Materials Transactions, Vol. 43, No. 3 (2002) pp. 428 to 431

Ternary Compound Ti_3SiC_2: Part I. Pulse Discharge Sintering Synthesis [*1]

ZhengMing Sun, ZheFeng Zhang [*2], Hitoshi Hashimoto and Toshihiko Abe

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

Pulse discharge sintering (PDS) technique was employed to synthesize the ternary compound Ti_3SiC_2 from four starting powder mixtures. The experimental results demonstrated that when the starting material of 3Ti/Si/2C or 3Ti/SiC/C was used high content of the secondary phase, TiC, higher than 30 mass%, was found in the sintered material. When TiC powder as starting material was used (Ti/Si/2TiC) in the same stoichiometric composition, however, the final sintered product contained low TiC content of a few percent. Further adjusting the composition to the off-stoichiometric of 2Ti/2Si/3TiC, the content of the secondary phase TiC was further controlled to be around 1 mass%. In the materials sintered from Ti/Si/2TiC and 2Ti/2Si/3TiC an optimum sintering temperature exists at 1573 K, at which the highest Ti_3SiC_2 phase purity was achieved. When sintered at the optimum temperature a density of higher than 99% was obtained. At the optimum sintering temperature, both the phase purity and the density of the material sintered from 2Ti/2Si/3TiC showed very little dependence on the sintering time ranging from a few minutes to four hours, indicating the phase stability at this temperature.

(Received October 22, 2001; Accepted December 19, 2001)

Keywords: *titanium silicon carbide, synthesis, pulse discharge sintering, stoichiometric composition, secondary phase, density*

1. Introduction

Ti_3SiC_2 was first synthesized via chemical reaction in 1967[1)] and was found to be atypical as a carbide in 1972[2)] and later.[3)] It exhibits a good combination of the properties of both metals and ceramics, which makes it promising candidate materials for high temperature applications. In recent decade, various processes[4–12)] were employed and developed to synthesize Ti_3SiC_2. Among these synthesis methods, the sintering process is proven to be a practical one to fabricate bulk Ti_3SiC_2 samples mainly by the following three reactions from powders of, (1) $3Ti+Si+2C \rightarrow Ti_3SiC_2$; (2) $3Ti+SiC+C \rightarrow Ti_3SiC_2$ and (3) $Ti + Si + 2TiC \rightarrow Ti_3SiC_2$. For the three reactions, the elemental powders Ti/Si/C were frequently employed for the synthesis of Ti_3SiC_2 by many researchers.[6–10)] Barsoum and El-Raghy[8,9)] often employed the second reaction and successfully synthesized the Ti_3SiC_2 samples with high phase-purity. However, their sintering process was conducted at relatively high temperature (1723–1973 K) for long time. Li and Miyamoto[11)] tried to synthesize Ti_3SiC_2 through cold isostatic pressing (CIP) and reactive sintering Ti/Si/TiC mixture powder at temperature near 1673 K. 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. With PDS process, powder particle surface is activated in the electrical field and the locally high temperature at the interfaces due to the high resistance improves the sintering process. In our previous work, mechanical alloying[13)] or adding the excess of Si,[14)] into Ti/Si/TiC powder have been considered, and also through some new reactions,[15,16)] by using this PDS technique to synthesize Ti_3SiC_2 at the temperature below 1673 K. The results showed that the approaches could not further improve the phase purity of Ti_3SiC_2, whereas the optimum sintering temperature was successfully decreased to below 1573 K, which is about 200–300 K lower than the common methods (such as HIP technique).

The objective of the present study is to compare the synthesis of Ti_3SiC_2 from the starting powder mixtures of 3Ti/Si/2C, 3Ti/SiC/C and Ti/Si/2TiC in stoichiometric composition and also the effect of off-stoichiometric composition 2Ti/2Si/3TiC, with the pulse discharge sintering technique. The effect of sintering temperature and sintering time is also investigated.

2. Experimental Procedures

Four groups of powders were selected as starting materials for this study: (1) 3Ti/Si/2C, with stoichiometric composition of $Ti : Si : C = 3 : 1 : 2$, (in molar ratios hereafter unless indicated); (2) 3Ti/SiC/C; (3) Ti/Si/2TiC; and (4) 2Ti/2Si/3TiC. The purity and particle size of the powders used are as follows: 10 μm and 99.9% for Ti, 10 μm and 99.9% for Si, 2–5 μm and 99% for TiC, 1 μm and 99% for C. The four groups of powders were respectively mixed in argon atmosphere with a Turbula mixer for 86.4 ks. The powder mixtures were sintered with a pulse discharge sintering (PDS) apparatus in vacuum of 10^{-3} Pa. The sintering temperature and holding time were changed to investigate the respective effects, while the pressure applied through the electrodes at the sintering temperature was selected to be 50 MPa for all the materials. The sintered compacts were polished and etched with a solution of $HNO_3 : HF : H_2O = 1 : 1 : 2$, and the microstructures were observed. X-ray diffraction was carried out with Cu Kα at 30 kV and 40 mA for the phase analysis. Density of the sintered samples was measured with the Archimedes method.

3. Results and Discussion

The X-ray diffraction profiles of the starting powder mixtures and the sintered samples are summarized in Fig. 1. In the results of 3Ti/Si/2C group samples (Fig. 1(a)), it can be found that the main peaks for starting elemental powders of Ti, Si and C disappeared after sintering at any temperature, indicating that in the sintering temperature range of 1523 to

[*1] This Paper was Presented at the Autumn Meeting of the Japan Institute of Metals, held in Fukuoka, on September 22nd, 2001.

[*2] JSPS postdoctoral fellow.

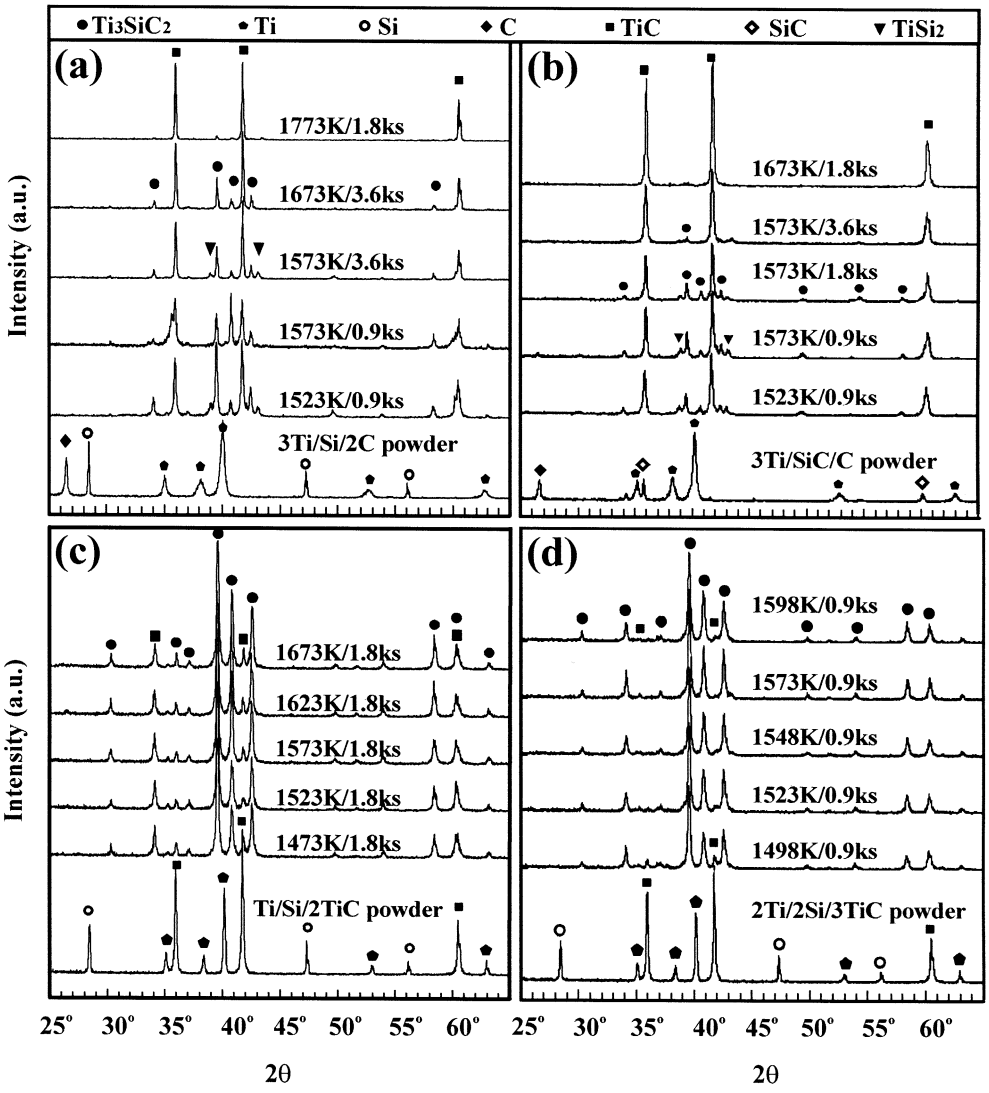

Fig. 1 X-Ray diffraction profiles of different powder mixtures and the compacts sintered with pulse discharge sintering technique at different temperatures for different sintering time with the starting powders of (a) 3Ti/Si/2C, (b) 3Ti/SiC/C, (c) Ti/Si/2TiC, (d) 2Ti/2Si/3TiC.

1773 K, reactions were thoroughly completed for the sintering time of longer than 0.9 ks. It can be seen that instead of the expected Ti_3SiC_2 peaks, TiC diffraction peaks with high intensities were obtained. This implies that with the starting powder mixture of 3Ti/Si/2C it is difficult to synthesize single phase Ti_3SiC_2. Figure 1(b) shows the result of 3Ti/SiC/C group samples. Similarly, the diffraction peaks of the starting powders of Ti, SiC and C disappeared after sintering in any of the conditions, and formation of a large fraction of TiC in the sintered compact is observed. When the starting materials were changed to Ti/Si/2TiC, also in the stoichiometric composition, the situation was improved considerably as shown in Fig. 1(c). The strong TiC peaks in the starting powder mixture were considerably lowered, though not vanished completely, while the diffraction peaks for Ti_3SiC_2 showed strong intensities. In Figure 1(d), the results of 2Ti/2Si/3TiC group, in an off-stoichiometric composition, are summarized. The diffraction intensities of the TiC peaks in the sintered samples were considerably decreased compared with those in the starting powders. It is worth noticing that the intensity of TiC peaks in the sample sintered at 1573 K for 0.9 ks are negligible.

The Ti_3SiC_2 and the TiC mass percentage in a Ti_3SiC_2–TiC two-phase compacts were calibrated and can be calculated according to the following equations:[17)]

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

Wherein, 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(200) to Ti_3SiC_2(104). With these two equations, the TiC contents in the four groups of materials are calculated and plotted as functions of sintering temperature in Fig. 2, where Fig. 2(b) is the enlarged graph of Fig. 1(a) at the lower part. It is obvious from Fig. 1(a) that the sintered samples contains large fraction of TiC when the starting material of 3Ti/Si/2C or 3Ti/SiC/C is employed. However when the powder mixture of Ti/Si/2TiC or 2Ti/2Si/3TiC is used, the sintered material contains very low fraction of TiC. Comparison between the two curves in Fig. 2(b) indicates that by adjusting the composition from stoichiometry of Ti : Si : C being 50 : 17 : 33 (3 : 1 : 2) to 50 : 20 : 30 (5 : 2 : 3), the TiC content in the synthesized compound was decreased in all the sintering conditions. One

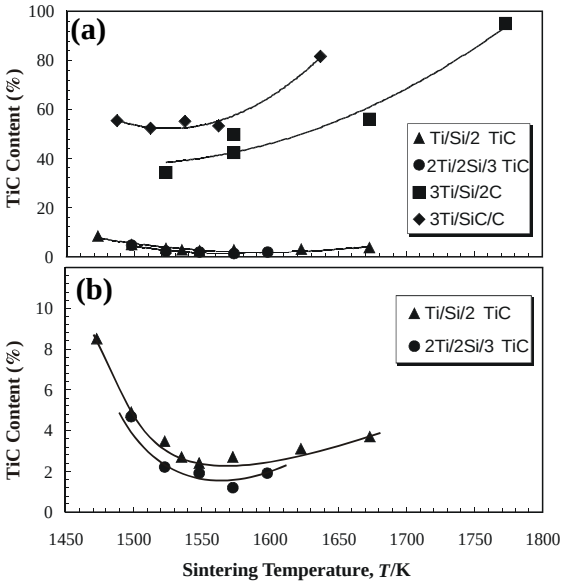

Fig. 2 TiC content in Ti_3SiC_2 compound sintered with pulse discharge sintering technique from different powder mixtures as indicated in the figure, as a function of sintering temperature. (b) is the enlarged lower part of (a).

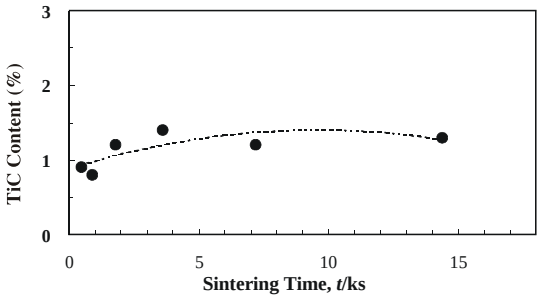

Fig. 3 TiC content in Ti_3SiC_2 compound sintered with pulse discharge sintering technique from 2Ti/2Si/3TiC powder mixture at 1573 K, as a function of sintering time.

Table 1 Density of the Ti_3SiC_2 compound sintered from 2Ti/2Si/3TiC powder mixture at different sintering temperature for a sintering time of 0.9 ks.

Temperature (K)	1498	1523	1548	1573	1598
Measured (Mg/m^3)	4.463	4.488	4.499	4.500	4.504
Theoretical (Mg/m^3)	4.552	4.538	4.536	4.533	4.537
Relative (%)	98.0	98.9	99.2	99.3	99.3

Table 2 Density of the Ti_3SiC_2 compound sintered from 2Ti/2Si/3TiC powder mixture at 1573 K for different sintering time.

Time (ks)	0.48	0.90	1.80	3.60	7.20	14.40
Measured (Mg/m^3)	4.491	4.499	4.501	4.511	4.509	4.512
Theoretical (Mg/m^3)	4.533	4.533	4.534	4.535	4.534	4.534
Relative (%)	99.1	99.3	99.3	99.5	99.4	99.5

point in common for the two groups of materials shown in Fig. 2(b) is that there is an optimum sintering temperature in terms of the Ti_3SiC_2 phase purity in the sintered compacts, at which the TiC content could be controlled to a low level of about 3 mass% for the Ti/Si/2TiC and of about 1 mass% for the 2Ti/2Si/3TiC materials. For the two groups of materials the optimum sintering temperatures were found to be near 1573 K. Whereas the high TiC content in the materials sintered at the low temperature side on the curves could be attributed to the insufficient reaction in the starting materials, the high content of TiC in the samples sintered at the high temperature side could be due to the decomposition of the Ti_3SiC_2 compound.

Figure 3 shows the sintering time dependence of the second phase content in Ti_3SiC_2 compounds sintered from 2Ti/2Si/3TiC at 1573 K, where it can be found that the TiC content in the sintered Ti_3SiC_2 compounds shows very little variation around 1 mass% in the large sintering time range from 0.48 ks to 14.4 ks. The requirement on only a short sintering time in this process is implying that a liquid phase may have occurred in the sintering process. In the Ti–Si system, there exist two eutectic reactions, Ti–Ti_5Si_3 and Si–$TiSi_2$, both at the eutectic temperature of 1603 K.[18] In pulse discharge sintering process the sample was heated by the Joule heat of the powder itself. Possible plasma happened among the particles, and also the locally over-heating at the particle-particle interfaces give rise to a locally high temperature. This locally high temperature is expected to exceed the eutectic temperature and hence liquid phases were induced into the system. These liquid phases further reacted with the TiC powder at a high rate and lead to the final product of Ti_3SiC_2 compound.

The results of density measurements are listed in Table 1 and Table 2. In these two Tables, beside the measured densities of the samples, the theoretical and relative density results are also listed. The theoretical densities were calculated by taking into account the Ti_3SiC_2 (4.53 Mg/m^3) and TiC (4.90 Mg/m^3) content into consideration. Table 1 shows that in the sintering temperature range density over 98% was achieved and the density increases with increasing temperature. At the optimum sintering temperature of 1573 K, the density was found to be higher than 99%. On the other hand, as can be seen in Table 2, at the optimum sintering temperature all the samples sintered for different time show densities over 99%.

Figure 4 shows the microstructure of the Ti_3SiC_2 compound sintered from 2Ti/2Si/3TiC powders at the optimum temperature of 1573 K for 3.6 ks. The microstructure consists of large plate-shaped grains and small equiaxed grains. From the scanning electron microscopy the single-phase microstructure was examined by the back-scattered electron imaging, no secondary phase was identified, indicating the high phase-purity material obtained.

In this study we have found that by adjusting the composition from Ti/Si/2TiC to 2Ti/2Si/3TiC the Ti_3SiC_2 content has been improved. Figure 5 shows the isothermal section at 1473 K of the Ti–Si–C ternary phase diagram.[5] In the enlarged part of the diagram, the stoichiometric composition is indicated as 1, corresponding to Ti : Si : C = 50 : 17 : 33. Also indicated is the off-stoichiometric composition, 2, at Ti : Si : C = 50 : 20 : 30. In other words, the composition is shifted along the Ti = 50% line to the Si side. As a matter of fact, many attempts have been made to adjust the compo-

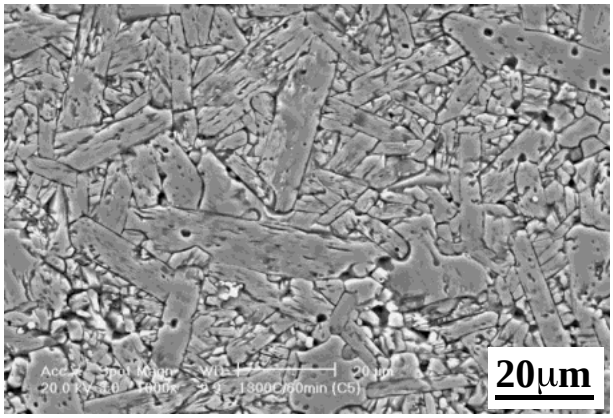

Fig. 4 Scanning electron micrograph showing the microstructure of the Ti_3SiC_2 compound sintered with pulse discharge sintering technique from 2Ti/2Si/3TiC powder mixture at 1573 K for 3.6 ks at a pressure of 50 MPa.

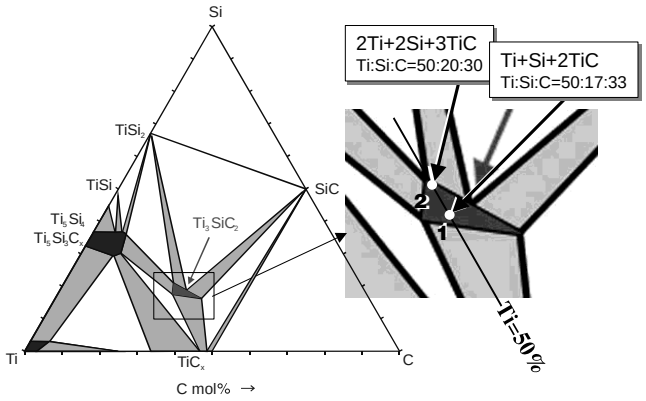

Fig. 5 Ti–Si–C ternary phase diagram at 1473 K and the schematic illustration on the off-stoichiometric composition adjustment.

sition by increasing the Si content,[14] which was found to be not effective in improving the Ti_3SiC_2 phase purity. Considering that the optimum sintering temperature in this study is near 1573 K, 100 K higher than the temperature for the phase diagram in Fig. 5, the result may indicate a different cross section of the phase diagram at this temperature.

4. Summary

By using the pulse discharge sintering (PDS) technique, ternary compound Ti_3SiC_2 was synthesized by sintering various powder mixtures and the main results can be summarized as follows.

(1) When the starting powder of 3Ti/Si/2C, 3Ti/SiC/C were used the sintered Ti_3SiC_2 contains high content of secondary phase TiC. However, when TiC is used in the starting powder the content of TiC, as a secondary phase, in the final sintered samples was substantially reduced.

(2) The Ti_3SiC_2 phase content can be further increased to over 99% by adjusting the composition from the stoichiometric Ti : Si : C = 50 : 17 : 33 (Ti/Si/2TiC) to the off-stoichiometric one of Ti : Si : C = 50 : 20 : 30 (2Ti/2Si/3TiC).

(3) An optimum sintering temperature at 1573 K was found for the material sintered from the powders containing TiC as starting powders.

(4) Ti_3SiC_2 content was found to receive limited effect of sintering time when sintered at the optimum temperature in the sintering time range of 0.48 ks to 14.4 ks.

REFERENCES

1) W. Jeitschko and H. Nowotny: Monath. Chem. **98** (1967) 329–337.
2) J. J. Nickl, K. K. Schweitzer and P. Luxenberg: J. Less Com. Met. **26** (1972) 335–353.
3) T. Goto and T. Hirai: Mater. Res. Bull. **22** (1987) 1195–1201.
4) M. Barsoum: Prog. Solid St. Chem. **28** (2000) 201–281.
5) S. Arunajatesan and A. H. Carim: J. Am. Ceram. Soc. **78** (1995) 667–672.
6) J. Lis, Y. Miyamoto, R. Pampuch and K. Tanihata: Mater. Lett. **22** (1995) 163–168.
7) J. F. Li, F. Sato and R. Watanabe: J. Mater. Sci. Lett. **18** (1999) 1595–1597.
8) M. W. Barsoum and T. El-Raghy: J. Am. Ceram. Soc. **79** (1996) 1953–1956.
9) T. El-Raghy and M. W. Barsoum: J. Am. Ceram. Soc. **82** (1999) 2849–2854.
10) Y. C. Zhou and Z. M. Sun: Scr. Mater. **41** (1999) 61–66.
11) J. T. Li and Y. Miyamoto: J. Mater. Synth. Proc. **7** (1999) 91–96.
12) J.-F. Li, W. Pan, F. Sato and R. Watanabe: Acta Mater. **49** (2001) 937–945.
13) Z. F. Zhang, Z. M. Sun, H. Hashimoto and T. Abe: Submitted to J. Am. Ceram. Soc. 2001.
14) Z. F. Zhang, Z. M. Sun, H. Hashimoto and T. Abe: Submitted to Mater. Res. Bull. 2001.
15) Z. F. Zhang, Z. M. Sun, H. Hashimoto and T. Abe: Scr. Mater. **45** (2001) 1461–1467.
16) Z. F. Zhang, Z. M. Sun, H. Hashimoto and T. Abe: Mater. Res. Innov. in press.
17) Z. F. Zhang, Z. M. Sun, H. Hashimoto and T. Abe: Submitted to Acta Mater. 2001.
18) L. Kaufman: Calphad **3** (1979) 45–76.