Fabrication and Microstructure Characterization of Ti₃SiC₂ Synthesized from Ti/Si/2TiC Powders Using the Pulse Discharge Sintering (PDS) Technique

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Ti/Si/2TiC powders were prepared using a mixture method (M) and a mechanical alloying (MA) method to fabricate Ti₃SiC₂ at 1200°–1400°C using a pulse discharge sintering (PDS) technique. The results showed that the Ti₃SiC₂ 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 Ti₃SiC₂ 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 Ti₃SiC₂ 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 Ti₃SiC₂ 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 Ti₃SiC₂ 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 Ti₃SiC₂ 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 each other by hexagonal nets of silicon; every fourth layers is a which almost close-packed planes of titanium are separated from

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<300 μm, and 2–5 μm, 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 μm 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. At the beginning of sintering, a rectangular pulse current (1) XRD Analysis of the Synthesized Samples

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Figure 1 shows the XRD results scanned at 2θ = 30°–80° in the MA powder and samples synthesized in the temperature range of 1200°–1400°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 structure supersaturated with titanium and silicon. The sintered MA powder showed that there were at least eight peaks in the scanned range, of which Ti₃SiC₂ was the main peak, except for the sample sintered at 1400°C. Therefore, Ti₃SiC₂ had formed in these samples after sintering. Besides the Ti₃SiC₂ peaks, there were three diffraction peaks marked as TiC at 2θ = 36°, 41.8°, and 60.5°. Meanwhile, the intensities of the TiC peaks in the MA samples increased with sintering temperature. Especially, when the sample was sintered at 1400°C, the TiC peak was higher than the Ti₃SiC₂ peak and became the main peak. From the XRD results above, it seemed that the purity of Ti₃SiC₂ 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°–1400°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 Ti₃SiC₂ 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 Ti₃SiC₂ could be synthesized with less TiC using the PDS technique. To determine the purity of Ti₃SiC₂ in all the synthesized samples, one bulk M sample sintered at 1300°C for 15 min was drilled to collect some Ti₃SiC₂ powder. The drilled Ti₃SiC₂ powder was incorporated into a pure-TiC powder to make various mixtures of Ti₃SiC₂/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/Ti₃SiC₂ peaks versus the content of TiC in these mixture powders. This procedure was often referred to as the standard additive method, and the quantitative results are to be reported elsewhere.

(2) Purity and Density of Ti₃SiC₂

Figure 3(a) shows the quantitative relationship of TiC content with sintering temperature in M and MA samples sintered at 1200°–1400°C for 30 min. At a lower sintering temperature of 1200°–1300°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°–1400°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 Ti₃SiC₂ did not have a higher purity by sintering the mechanically alloyed Ti/Si/TiC powders. One reason 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
The relative density of the MA samples from the ratio $H_9267$ was relatively low at temperatures. It has been reported that the density of the Ti$_3$SiC$_2$ with high purity is 4.9 g/cm$^3$.17 If the content and density of TiC impurity, whose density has been confirmed to be higher than for those sintered from the Ti/Si/C and Ti/SiC/C powders,21 the TiC content was almost independent of the sintering time at lower than the previous temperatures.

Figure 4 shows the dependence of density of the MA and M samples sintered for 30 min. 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$_3$SiC$_2$ 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 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$_3$SiC$_2$, and was not a practicable method. Recently, by reactive sintering Ti/Si/TiC powder, Li and Miyamoto31 also synthesized Ti$_3$SiC$_2$ 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$_3$SiC$_2$ with high purity. In particular, by using the PDS technique, the present optimized sintering temperature was ~200–300°C lower than the previous temperatures.

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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$^3$, 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$^3$ of the pure Ti$_3$SiC$_2$. 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$^3$.17 If the content and density of the TiC phase were taken into account, the theoretical density ($p_{\text{th}}$) of the synthesized MA samples could be calculated, as shown in Fig. 4(a). It was apparent that the measured densities ($p_{\text{ma}}$) of the MA samples were lower than $p_{\text{th}}$. Furthermore, we could calculate the relative density of the MA samples from the ratio $p_{\text{ma}}/p_{\text{th}}$. Figure 4(a) shows that the relative density ($p_{\text{ma}}/p_{\text{th}}$) of the MA samples synthesized at 1250–1400°C was always >98%, which indicated a good densification process produced by the PDS technique.

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$_3$SiC$_2$ was >4.50 g/cm$^3$ 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.24 compared the mechanical-alloying effect of Ti/Si/C powders; they also found that the content of Ti$_3$SiC$_2$ 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$_3$SiC$_2$, and was not a practicable method. Recently, by reactive sintering Ti/Si/TiC powder, Li and Miyamoto31 also synthesized Ti$_3$SiC$_2$ 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$_3$SiC$_2$ 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$_3$SiC$_2$ 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 μm 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 μm in length, as shown in Fig. 5(b). Ti$_3$SiC$_2$ 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 μm in length and 5–10 μm 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.
The microstructure of Ti$_3$SiC$_2$ could be controlled to have various types. In turn, the performance of the synthesized Ti$_3$SiC$_2$ could be adjusted and optimized by controlling the sintering temperature and time, by which the microstructure of Ti$_3$SiC$_2$ also could be controlled to have various types.

(4) Comparison of Various Sintering Methods for Ti$_3$SiC$_2$

During the past decade, Ti$_3$SiC$_2$ samples with various purities have been synthesized by many investigators using various methods. Liu and co-workers$^{18,19}$ sintered Ti$_3$SiC$_2$ samples using HIPing or SHS-HIPing methods by using Ti/Si/C powders at 1200°–1800°C. They found that dense Ti$_3$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$^{20,21}$ synthesized Ti$_3$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 Ti$_3$SiC$_2$ at a lower temperature range.$^{26,27}$

The purity in all the samples synthesized by the two methods was ≤90%. Radhakrishnan and co-workers$^{20,21}$ also prepared Ti/Si/C powders with excess silicon and then sintering them at 1350°C for 5 h; the purities of Ti$_3$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.$^{22}$ Li et al.$^{23}$ and Sato et al.$^{24}$ also found that Ti$_3$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$^{28,29}$ synthesized Ti$_3$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 TiC, and the grain size varied with the sintering temperature and time. Recently, the third mixture powder of Ti/Si/TiC was used to fabricate Ti$_3$SiC$_2$ with purity >98 wt% at temperature >1400°C for >2 h.$^{31}$ From the synthesis processes available, it was suggested that Ti$_3$SiC$_2$ should be sintered at temperatures >1350°C, independent of the Ti/Si/C, Ti/SiC/C, or Ti/Si/TiC
powder mixture used. In the present synthesis process of Ti$_3$SiC$_2$, the sintering temperature was decreased to $<1300^\circ$C when the PDS technique was used. The difference in the synthesis processes of Ti$_3$SiC$_2$ 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 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$_3$SiC$_2$. On the other hand, Sato et al. for the synthesis of Ti$_3$SiC$_2$ from Ti/Si/C powder, reported that they

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

Fig. 7. Microstructure distribution of Ti$_3$SiC$_2$ in M samples sintered at various temperatures and times.
assumed that the TiC phase would form first, i.e., Ti + C → 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: Ti + Si → TiSi(l). Third, Ti3SiC2 formed at the interfaces between the Ti–Si liquid phase and TiC particles, i.e., 2TiC + Ti–Si(l) → Ti3SiC2. Because TiC has an octahedral structure, whereas Ti3SiC2 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 layer is a silicon layer.1,2 In the present Ti/Si/TiC mixture, the TiC had existed in advance; therefore, Ti3SiC2 could form by connecting the Ti–Si(l) and existing TiC, which was a more simple reaction process than for Ti/SiC powder. Li and Miyamoto synthesized Ti3SiC2 from the same Ti/Si/TiC powder at a temperature of ~1400°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°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 Ti3SiC2 at lower temperatures and shorter times. Meanwhile, Ti/Si/TiC powder is a favorable mixture to synthesize Ti3SiC2 in comparison with Ti/SiC and Ti/Si/C powders,6–9 especially by using the PDS technique. Furthermore, the Ti/Si/TiC powder should be considered as another new candidate mixture to synthesize Ti3SiC2 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 Ti3SiC2 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 1200–1400°C. However, at 1250–1400°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 1250–1300°C, the TiC content is further decreased to ~3 wt%. The grain size of Ti3SiC2 changes little in the temperature range of 1200–1250°C, and it is sensitive to the sintering temperature at 1250–1300°C.

2. In the temperature range of 1250–1400°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 Ti3SiC2 polycrystals that have high performance through sintering Ti/Si/TiC powder in the temperature range for a short time. It is suggested that the PDS technique is a rapid method for the synthesis of Ti3SiC2 at lower temperatures and shorter times. Furthermore, Ti/Si/TiC powder can be considered as a new candidate mixture to fabricate Ti3SiC2 products in the future.

References