Synthesis of High-Purity Ti_3SiC_2 through Pulse Discharge Sintering of $\text{TiH}_2/\text{SiC}/\text{C}$ Powder Mixture

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Ternary compound Ti_3SiC_2 was successfully synthesized by pulse discharge sintering the powder mixture of $\text{TiH}_2/\text{SiC}/\text{C}$. When the molar ratio of the starting powder mixture was selected to be $\text{TiH}_2 : \text{SiC} : \text{C} = 2.8 : 1 : 0.8$, single-phase dense Ti_3SiC_2 was synthesized at 1400°C for 20 min. The grain size of synthesized Ti_3SiC_2 strongly depends on the sintering temperature. The synthesis mechanism of Ti_3SiC_2 was revealed to be completed via the reactions among the intermediate phases of $\text{Ti}_5\text{Si}_3\text{C}_x$ and TiC . It is found that dehydrogenation was accelerated by the synthesis reaction during sintering progress. Compared with $\text{Ti}/\text{SiC}/\text{C}$ powder mixture, the $\text{TiH}_2/\text{SiC}/\text{C}$ mixed powder is favorable for synthesizing Ti_3SiC_2 through PDS technique. [doi:10.2320/matertrans.48.133]

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1. Introduction

Recently, ternary carbide Ti_3SiC_2 has attracted attention as a novel material which possesses many best attributes of both metals and ceramics.^{1–6} It possesses low density (4.52 g/cm^3), high melting point ($\sim 3000^\circ\text{C}$),⁷ good electrical and thermal conductivity (being about $4.5 \times 10^6 \Omega^{-1} \text{ m}^{-1}$ and 37 W/mK),^{8,9} and excellent resistance to thermal shock.¹⁰ In recent years, hot-isostatic-pressing (HIP)^{11–14} or hot-pressing (HP),^{15,16} pressureless sintering,^{17–19} self-propagating high temperature synthesis (SHS)^{20–22} and pulse discharge sintering (PDS) (also called spark plasma sintering (SPS))^{23–31} were employed to synthesize Ti_3SiC_2 . In these synthesis methods, four reactions were used: (1) $\text{Ti} + \text{SiC} + \text{C} \rightarrow \text{Ti}_3\text{SiC}_2$, (2) $\text{Ti} + \text{Si} + \text{C} \rightarrow \text{Ti}_3\text{SiC}_2$, (3) $\text{Ti} + \text{Si} + \text{TiC} \rightarrow \text{Ti}_3\text{SiC}_2$ and (4) $\text{Ti} + \text{SiC} + \text{TiC} \rightarrow \text{Ti}_3\text{SiC}_2$.

However, it is noted that these sintering processes employed metallic Ti powder as a starting material. TiH_2 powder is the intermediate product of producing crashed metallic Ti powder, so it is lower in cost than metallic Ti powder and its price is only half of metallic Ti powder with the same grain size. Therefore, the synthesis of Ti_3SiC_2 from TiH_2 powder is a practical attempt to bring this fascinating ternary compound closer to application with lower cost. But the reports of adopting TiH_2 as starting materials are seldom,^{15,32,33} where the mixture powders containing TiH_2 were annealed at 900°C for 6 hours to remove hydrogen prior to powder blending.³³ When TiH_2 was used directly as a substitution for Ti in starting mixtures, without preliminary dehydrogenation, single-phase Ti_3SiC_2 was not available after synthesis.^{15,32} Pulse discharge sintering (PDS) technique,³⁴ is a recent innovation and its versatility allows quick densification to nearly theoretical density in a number of metallic, ceramic and other engineering components.^{35,36} In our previous work, PDS had been successfully employed to synthesize fully-dense single-phase Ti_3SiC_2 in a short time.^{5,6,25} The main purpose of the present work is to focus on the following issues: (1) the possibility of synthesizing

single-phase dense Ti_3SiC_2 with $\text{TiH}_2/\text{SiC}/\text{C}$ powder mixture without preliminary dehydrogenation by PDS process, (2) understanding of the mechanism of the Ti_3SiC_2 synthesis and dehydrogenation reactions during the process, (3) comparison of the present process with that employing $\text{Ti}/\text{SiC}/\text{C}$ powder mixture.

2. Experimental Procedures

Starting powders of TiH_2 ($-45 \mu\text{m}$, 99%), Ti ($-45 \mu\text{m}$, 99%), SiC ($2-3 \mu\text{m}$, 99.9%), and C ($-5 \mu\text{m}$, 99.7%) were used in this study. For the $\text{TiH}_2/\text{SiC}/\text{C}$ mixtures, three molar ratios were selected for this study, that is, the stoichiometric one with $\text{TiH}_2 : \text{SiC} : \text{C} = 3 : 1 : 1$ (named M1), and the off-stoichiometric ones with $\text{TiH}_2 : \text{SiC} : \text{C} = 5 : 2 : 1$ named as M2, and $\text{TiH}_2 : \text{SiC} : \text{C} = 2.8 : 1 : 0.8$ named as M3. For comparison, the $\text{Ti}/\text{SiC}/\text{C}$ with molar ratio of $5 : 2 : 1$ was also studied. These powders were mixed in a Turbula shaker mixer in Ar atmosphere for 24 hours. The powder mixture was filled in a graphite mold (20 mm in diameter) and sintered in vacuum by using PDS technique (PAS-V, Sodick Co. Ltd.). The sintering temperature was monitored and controlled through an infrared camera. The heating rate was controlled at $50^\circ\text{C}/\text{min}$, and the sintering temperature was selected in the range of $800-1450^\circ\text{C}$ and held for 0 to 20 min. Sintering temperature, axial pressure as well as the ram displacement were recorded to monitor the shrinkage of the powder compact during sintering process. The powder compact was kept under a constant axial pressure of 50 MPa during sintering. After sintering, the samples were ground to remove the surface layer for 1 mm in order to eliminate the reaction layer with graphite. Then the samples were analyzed to identify the phase constitution by X-ray diffractometry (XRD) with $\text{CuK}\alpha$ radiation at 30 kV and 40 mA. The microstructure of the synthesized samples were observed and analyzed by using scanning electron microscopy (SEM) equipped with an energy-dispersive spectroscopy (EDS) system.

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Fig. 1 X-ray diffraction patterns of M1 samples sintered at various temperatures for 20 min.

Fig. 2 X-ray diffraction patterns of M3 samples sintered at various temperatures for 20 min.

3. Results and Discussion

3.1 X-ray diffraction results of synthesized samples

Figure 1 shows the XRD patterns of M1 samples synthesized in the temperature range of 1250–1450°C for 20 min. It can be seen that the strong peaks in all the samples correspond to Ti_3SiC_2 phase. But TiC and Ti_5Si_3 can also be observed as impurity phases in all samples. Although the relative intensity of impurity phases decreased with increasing sintering temperature, the peaks of TiC are still high even when the sample was sintered at the highest

Fig. 3 (a) TiC and (b) Ti_5Si_3 contents in all samples as functions of sintering temperature.

temperature of 1450°C for 20 min. It seems the contents of impurity phases are high in all the M1 samples. For the M2 samples, similar results were observed (not shown), but the peaks of TiC and Ti_5Si_3 are very low when the samples were sintered at high end of the temperature range, that is, at 1400–1450°C for 20 min, resulting in no availability of single-phase Ti_3SiC_2 .

Figure 2 shows the XRD results of M3 samples sintered at temperatures ranged 1250–1450°C for 20 min. Similar to the results of M1 samples, the strong peaks also correspond to Ti_3SiC_2 . However, unlike the case of M1, the peaks of TiC and Ti_5Si_3 are very low and can't be detected in the sample after being sintered at 1400°C for 20 min. In other words, single-phase Ti_3SiC_2 was synthesized in M3 sample sintered at 1400°C for 20 min.

3.2 Phase purity and density of synthesized samples

In order to determine the content of Ti_3SiC_2 in all the synthesized samples, equations for quantitative evaluation of the contents of three coexisting phases (Ti_3SiC_2 , Ti_5Si_3 and TiC) were derived based on experimental calibration. The details of calibration will be reported elsewhere.³⁷⁾ The content of Ti_3SiC_2 , TiC and Ti_5Si_3 can be calculated from the intensity of Ti_3SiC_2 (104) peak, TiC (111) peak and Ti_5Si_3 (102) peak by the following equations:

$$\omega_{TSC} = \frac{I_{TSC}}{I_{TSC} + 4.159I_{TS} + 0.818I_{TC}} \quad (1)$$

$$\omega_{TS} = \frac{I_{TS}}{0.24I_{TSC} + I_{TS} + 0.197I_{TC}} \quad (2)$$

$$\omega_{TC} = \frac{I_{TC}}{1.22I_{TSC} + 5.072I_{TS} + I_{TC}} \quad (3)$$

Figures 3(a) and 3(b) showed the quantitative relationship between phase contents and sintering temperature for TiC and Ti_5Si_3 in all samples sintered at 1250–1450°C for 20 min, respectively. At a lower sintering temperature of 1250–1300°C, high contents of TiC and Ti_5Si_3 were found in all samples. When the sintering temperature is increased to above 1350°C, the content of TiC decreased prominently in M2 and M3 samples, while it remained a value of 9–10 mass% in M1 samples. The content of Ti_5Si_3 decreased to near 0 in M3 samples when the sintering temperature is higher than 1350°C, and the value of Ti_5Si_3 content is about 5–7 mass% in M1 and M2 samples.

Figure 4 shows the variation in relative density of the M1, M2 and M3 samples with sintering temperature. The relative density was calculated by dividing the measured density with the theoretical density of each sample by taking account of the theoretical density of TiC (4.90 g/cm³), Ti_5Si_3 (4.32 g/cm³), Ti_3SiC_2 (4.52 g/cm³), and the mass fraction (Fig. 3) of the three constituent phases. The relative density of samples increases with sintering temperature in all samples.

When the sintering temperature is higher than 1350°C, the relative densities of M2 and M3 samples were higher than 99%.

3.3 Microstructures of sintered samples

Figure 5 shows the SEM micrographs of the M3 samples sintered at 1300–1450°C for 20 min. Most grains were very fine, 2–3 μm in the sample sintered at 1300°C for 20 min (Fig. 5(a)). At 1350°C, some grains grown up to 5–10 μm in

Fig. 4 Dependence of the relative density of M1, M2 and M3 samples on sintering temperature.

Fig. 5 SEM micrographs showing the microstructure of the samples sintered at different temperatures for 20 min: (a) 1300°C, (b) 1350°C, (c) 1400°C and (d) 1450°C.

Fig. 6 X-ray diffraction patterns of the $\text{TiH}_2/\text{SiC}/\text{C}$ powder mixture and the samples sintered at 800–1300°C and cooled down.

length (Fig. 5(b)) were found together with the 2–3 μm fine grains. When the sample was sintered at 1400°C for 20 min, the coarse grains with width of 5–10 μm and length of beyond 20 μm were observed. The microstructure at 1450°C dominantly consists of the coarse grains of 10–20 μm in width and 20–50 μm in length. For the nearly single-phase Ti_3SiC_2 in M3 samples, the microstructure with different grain size could be adjusted by controlling the sintering temperature.

3.4 Synthesis mechanism

In order to understand the reaction route during sintering process, samples of the powder mixture were heated to various intermediate temperatures under the same heating and loading procedures as in the aforementioned experiments, and cooled down immediately when the programmed temperature was reached. The high cooling rate (300°C/min) will enable the “freezing” of the intermediate phases during the sintering process. Figure 6 shows the X-ray diffraction patterns of the starting powder and these samples heated to, and then immediately cooled down from 800°C, 900°C, 1000°C, 1100°C, 1200°C and 1300°C, respectively. When the sample was heated to 800°C, the peaks of TiH_2 disappeared and strong Ti peaks were observed. At the same time, the peaks of intermetallic compounds Ti_5Si_3 were detected, despite their low intensities. With increasing sintering temperature, relative intensity of Ti_5Si_3 increased. When the temperature was increased to 1000°C, TiC_x peaks were detected. When the sample was heated to 1200°C, the main peak of Ti_3SiC_2 at about $2\theta = 39.5^\circ$ appeared and the peaks of SiC almost disappeared. When heated to 1300°C, the main peak of Ti_3SiC_2 became the highest and the peaks of Ti disappeared. However, the analysis results of energy-dispersive spectroscopy (EDS) showed that these intermediate Ti_5Si_3 phase is not pure Ti_5Si_3 but contains some carbon, and hence should be designated as $\text{Ti}_5\text{Si}_3\text{C}_x$, although it can’t be distinguished from X-ray results. Figure 7 showed the

Fig. 7 SEM microstructure of a sample sintered at 1000°C and cooled down.

SEM image of the sample sintered at 1000°C and cooled down immediately. The SiC, Ti and $\text{Ti}_5\text{Si}_3\text{C}_x$ were marked in this figure. The reactions during the synthesis process for Ti_3SiC_2 can be expressed as follows,

3.5 Dehydrogenation reaction

In Fig. 6, it is noted that the peaks of TiH_2 disappeared completely when the sample was heated to 800°C and cooled down immediately. However, it is not clear whether the rapid dehydrogenation reaction is caused by heating alone or due to other reasons. In order to clarify this issue, TiH_2 powder with same mass as used in the powder mixture for reactive sintering was sintered at 1300°C for 20 min with the same sintering program. The X-ray result showed that the peaks of TiH_2 still exist beside the Ti peaks, as shown in Fig. 8. This indicated that the simple heating couldn’t finish the dehydrogenation reaction in a short time, even at a temperature much higher than 800°C. Therefore, the above-mentioned rapid dehydrogenation reaction is caused by synthesis reaction. The possible reason is the carbon atoms in graphite or SiC diffused into TiH_2 , resulting in the expansion of TiH_2 lattice. The increased lattice spacing is favorable for the detachment of H atoms from the TiH_2 structure. As an adjuvant evidence, EDS results indicated that the Ti area was not pure Ti in sample heated to 800°C and cooled down, it always contained some carbon. It is our understanding that by the employment of TiH_2 in the starting materials the reactions to form intermediate phase not only prompt the synthesis of Ti_3SiC_2 , but also accelerate the dehydrogenation reaction in short time.

3.6 Comparison with the synthesis using metallic Ti powder

In our previous work,³⁰⁾ $\text{Ti}/\text{SiC}/\text{C}$ mixture powders with different molar ratios were sintered through PDS technique.

Fig. 8 X-ray diffraction patterns of the TiH_2 powder and the sample sintered at 1300°C for 20 min.

Fig. 9 Variation of ram displacement with sintering time at 1400°C for 20 min when sintering $\text{TiH}_2/\text{SiC}/\text{C}$ and $\text{Ti}/\text{SiC}/\text{C}$ samples.

However, no single-phase Ti_3SiC_2 was synthesized, although the molar ratios were optimized. In order to understand this question, we recorded and analyzed the shrinkage displacement curve when sintering $\text{TiH}_2/\text{SiC}/\text{C}$ and $\text{Ti}/\text{SiC}/\text{C}$ mixture powders. Figure 9 shows the shrinkage displacement with sintering time during sintering $\text{TiH}_2/\text{SiC}/\text{C}$ and $\text{Ti}/\text{SiC}/\text{C}$ mixture powders. The shrinkage in $\text{TiH}_2/\text{SiC}/\text{C}$ curve is smooth, but there is an abrupt shrinkage in $\text{Ti}/\text{SiC}/\text{C}$ curve. Further experiments showed that the abrupt shrinkage in $\text{Ti}/\text{SiC}/\text{C}$ powder mixture was caused by self-propagating reaction, resulting in liquid phase which immediately fills the gaps in the powder or mold under applied pressure. This deteriorates the quality of the synthesized products. Therefore, the $\text{TiH}_2/\text{SiC}/\text{C}$ mixed powder is favorable for synthesizing Ti_3SiC_2 through PDS technique, because self-propagating reaction is avoided due to the effect of dehydrogenation reaction, which consumes

some energy that will otherwise be accumulated for self-propagating reaction.

4. Conclusion

- (1) Ternary compound Ti_3SiC_2 was successfully synthesized by pulse discharge sintering of the powder mixture of $\text{TiH}_2/\text{SiC}/\text{C}$ without preliminary dehydrogenation. When the molar ratio of the starting powder mixture was selected to be $\text{TiH}_2 : \text{SiC} : \text{C} = 2.8 : 1 : 0.8$, single-phase dense Ti_3SiC_2 was synthesized when sintered at 1400°C for 20 min.
- (2) The grain sizes of synthesized Ti_3SiC_2 polycrystals strongly depend on the sintering temperature, and the microstructure with different grain size could be adjusted by controlling the sintering temperature. The synthesis mechanism of Ti_3SiC_2 was revealed to be completed via the reactions among the intermediate phases of $\text{Ti}_5\text{Si}_3\text{C}_x$ and TiC .
- (3) The rapid dehydrogenation reaction during sintering progress is not only caused by heating, but also was accelerated by intermediate synthesizing reaction. Compared with $\text{Ti}/\text{SiC}/\text{C}$ powder mixture, the $\text{TiH}_2/\text{SiC}/\text{C}$ mixed powder is favorable for synthesizing Ti_3SiC_2 through PDS technique, because it avoids the self-propagating reaction due to the effect of dehydrogenation reaction.

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