approximately constant (<1.5 wt pct over a wide sintering-time range of 8 to 240 minutes), which would be favorable for controlling the microstructure and optimizing the performance of Ti$_3$SiC$_2$ samples or products. This indicates that the present optimum sintering temperature (1300 °C) through the PDS technique is about 200 °C to 300 °C lower than that of the synthesized samples from Ti/Si/C and Ti/Si/C powders by the HIP technique. In addition, the relative content of Ti$_3$SiC$_2$ can be further...
Fig. 7—Microstructure of the M2 samples sintered from 2Ti2Si3/TiC powders at different temperatures: (a) microstructure of the fine grains ($T = 1250 \, ^\circ C$, $t = 30 \, \text{min}$); (b) microstructure of the fine and plateletlike grains ($T = 1300 \, ^\circ C$, $t = 30 \, \text{min}$); (c) microstructure of the plateletlike grains ($T = 1300 \, ^\circ C$, $t = 120 \, \text{min}$); and (d) microstructure of the coarse grains ($T = 1400 \, ^\circ C$, $t = 30 \, \text{min}$).

D. Microstructure and Density of Ti$_3$SiC$_2$ Samples

It was found that the microstructure of Ti$_3$SiC$_2$ samples was not influenced by the molar ratio of Ti/Si/TiC in the M1 and M2 samples. Figure 7 shows a typical microstructure of the M1 and M2 samples sintered at different temperatures and times. When the sintering temperature was 1200 $^\circ C$, the microstructure consists of homogeneous fine grains of 5 to 10 $\mu m$ in length and 2 to 5 $\mu m$ in width. When the sintering temperature was increased to 1250 $^\circ C$, some grains began to grow and appeared in a plateletlike shape of more than 10 $\mu m$ in length, as shown in Figure 7(a). At an increased sintering temperature of 1300 $^\circ C$, the plateletlike grains could continue to grow with increased sintering time. As shown in Figures 7(b) and (c), the grain size can reach about 30 to 40 $\mu m$ ($t = 30 \, \text{minutes}$) and 40 to 50 $\mu m$ ($t = 120 \, \text{minutes}$), respectively. Meanwhile, the volume fraction of the plateletlike grains increased with sintering time. At higher sintering temperatures of 1350 $^\circ C$ and 1400 $^\circ C$, the size of the plateletlike grains can grow to more than 80 to 100 $\mu m$ in length and 30 to 50 $\mu m$ in width, as shown in Figure 7(d). From the previous micrography results, it can be concluded that the grain size and volume fraction of the coarse grains strongly depend on the sintering temperature. In the optimum sintering temperature of 1300 $^\circ C$, the typical microstructure consists of fine grains (5 to 10 $\mu m$) and plateletlike grains (30 to 50 $\mu m$), which was defined as a duplex microstructure.

Figure 8 shows the dependence of density in the M2 samples on the sintering temperature and time. It can be seen that when the sintering temperature is below 1250 $^\circ C$, the measured density ($\rho_m$) is less than 4.50 g/cm$^3$. When the sintering temperature increased to above 1275 $^\circ C$, the measured density increased to 4.50 to 4.52 g/cm$^3$, which is quite close to the theoretical density of pure Ti$_3$SiC$_2$ (4.53 g/cm$^3$). Since the theoretical density of TiC is equal to 4.90 g/cm$^3$, the theoretical density ($\rho_T$) of the synthesized M2 samples was calculated by taking the relative content of Ti$_3$SiC$_2$ in Figure 6 into account, and the results are also shown in Figure 8(a). Therefore, the relative density of the M2 samples can be obtained from the ratio $\rho_m/\rho_T$ of the measured density to the theoretical density. It is apparent that the relative density of the M2 samples is quite high (97.7 to 99.4 pct) at all the sintering temperatures. At sintering temperatures above 1275 $^\circ C$, the relative density of the M2 samples is greater than 99 pct. For the M2 samples sintered at 1300 $^\circ C$ for different times, the relative densities are quite high even after short-time sintering (Figure 8(b)). Recently, high-temperature compressive tests were conducted on the...
Ti$_3$SiC$_2$ samples sintered at the temperature of 1300 °C for 15 minutes. It was found that the Ti$_3$SiC$_2$ samples began to display plastic deformation behavior in compression at the temperature of 900 °C,[28] which is about 200 °C to 300 °C less than the samples made from Ti/SiC/C powder by the HIP technique.[29] Meanwhile, when the same samples were subjected to four-point bending, the Ti$_3$SiC$_2$ samples displayed large plastic deformation at temperatures higher than 1200 °C.[30] From the aforementioned results, it can be concluded that high-performance Ti$_3$SiC$_2$ samples can be synthesized from the 2Ti/2Si/3TiC powder in the relatively low sintering temperature range of 1250 °C to 1300 °C.

E. Synthesis Processes of Ti$_3$SiC$_2$

During the past decade, Ti$_3$SiC$_2$-rich samples were synthesized by many investigators through various powder mixtures and sintering processes, as listed in Table II. It can be seen that, in general, the sintering temperature is higher than 1350 °C for most synthesis processes, and a long sintering time was necessary regardless of the starting powders (i.e., Ti/SiC, Ti$_3$SiC$_2$/C, or Ti/Si/TiC). To explain the synthesis processes of Ti$_3$SiC$_2$, several reaction mechanisms were proposed. Zhou et al.[18] synthesized Ti$_3$SiC$_2$ from Ti/SiC powder through a hot-pressing process in the range of 1450 °C to 1600 °C. They proposed a solid-liquid reaction mechanism of Ti$_3$SiC$_2$ among the liquid Si and solid Ti and C. Recently, Li et al.[11] and Sato et al.[12] proposed another possible reaction path for the synthesis of Ti$_3$SiC$_2$ from Ti/Si/C powders. They concluded that (1) Ti first reacted with C to form TiC particles; (2) Ti and Si reacted to form a liquid phase of Ti-Si; and (3) the final formation of Ti$_3$SiC$_2$ was from the solid-liquid reaction between the TiC particles and the Ti-Si liquid phase. For the synthesis reaction from Ti/SiC/C powder, Barsoum and El-Raghy[13,14] proposed that C and Si diffuse into Ti particles to form TiC, and Ti$_3$SiC$_2$, then those phases, in turn, react to form Ti$_3$SiC$_2$. Radhakrishnan et al.[16] employed the reaction 3TiC + 2Si $\Rightarrow$ Ti$_3$SiC$_2$ + 2SiC to form a composite of Ti$_3$SiC$_2$ and SiC from a mixture of TiC and Si. From the aforementioned synthesis processes, it is apparent that Ti$_3$SiC$_2$ can be formed by different starting powders and sintering processes. But, when the powders were sintered by the PDS technique, the sintering temperature could be decreased to a lower range (below 1350 °C) for a short time, regardless of the starting powders used (i.e., Ti/SiC/TiC, Ti/TiSi$_2$/TiC, or Ti/Si/TiC).[11,12,21] As listed in Table II, it indicates that the PDS technique can effectively improve the reaction process of Ti$_3$SiC$_2$ from different powders.

For the present synthesis processes, we considered that there might be three possible reaction paths to synthesize Ti$_3$SiC$_2$ from the starting powders of Ti/Si/TiC. One is the liquid-solid reaction among Ti, TiC particles, and liquid Si, as proposed by Zhou and co-workers.[18,19] In addition, from the reaction by Radhakrishnan et al.[16] Ti$_3$SiC$_2$ can be formed by TiC and Si particles in the first step. Then, another reaction between SiC and Ti can result in the formation of Ti$_3$SiC$_2$, as reported in a diffusion couple of SiC/Ti by Iseki et al.[22] Therefore, the Ti powder will react with the released SiC to form Ti$_3$SiC$_2$. This process can be understood to mean that all the Ti/Si/TiC powders will alternately react to be synthesized Ti$_3$SiC$_2$, which can be regarded as the second possible reaction path from Ti/Si/TiC powders. The third possible reaction path to form Ti$_3$SiC$_2$ might result from the Ti-Si liquid phase and TiC particles. For the Ti-Si system, there are two eutectic reactions for the Si-TiSi$_2$ and Ti$_3$Si$_4$ compositions, both at a temperature of 1333 °C.[11,12,20] When the sintering processes were controlled at the eutectic temperature, the eutectic liquid phase may begin to appear between Ti and Si particles. Finally, Ti$_3$SiC$_2$ will be easily formed at the interfaces between the Ti-Si liquid and TiC particles, i.e.,

$$2\text{TiC} + \text{Ti-Si (liquid)} \Rightarrow \text{Ti}_3\text{SiC}_2$$

(6)

To confirm the formation of the Ti-Si liquid phase, a 2Ti/3Si/4TiC powder (M3) with more excess Si was sintered at 1250 °C and 1300 °C for 15 minutes through the PDS technique. The XRD patterns of the M3 samples are shown in Figure 9. It can be seen that, except for the Ti$_3$SiC$_2$ and TiC phases, there were other kinds of diffraction peaks at 2θ = 39 and 43.2 deg, respectively. They were identified to correspond to TiSi$_2$ phase, which is close to the formation of the Ti-Si eutectic phase. This indicates that the eutectic phase of the Si-TiSi$_2$ had formed during sintering at 1250 °C to 1300 °C, which would provide direct evidence for the proposed synthesis process of Ti$_3$SiC$_2$ by Reaction [6].
Table II. Recent Work on the Synthesis of Ti₃SiC₂ from Different Mixtures and the Present Results

<table>
<thead>
<tr>
<th>Investigators</th>
<th>Molar Ratio</th>
<th>Synthesis Methods</th>
<th>Sintering Conditions</th>
<th>Content</th>
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</thead>
<tbody>
<tr>
<td>Lis et al.⁹¹</td>
<td>Ti:Si:C = 3:1:2</td>
<td>SHS-HIP</td>
<td>1400 °C/3 h</td>
<td>82 vol pct</td>
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<tr>
<td>Zhou and Sun¹⁸¹⁹</td>
<td>Ti:Si:C = 6:3:3:5</td>
<td>hot pressing</td>
<td>1550 °C/1 h</td>
<td>93 wt pct</td>
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<tr>
<td>Gao et al.¹⁰³</td>
<td>Ti:Si:C = 3:1:1</td>
<td>HIP</td>
<td>1500 °C/30 min</td>
<td>97 vol pct</td>
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<tr>
<td>Radhakrishnan et al.¹⁵¹⁶</td>
<td>Ti:Si:C = 3:1:1:2</td>
<td>hot pressing</td>
<td>1350 °C/5 h</td>
<td>96 vol pct</td>
</tr>
<tr>
<td>Li et al.¹¹¹</td>
<td>Ti:Si:C = 3:1:1:2</td>
<td>hot pressing</td>
<td>1350 °C/5 h</td>
<td>98.7 vol pct</td>
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<tr>
<td>Sato et al.¹²¹</td>
<td>Ti:Si:C = 3:1:2</td>
<td>HIP</td>
<td>1500 °C/1 h</td>
<td>97 vol pct</td>
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<tr>
<td>Barsoum et al.¹³¹⁴</td>
<td>Ti:Si:C = 3:1:1</td>
<td>PDS</td>
<td>1600 °C/1 to 4 h</td>
<td>98 vol pct</td>
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<tr>
<td>Zhang et al.²²²³</td>
<td>Ti:Si:C = 5:2:3</td>
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<td>1300 °C/15 min</td>
<td>93.6 wt pct</td>
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<td>Present work</td>
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<td></td>
<td>Ti:Si:TiC = 1:1:3</td>
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<td></td>
<td>Ti:Si:TiC = 2:2:3</td>
<td>PDS</td>
<td>1300 °C/15 min</td>
<td>99 wt pct</td>
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Fig. 9—XRD patterns of the M3 samples sintered from Ti/1.5Si/2TiC powder at 1250 °C and 1300 °C for 15 min.

IV. CONCLUSIONS

1. The standard additive method was calibrated to calculate the relative content of Ti₃SiC₂ in the synthesized products. In the present investigation, the relative weight percentages of Ti₃SiC₂ and TiC can be calculated from the intensity ratio I_TiC/I_TiC(200) main peak to the Ti₃SiC₂(104) main peak by the following equations:

\[ W_{TiC} = \frac{I_{TiC}}{1.80 + I_{TiC}/I_{TSC}} \quad \text{and} \quad W_{TiC} = \frac{I_{TiC}/I_{TSC}}{1.80 + I_{TiC}/I_{TSC}} \]

2. When Ti/Si/2TiC (M1) and 2Ti/Si/3TiC (M2) powders were sintered by the PDS technique, the relative weight percentages of Ti₃SiC₂ in the M1 and M2 samples can, respectively, be increased to 96 to 97 wt pct and 99 wt pct in the optimum sintering temperature of 1250 °C to 1300 °C. At 1300 °C, the TiC content in the samples made from the 2Ti/2Si/3TiC powder is approximately constant (0.8 to 1.5 wt pct) over a long sintering time range of 8 to 240 minutes. With the PDS technique, the synthesis process of Ti₃SiC₂ samples can be substantially shortened to 15 minutes, and the synthesized samples have a good densification at the sintering temperature above 1275 °C. It is suggested that the Ti/Si/TiC powder is a practical mixture for synthesizing a Ti₃SiC₂ mixture with high content through the PDS technique.

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