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Application of pulse discharge sintering (PDS) technique to rapid synthesis of Ti_3SiC_2 from Ti/Si/C powders

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Abstract

To synthesize Ti_3SiC_2 samples, pulse discharge sintering (PDS) technique was utilized to sinter elemental powders of Ti/Si/C with stoichiometric and off-stoichiometric ratios in a temperature range of 1200–1500 °C. The results showed that high purity Ti_3SiC_2 could not be obtained from the Ti/Si/C powder with molar ratio of 3:1:2, and Ti_3SiC_2 preferred to form at relatively low sintering temperature for a short time. When 5Ti/2Si/3C and 3Ti/1.5Si/2C powders were sintered for 15 min, the TiC content was respectively decreased to 6.4 and 10 wt.% at 1250–1300 °C. The corresponding relative density of the samples sintered from 5Ti/2Si/3C powder was calculated to be as high as 99% at the temperature above 1300 °C. It is suggested that low-temperature rapid synthesis of Ti_3SiC_2 would be possible through the PDS technique, provided that the composition of the starting powders should be adjusted to be off-stoichiometric ratio from 3:1:2. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ti_3SiC_2; TiC; Pulse discharge sintering (PDS); Sintering

1. Introduction

Ternary carbide Ti_3SiC_2 is one of the most interesting materials because of its unique characteristics, such as low density (~4.53 g/cm^3), low hardness (4–6 GPa), high melting point, good electrical and thermal conductivity, excellent resistance to thermal shock and unusual damage tolerance.[1] In recent decades, to synthesize Ti_3SiC_2 samples, various processes including: (1) chemical vapor deposition;[2] (2) arc-melting method;[3] (3) Hot-isolated-pressing (HIP) or spark plasma sintering (SHS) method;[4–9] and (4) reactive sintering method;[10–13] were employed or developed. In the earlier sintering methods, most investigators preferred to fabricate this material by using the elemental powders of Ti/Si/C with different molar ratios, such as Lis et al., [5,6] Li et al.,[7,8] Gao et al ,[9] Racault et al., [10] Radhakrishnan et al., [11] Zhou and Sun. [12,13] However, it is noted that their sintering processes were often performed at relatively high temperature (more than 1400 °C) for a long time. Recently, an innovative technique for rapid sintering, i.e. pulse discharge sintering (PDS) or spark plasma sintering (SPS) was developed for sintering ceramics and metallic materials, for example: Ti-Al,[14] nano-materials[15] etc. It is assumed that metals and ceramics can be rapidly sintered under a relatively lower temperature and short time, with fine grains and high performances. Therefore, the materials prepared by PDS often represent better mechanical properties than those prepared by existing sintering methods. [16] In our previous work,[17,18] it was found that the PDS technique could effectively decrease the sintering temperature of Ti_3SiC_2 to 1250–1300 °C by using Ti/Si/TiC powders. However, up to now, it was never reported that Ti_3SiC_2 was synthesized by the PDS technique through sintering elemental powders of Ti/Si/C. The main purpose of the present research is to synthesize Ti_3SiC_2 from Ti/Si/C powders with different molar ratios by using the PDS technique at relatively lower temperature.

2. Experimental procedure

This work was conducted by using commercially available powders of Ti ($d=10$ μm, 99.9%), Si ($d=10$

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Table 1
Molar ratios of Ti:Si:C in the selected mixture powders M1–M6

	M1	M2	M3	M4	M5	M6
Ti:Si:C (Molar ratio)	3:1:2	3:1.05:2	3:1.10:2	3:1.15:2	5:2:3	3:1.5:2

μm, 99.9%) and C ($d = 1$ μm, 99%) to yield mixtures with different molar ratios of Ti:Si:C as listed in Table 1. The excess of Si in the powders M2–M6 was used to decrease the content of TiC impurity in the synthesized products. Before sintering, all the powders were mixed in a Turbula mixer for 24 h in Ar atmosphere. Then, the powders were compacted into a graphite mold (20 mm in diameter) and sintered in vacuum (10^{-4} Pa) in the temperature range of 1200–1500 °C for 15–60 min by using the PDS technique. The heating rate was controlled in the range of 50–60 °C/min and the applied pressure was maintained constant at 50 MPa during sintering. After sintering, the surfaces of samples were ground to remove the graphite layer and analyzed by X-ray diffractometry (XRD) with Cu$K\alpha$ radiation at 30 KV and 40 mA to determine the purity of Ti_3SiC_2 by means of standard additive method. The densities of the synthesized samples were measured by means of the Archimedes method to show the degree of densification.

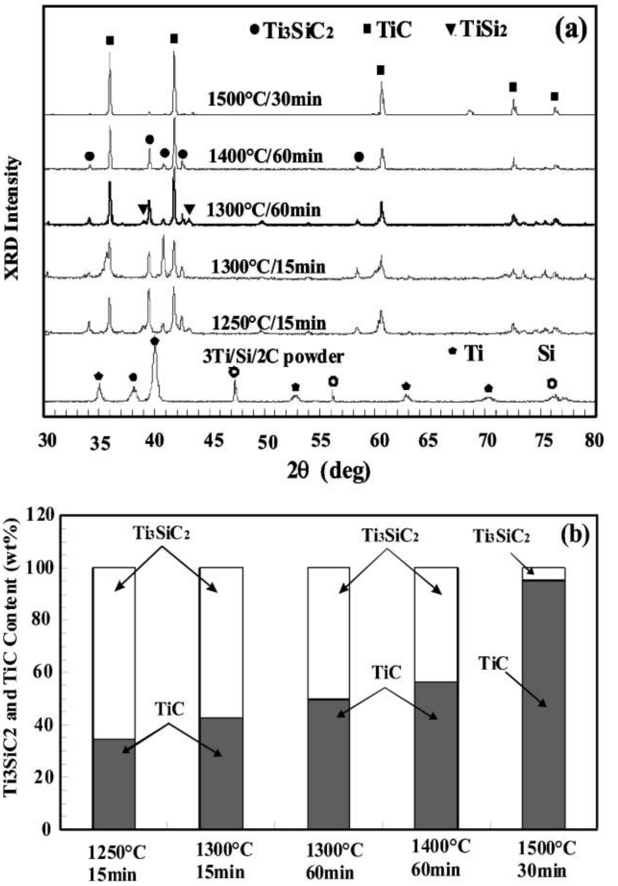

Fig. 1. (a) X-ray diffraction (XRD) patterns of 3Ti/Si/2C powder and M1 samples (Ti:Si:C = 3:1:2) sintered at 1250–1500 °C for different times; (b) relative weight percentages of Ti_3SiC_2 and TiC in the M1 samples.

3. Experimental results

Fig. 1(a) shows the XRD patterns of 3Ti/Si/2C powder and the M1 samples sintered at 1250–1500 °C. For the 3Ti/Si/2C powder, Ti and Si peaks can be clearly seen from the XRD pattern, while C peak only appears at $2\theta = 26.5°$ and is not shown in the XRD pattern. For the M1 samples, all the peaks of Ti, Si and C cannot be seen in their XRD patterns, indicating that all the elemental powders have reacted with each other to form compounds during sintering. At the low sintering temperature of 1250 °C for 15 min, both Ti_3SiC_2 and TiC main peaks can be seen in the XRD pattern and they nearly have the same intensity. Besides, two $TiSi_2$ peaks with low intensity appeared at $2\theta = 39°$ and 43.2°. When the sintering temperature rose to 1300 and 1400 °C, Ti_3SiC_2 peaks were decreased and the intensity of TiC peaks become stronger. At the highest sintering temperature of 1500 °C, almost all the peaks correspond to TiC phase with very limited intensity of Ti_3SiC_2, indicating that Ti_3SiC_2 cannot be synthesized at this temperature. The earlier results demonstrate that increasing sintering temperature and time would decrease the purity of Ti_3SiC_2. To compare the content of Ti_3SiC_2 and TiC in the synthesized products, Fig. 1(b) shows the relative weight percentages of Ti_3SiC_2 and TiC, which were calculated by the calibrated standard addition method [18] from the following equations:

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

and

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

where, W_{TSC} and W_{TC} are the weight percentages of Ti_3SiC_2 and TiC phases, respectively. I_{TC}/I_{TSC} is the integrated diffraction intensity ratio of TiC to Ti_3SiC_2 main peaks, which were obtained from the X-ray diffraction patterns scanned in a narrower diffraction range of 32–44° at a scanning speed of one fourth that used for the results in Fig. 1(a). It can be seen that the relative content of TiC increases with sintering temperature and the highest content of Ti_3SiC_2 is only 65.4 wt.% in the sample sintered at 1250 °C for 15 min. From the present results, it can be concluded that high purity Ti_3SiC_2 cannot be synthesized from Ti/Si/C powder with the molar ratio of 3:1:2 through the PDS technique. In particular, when the sintering temperature is above 1400 °C, the content of Ti_3SiC_2 will be remarkably reduced, which is distinctly different from the previous results obtained by other methods. [5–13] To further improve the purity of Ti_3SiC_2, one of the usual methods is to add an excess of Si in the starting powder in order to balance the evaporation of Si. [6,7,11–13] In the present study, the M2–M4 powders with excess of Si were also sintered, respectively at 1300 and 1400 °C. However, from their XRD patterns, it was found that the intensity of TiC peaks were not decreased even in the M4 samples, in which the excess of Si is as high as 15%. The weight percentages of TiC in M2–M4 samples sintered at two temperatures nearly have the same value as that of the M1 samples.

To further determine the effect of Si content on reactant products, the M6 powder with a higher excess of Si (Ti:Si:C = 3:1.5:2) was sintered at 1200–1300 °C for 15 min. Fig. 2(a) shows the X-ray diffraction patterns scanned in the range of $2\theta = 32$–$44°$ at a low scanning rate of 0.02°/s. It is noted that all the main peaks correspond to Ti_3SiC_2 phase and TiC peaks were obviously decreased in comparison with the M1 samples in Fig. 1(a). However, two $TiSi_2$ peaks were found to appear at $2\theta = 39°$ and 43.2°, and the intensity of $TiSi_2$ peaks increases with sintering temperature. It is indicated that if Si content is too high, the excess of Si reacted with Ti to form $TiSi_2$ phase during sintering. Therefore, the composition of the starting powder was further adjusted to have the molar ratio of Ti:Si:C = 5:2:3 (M5). The sintering process was conducted at temperature below 1400 °C for a short time. Fig. 2(b) shows the X-ray diffraction patterns of the M5 samples sintered at 1200–1400 °C for 15 min in the diffraction range of $2\theta = 32$–$44°$. It is clear that the TiC peaks become lower than those of the M6 samples in Fig. 2(a) even though the M5 powder has a lower Si content than the M6 powder. Besides, only little $TiSi_2$ peaks can be seen at $2\theta = 39°$ and 43.2°, in the M5 samples sintered at 1250 and 1300 °C. However, when the sintering is conducted at other temperatures, there are only two kinds of peaks, corresponding to Ti_3SiC_2 and TiC phases. Fig. 3 demonstrates the dependence of TiC content in the M5 and M6 samples on sintering temperature. The TiC content in the M5 samples was effectively decreased to 6.4 wt.% at 1250–1300 °C, while it was only reduced to about 10 wt.% in M6 samples. This result implies that the excess of Si cannot monotonically reduce the TiC content in the synthesized products. When more excess of Si was added into the starting powder, the impurity of $TiSi_2$ was formed after sintering, like in M6 samples. Even though the purity of Ti_3SiC_2 in the present synthesis process was not very high, it is assumed that Ti_3SiC_2 can be purified by optimizing sintering conditions, such as by using fluctuation method[13] or further adjusting the molar ratio of Ti:Si:C. Nevertheless, the most important fact is that, by using the PDS technique, Ti_3SiC_2 can be rapidly synthesized at the sintering temperature near 1300 °C, which is about 100–200 °C lower than those used by other techniques.

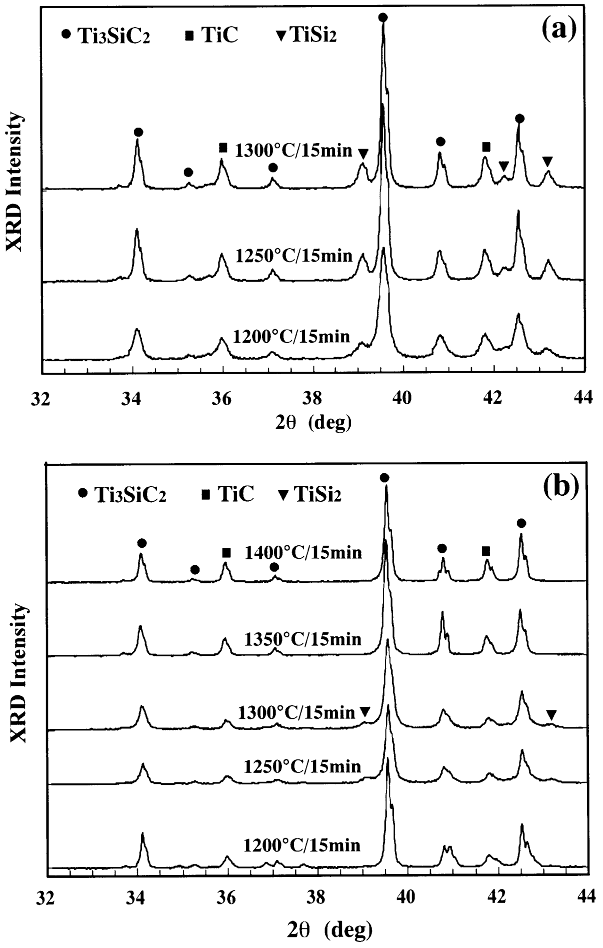

Fig. 2. (a) X-ray diffraction (XRD) patterns of the M6 samples sintered at 1200–1300 °C for 15 min. (a) X-ray diffraction (XRD) patterns of the M5 samples sintered at 1200–1400 °C for 15 min.

Fig. 4 shows the variation of the measured density (ρ_M), theoretical density (ρ_T) and relative density

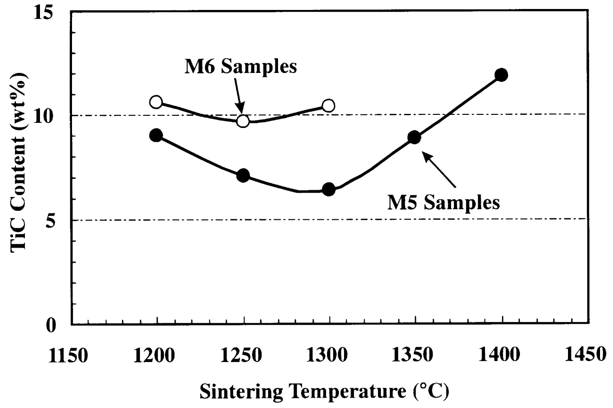

Fig. 3. TiC content in the M5 and M6 samples sintered at 1200–1400 °C for 15 min.

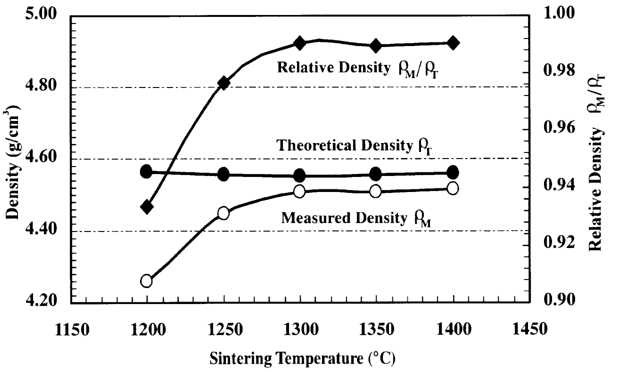

Fig. 4. Dependence of the measured density, theoretical density and relative density of the M5 samples on sintering temperature.

(ρ_M/ρ_T) of the M5 samples with sintering temperature. It can be seen that the measured density (ρ_M) of the M5 samples increases from 4.24 to 4.52 g/cm^3 in the temperature range of 1200–1400 °C. It was reported that the theoretical densities of Ti_3SiC_2 and TiC are equal to 4.53 and 4.90 g/cm^3, respectively. Accordingly, the theoretical densities of the synthesized samples were calculated from the densities of Ti_3SiC_2 and TiC by taking the composition of the samples (shown in Fig. 3) into account. It is apparent that the relative density of the M5 samples is quite high (97.4–99.2%) at the sintering temperature above 1250 °C. When the sintering temperature rose to above 1300 °C, the relative density of the M5 samples can be higher than 99%, indicating a good densification effect of the PDS process conducted at a pressure of 50 MPa for a short sintering time of 15 min.

4. Discussion

To synthesize Ti_3SiC_2 samples, elemental powders of Ti/Si/C have been frequently employed by various sintering process. Table 2 lists recent work available on the synthesis of Ti_3SiC_2 from Ti/Si/C powders with different molar ratios by using different methods along with the present results. Lis et al. [5] tried to utilize the SHS–HIP, HIP and gas-pressure combustion synthesis (GPCS) techniques to synthesize Ti_3SiC_2 from Ti/Si/C powder. In their HIP experiment, the best result, i.e. dense Ti_3SiC_2 material with the purity of 82 wt.%, was obtained by sintering at 1400 °C for 3 h at a pressure of 25 MPa. They concluded that for the preparation of Ti_3SiC_2-rich materials generally low-temperature and low-pressure densification should be used. At high temperature, the composition of the synthesized products became more complicated, including the formation of Ti_5Si_3, $TiSi_2$, TiC and SiC phases, which would decrease the purity of Ti_3SiC_2. Li et al.[7] and Sato et al.[8] fabricated Ti_3SiC_2 from Ti/Si/C powders by HIP technique and nearly obtained the same purity of 96–97 vol.% in the temperature range of 1400–1500 °C. They observed that the purity of Ti_3SiC_2 decreased remarkably when the holding time was extended from 1 to 3 h. They suggested that the formed Ti_3SiC_2 was not stable at high temperature. In the present result in Fig. 1(a), it can be seen that in addition to TiC phase, $TiSi_2$ phase was formed in the M1 samples at temperature higher than 1300 °C. Meanwhile, with increasing sintering time from 15 to 60 min at 1300 °C, the TiC peaks were obviously enhanced and the corresponding weight percentage of TiC became higher. It is indicated that low-temperature rapid sintering for the synthesis of Ti_3SiC_2 by using the PDS technique is necessary, which is in agreement with the observations by Sato et al.[8] The difference is that the present optimized sintering temperature and time by the PDS technique can be further decreased in comparison with those by the HIP technique.

Concerning the synthesis reaction of Ti_3SiC_2 from Ti/Si/C powder, Zhou and Sun[12] took the melting point (1420 °C) of Si into account to synthesize Ti_3SiC_2. Therefore, they sintered Ti/Si/C powder at temperature higher than 1450 °C so that the melting Si would wet the Ti and C particles during sintering. However, they only obtained the Ti_3SiC_2 samples with highest purity of 93 wt.% at 1550 °C. To explain the formation of Ti_3SiC_2 from Ti/Si/C powders, Sato et al.[8] proposed other reaction processes. They assumed that the TiC phase would be formed from Ti and C at first because thermodynamically this reaction is the most probable among all the reactions. Then, they considered the eutectic point (1333 °C) of the Ti–Si system, and pro-

Table 2
Recent work on the synthesis of Ti_3SiC_2 from elemental powders of Ti/Si/C made from several different research groups and the present results

Authors	Ti:Si:C	Synthesis methods	Sintering conditions	Purity
Lis et al.[5]	3:1:2	HIP	1400 °C/3 h	82 vol.%
Zhou and Sun[12]	0.42:0.23:0.35	Hot pressing	1550 °C/1 h	93 wt.%
Gao et al.[9]	3:1:2	HIP	1100 °C/3 h	85.7 vol.%
	3:1:2	HIP	1400 °C/3 h	65.3 vol.%
Radhakrishnan et al.[11]	3:1.1:2	Reactive sintering	1350 °C/5 h	96 vol.%
	3:1.2:2	Reactive sintering	1350 °C/5 h	98.7 vol.%
Li et al.[7]	3:1.1:2	HIP	1500 °C/1 h	97 vol.%
Sato et al.[8]	3:1:2	HIP	1400 °C/1 h	96 vol.%
Present work	5:2:3	PDS	1300 °C/15 min	93.6 wt.%

posed that Ti_3SiC_2 will be synthesized at the interfaces between the Ti–Si liquid phase and the formed TiC particles. In the present synthesis process, the optimized sintering temperature is near 1300 °C, therefore, it is suggested that the reaction process between Ti–Si liquid phase and TiC particles might be possible. The appearance of $TiSi_2$ phase in M1 and M6 samples should provide direct evidence on the proposed reaction processes by Sato et al.[8]

From Table 2, one of the common phenomenon is that the synthesis process often conducted at relatively high temperature ($\geqslant$1400 °C) for a long time ($\geqslant$1 h) no matter by using the HIP process or reactive sintering method. For a special case by Gao et al ,[9] they sintered Ti/Si/C powder at 1100 °C for 3 h and obtained the Ti_3SiC_2 with purity of 85.7 vol.%. However, the density of the synthesized sample is only 3.73 g/cm^3, indicating that the densification of the samples is very poor even at a high pressure of 100 MPa. In the present sintering process, the sintering temperature was effectively decreased to below 1300 °C, which is about 100–200 °C lower than that by other methods. Meanwhile, the sintering time was distinctly shortened to be only 15 min due to the application of the PDS technique. The reason why PDS can sinter samples with low sintering temperature and short time can be explained as follows. It is reported that the plasma environment created by electrical discharge can cause a removal of surface oxides on the particles, which results in the concentration of heat effect, and hence, possibly an activation of the particle surface and a rapid neck formation. In the next stage, intense joule heat is produced at the inter-particle contact zone as conventional direct current flows at the particle. During sintering, the pulse electric field may activate the surface of the powder particles which enable an easy sintering process, and the plasma occurring between the particles may locally increase the temperature to a much higher level than the controlled average temperature, which could effectively promote the synthesis reaction of Ti_3SiC_2.[14–16]

5. Conclusions

The pulse discharge sintering technique can be employed for rapid synthesis of Ti_3SiC_2 samples from elemental powders of Ti/Si/C at relatively low sintering temperature range of 1250–1300 °C, which is about 100–200 °C lower than those made by other methods. With this PDS technique a good densification effect can be achieved with sintering at low temperature and short time, which will be favorable for industrial application. However, to fabricate high purity Ti_3SiC_2, the composition of the starting powder should be adjusted to be off-stoichiometric ratio from 3:1:2. By using the 5Ti/2Si/3C powder, the content of TiC impurity was decreased to 6.4 wt.% in the samples sintered at 1300 °C for 15 min.

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