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Ti_3SiC_2 powder synthesis

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Abstract

In this article, we report the successful synthesis of single phase Ti_3SiC_2 powder through a simple process by heat treating powder mixtures of Ti, Si, and TiC. By adjusting the composition of the starting powders and the condition of heat treatment, resultant powder with Ti_3SiC_2 content over 99% was obtained. The intermediate phase of Ti_5Si_3 was found to form which subsequently assisted the formation of the Ti_3SiC_2 phase.

Keywords: A. Powder; Titanium silicon carbide; Synthesis

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1. Introduction

Ternary compound Ti_3SiC_2, with a crystal structure comprised of hexagonal nets of Si atoms separated by three nearly closed-packed Ti layers that accommodate C atoms in the octahedral sites between them [1], is a promising candidate for high temperature applications as either a structural or a functional material. It possesses good electrical conductivity ($4.3 \times 10^6 \Omega^{-1} m^{-1}$) at RT and thermal conductivity ($39.9 W m^{-1} K^{-1}$), is relatively soft (HV, 4 GPa), machinable, damage tolerant, and resistant to thermal shock, like a metal [2–4]. On the other hand, it shows good high temperature mechanical properties and oxidation resistance like a ceramic [4]. We, therefore, referred to this compound as a metallic ceramic material [3]. Ti_3SiC_2 was firstly synthesized via a chemical reaction in 1967 [1], and then by CVD in 1987 [5]. In recent years, various processes were employed for the synthesis of bulk Ti_3SiC_2 material. In most cases, it is difficult to obtain single phase Ti_3SiC_2, and TiC exists as the ancillary second phase [2–4]. In practice, the synthesis of Ti_3SiC_2 powder provides an alternate route for the development of bulk single phase Ti_3SiC_2 as well as Ti_3SiC_2-based composite materials. Furthermore, the application of some potential high temperature candidate materials, such as NiAl and $MoSi_2$, is limited by their poor mechanical properties. The synthesis of Ti_3SiC_2 powder enables the development of Ti_3SiC_2 dispersion-strengthened materials. To synthesize Ti_3SiC_2 powder, a solid–liquid (S–L) reaction process [6] and a fluctuation synthesis (FS) method [7] were applied by using Ti, Si, and graphite powder mixture with NaF addition. In both cases, the Ti_3SiC_2 content of as synthesized powders is less than 85 wt.%. Moreover, it is deleterious to the environment with the addition of NaF. Table 1 summarizes this result and some other results reported on Ti_3SiC_2 powder synthesis [6–9]. It can be seen that even by a complicated process incorporating mechanical alloying and high temperature annealing, the content of Ti_3SiC_2 in the synthesized powder reaches not more than 95.8% [9]. It is, therefore, the objective for this study to establish a process for the synthesis of single phase Ti_3SiC_2 powder with a relatively simple process.

2. Experimental

Powders of Ti (10 μm in average size, 99.9% in purity), Si (2–3 μm in average size, 99% in purity), and TiC (2–5 μm in average size, 99% in purity) were used as starting powders. These powders weighed in various molar ratios, as shown in Table 2, were mixed using a Tubular shaker mixer in argon atmosphere for 24 h. These powder mixtures were designated as Ti/Si/2TiC, 2Ti/2Si/3TiC, Ti/1.05Si/2TiC, Ti/1.10Si/2TiC, and Ti/1.15Si/2TiC, respectively. Mixed powders were put into alumina crucible and heat treated in a vacuum furnace at different temperatures for various holding durations. The heating rate was 15 °C min^{-1}. The synthesized powders were analyzed by X-ray diffractometry

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Table 1
Reported synthesis of Ti_3SiC_2 powders

Starting material	Method	Treatment	Ti_3SiC_2 content (wt.%)	Reference
Ti/Si/C + NaF	S–L	1200 °C/2 h	<10	[6]
		1250 °C/2 h	81	
		1300 °C/2 h	48	
Ti/Si/C	FS	1200–1300 °C/2 h	82.5	[7]
Ti/Si/C	SHS	W coil ignition	58	[8]
Ti/Si/C	MA	MA/400 h + 1000 °C/1 h annealing	95.8	[9]

Table 2
Molar ratios for starting powders used for Ti_3SiC_2 synthesis

	Starting powders	Ti	Si	TiC
1	(Ti/Si/2TiC)	1	1	2
2	(2Ti/2Si/3TiC)	2	2	3
3	(Ti/1.05Si/2TiC)	1	1.05	2
4	(Ti/1.10Si/2TiC)	1	1.10	2
5	(Ti/1.15Si/2TiC)	1	1.15	2

(XRD) with Cu Kα radiation at 30 kV and 40 mA at a scanning speed of 0.01° s^{-1}. Morphologies of powders were analyzed by scanning electron microscopy (SEM) equipped with an energy-dispersive spectroscopy (EDS) system.

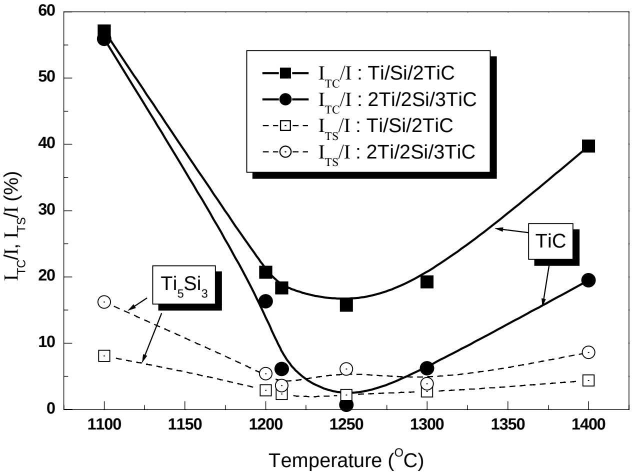

Fig. 2. Temperature dependence of the relative intensity for TiC(2 0 0) and Ti_5Si_3(3 0 0) (TC, TiC; TS, Ti_5Si_3).

3. Results and discussion

Fig. 1 shows the XRD patterns of 2Ti/2Si/3TiC powder mixture before and after heating at 1100–1400 °C for 2 h in vacuum. Except those peaks from Ti_3SiC_2, peaks of TiC and Ti_5Si_3 were also detected in the samples after heat treatment. Similar phases were also identified in the samples heat treated from Ti/Si/2TiC powder. For 2Ti/2Si/3TiC powder, after heating at 1250 °C in vacuum for 2 h, it was difficult to detect the existence of TiC, indicating its low content in the synthesized powder. Fig. 2 shows the temperature dependence of the relative intensity of the rep-

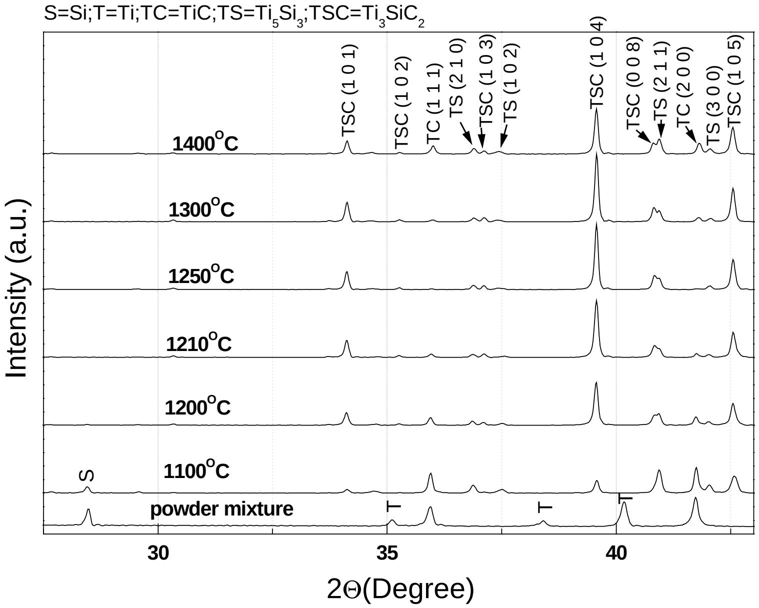

Fig. 1. XRD profiles of 2Ti/2Si/3TiC powders before and after heating at 1100–1400 °C for 2 h in vacuum.

resentative peak of TiC (I_{TC}/I) and Ti_5Si_3 (I_{TS}/I), respectively, with I_{TC} and I_{TS} being the integrated intensity for the representative peaks of TiC and Ti_5Si_3, and I being the sum of the integrated intensity for representative peaks of Ti_3SiC_2, TiC, and Ti_5Si_3. Ti_3SiC_2(1 0 4), TiC(2 0 0), and Ti_5Si_3(3 0 0) were chosen as the representative peaks for the respective phases. Calculations based on the assumption of Ti_3SiC_2–TiC two-phase system [4] showed that for treated 2Ti/2Si/3TiC and Ti/Si/2TiC powders, the highest Ti_3SiC_2 content was about 99.3 and 88.6 wt.%, respectively, after heating in vacuum at 1250 °C for 2 h. The decrease in the relative intensity of TiC with increasing temperature was obvious below 1210 °C. In the temperature range from 1210 to 1300 °C, the change was slight, and reached the minimum at 1250 °C, being about 0.7 and 15.7% for heat treated 2Ti/2Si/3TiC and Ti/Si/2TiC powders, respectively. At temperature above 1300 °C, the relative intensity of TiC increased obviously with increasing temperature. It implies that for the two different powders, the optimal temperature for the formation of Ti_3SiC_2 is in the range of 1210–1300 °C. For the two powder mixtures, the relative intensity of Ti_5Si_3 decreased with increasing temperature below 1210 °C, reaching a minimum at temperature between 1210 and 1300 °C, followed by an increase with the further temperature increasing above 1300 °C. In each case, the relative intensity of Ti_5Si_3 in the powder synthesized from 2Ti/2Si/3TiC is higher than that from Ti/Si/2TiC, which should be attributed to the difference in the starting composition. The fact that some Ti_5Si_3 was also found in the heat treated Ti/Si/2TiC powder together with Ti_3SiC_2 and TiC indicated that the existence of Ti_5Si_3 in the heat treated 2Ti/2Si/3TiC powder was not simply due to the excess of titanium and silicon. The reaction to form Ti_5Si_3 and Ti_3SiC_2 are exothermic, giving rise to heat release which may increase the local temperature to higher than the melting point of silicon, 1414 °C. As a result, evaporation of silicon may occur. Previous research showed that, Ti_5Si_3, TiC, and silicon are prerequisite reactants for the formation of Ti_3SiC_2 through the following reaction [10]

$$Ti_5Si_3 + TiC + Si \rightarrow Ti_3SiC_2 \qquad (1)$$

As a matter of fact, the growth of Ti_3SiC_2 from the TiC powder and from the intermediate phase of Ti_5Si_3 was observed in this study, as shown in Fig. 3. Fig. 3a shows a few Ti_3SiC_2 grains growing from a TiC particle, whereas in Fig. 3b, it is evident that a layered Ti_3SiC_2 grain was growing from the intermediate phase Ti_5Si_3 with a nodule shaped morphology. The phase identities were also confirmed by EDS analysis.

According to Eq. (1), therefore, the evaporation of silicon is not in favor of the formation of single phase Ti_3SiC_2. In case of silicon deficiency, it is not surprising that some TiC as well as Ti_5Si_3 were found in the final synthesized powders together with Ti_3SiC_2. This implies the possibility that the adjustment of silicon content based on the stoichiometric composition of Ti/Si/2TiC is an effective route to synthesize higher Ti_3SiC_2 content powder.

Based on this hypothesis, the powder mixtures of Ti/$(1 + x)$Si/2TiC($x = 0.00$, 0.05, 0.10, and 0.15) were heat treated at 1100–1300 °C for 2 h in vacuum. The XRD results demonstrated that after treatment at 1100 °C, the relative intensity for peaks of Si and $TiSi_2$ increased with increasing Si content in the starting material. The effect of Si content on the content of Ti_3SiC_2, TiC, and Ti_5Si_3 was found to be unobvious. After 2 h heating at 1200 °C, peaks of Si disappeared for all the treated powders, indicating its low content. The relative intensity of TiC decreased gradually with increasing Si content. Weak peaks of $TiSi_2$ appeared in the powder synthesized from Ti/1.15Si/2TiC mixture. Among all the heat treated powders, the strongest Ti_5Si_3 peak existed in the XRD profile of the powder synthesized from Ti/Si/2TiC mixture, while the difference in the intensity of Ti_5Si_3 peaks for the other three mixtures was unclear. After 2 h vacuum treatment at further higher temperature,

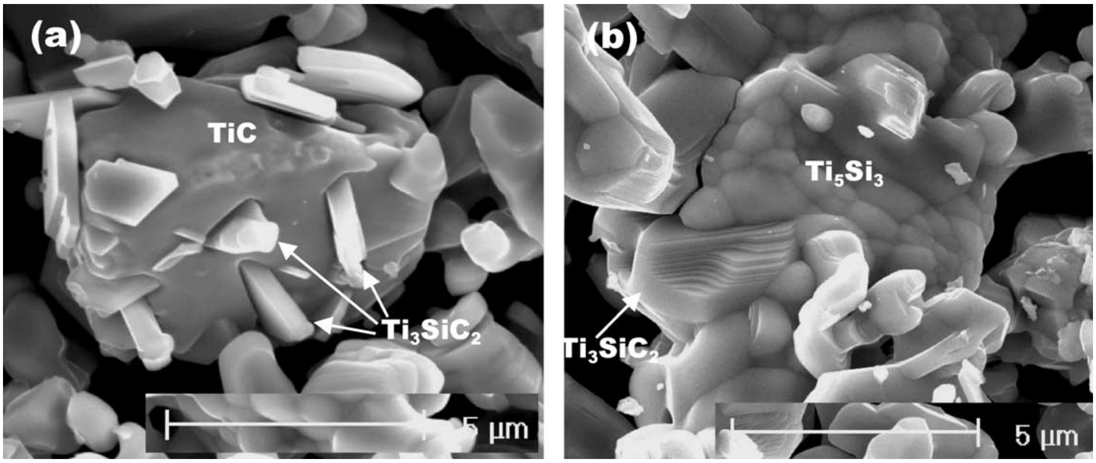

Fig. 3. SEM micrographs showing the growth of Ti_3SiC_2 grains from (a) TiC particle and (b) intermediate phase Ti_5Si_3. (starting powder 2Ti/2Si/3TiC and heat treated at (a) 1200 °C/2 h and (b) 1300 °C/2 h).

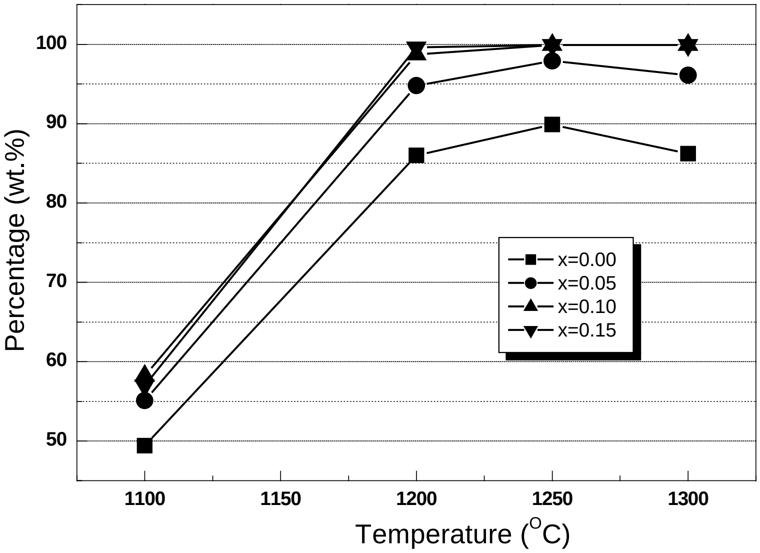

Fig. 4. Temperature dependence of Ti_3SiC_2 content synthesized from powder mixtures of Ti/(1 + x)Si/2TiC powder mixtures.

for example, at 1250 and 1300 °C, the content of TiC was too low to be detected by XRD for those powders developed from Ti/1.10Si/2TiC as well as Ti/1.15Si/2TiC mixture, while main peak of $TiSi_2$ can still be detected for powder which resulted from Ti/1.15Si/2TiC mixture after treatment at 1250 °C for 2 h despite its weak intensity. Fig. 4 summarizes the temperature dependence of calculated weight content of Ti_3SiC_2 based on the relative intensity of TiC(1 1 1) and Ti_3SiC_2(1 0 4). The Ti_3SiC_2 content in the heat treated powder increased obviously with increasing Si content. About 99.9 wt.% Ti_3SiC_2 powder was synthesized with Ti/1.10Si/2TiC and Ti/1.15Si/2TiC powders after heating at 1250–1300 °C in vacuum for 2 h. The overall morphology of the single phase Ti_3SiC_2 powder is shown in Fig. 5, where fine grained Ti_3SiC_2 particles with layered morphology are clearly seen.

As mentioned above, among powders after heat treatment at these temperatures, strongest peaks of TiC and Ti_5Si_3 appeared in those resulted from Ti/Si/2TiC mixture, even though its original composition is stoichiometric. According to the reaction described in Eq. (1), it is reasonable to find that with the addition of excessive Si, the peak intensity for TiC and Ti_5Si_3 in the XRD profiles become weaker compared to the powder synthesized from Ti/Si/2TiC mixture. However, too much Si addition can induce the formation of some Si-rich titanium-silicides, such as $TiSi_2$. According to

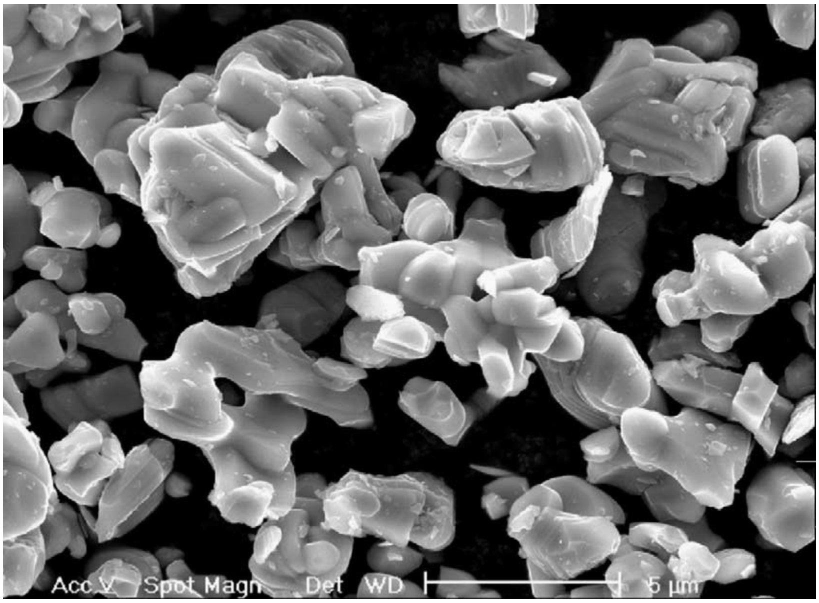

Fig. 5. SEM morphology of Ti/1.10Si/2TiC powder after heating in vacuum at 1250 °C for 2 h.

the present results, about 10% Si excess is appropriate for the single phase Ti_3SiC_2 powder synthesis.

4. Conclusions

(1) Single phase Ti_3SiC_2 powder was synthesized by heat treating the powder mixtures consisting Ti, Si, and TiC.
(2) The best starting powders for the Ti_3SiC_2 powder synthesis was found to be Ti/1.10Si/2TiC, or Ti/1.15Si/2TiC. When heat treated at a temperature of 1250 °C or higher for 2 h, powder with Ti_3SiC_2 content higher than 99% is obtained.
(3) Intermediate phase Ti_5Si_3 was found during the reaction and the growth of Ti_3SiC_2 grain from Ti_5Si_3 was observed. The Ti_3SiC_2 grain growth from the TiC particles was also observed.

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