

Synthesis of single-phase Ti_3SiC_2 powder

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Abstract

In this study, free 2Ti/2Si/3TiC powder mixture was heated at high temperatures in vacuum, in order to reveal the possibility for the synthesis of high Ti_3SiC_2 content powder. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used for the evaluation of phase identities and the morphology of the powder after different treatments. Results showed that almost single phase Ti_3SiC_2 powder (99.3 wt.%) can be synthesized by heat treatment with free 2Ti/2Si/3TiC powders in vacuum at 1210 °C for about 3 h. The nucleation and growth of Ti_3SiC_2 within TiC particles was observed. The typical appearance of the formed Ti_3SiC_2 is equiaxed with particle size of 2–4 μm . Effects of temperature and heating time on the morphology and the particle sizes of the synthesized Ti_3SiC_2 powders are not obvious.

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1. Introduction

Titanium silicon carbide (Ti_3SiC_2), the crystal structure of which is 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 material for high temperature applications. Its room-temperature electrical and thermal conductivities are excellent, being about $4.5 \times 10^{-6} \Omega^{-1} \text{m}^{-1}$ and 37 W/mK, respectively.^{2,3} It is relatively soft (the Vickers hardness of which is about 4 GPa), damage tolerant and resistant to thermal shock,^{3,4} and easily machinable.⁵ Furthermore, its density is relatively low (4.5 g/cm³) and it is stable up to at least 1700 °C in inert atmospheres and vacuum.⁶

Ti_3SiC_2 was firstly synthesized via chemical reaction in 1967,¹ and then by CVD in 1987.⁷ In recent years, various methods, such as arc-melting,⁸ chemical reaction,⁷ HIP or SHS-HIP,^{9–14} and reactive sintering,^{15–19}

have been employed for the synthesis of bulk Ti_3SiC_2 material using Ti/Si/C^{9–12,15–19} or Ti/SiC/C^{13,14} at relatively high temperature (1450–1700 °C) for a long time. The Ti_3SiC_2 content in the synthesized material is different depending on the process. In most cases, TiC is the ancillary second phase. Generally, the content of Ti_3SiC_2 is calculated from the relative intensity ratio for Ti_3SiC_2 and TiC peaks in X-ray diffraction (XRD) profiles.

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, it is well known that, the application of some potential high temperature candidate materials, for example, NiAl and MoSi₂, is limited by poor mechanical properties, such as tensile ductility, fracture toughness, impact resistance, and creep resistance. The synthesis of Ti_3SiC_2 powder enables the development of Ti_3SiC_2 dispersion-strengthened alloys. To synthesize Ti_3SiC_2 powder, a solid–liquid (S–L) reaction process²⁰ and a fluctuation synthesis (FS) method²¹ were applied by Zhou and co-workers using titanium, silicon and graphite powder mixture with or without some 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

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addition of NaF. To improve the Ti_3SiC_2 content, following treatments, including the removal of TiSi_2 by HF solution and the removal of TiC by oxidation at 500 °C in air followed by the dissolution in hot $(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{SO}_4$ solution, were used. By self-propagating high-temperature synthesis (SHS) with Ti/Si/C powders, J. Lis et al. synthesized Ti_3SiC_2 -based materials with significant amount of TiC.¹⁰ Table 1 summarizes the reported results for the synthesis of Ti_3SiC_2 -based powders.

In our previous work, high Ti_3SiC_2 phase content bulk material can be synthesized from 2Ti/2Si/3TiC powders (the molar ratios of which is 2:2:3) using pulse discharge sintering (PDS) technique.^{22–24} In this study, free 2Ti/2Si/3TiC powders were mixed and heated in vacuum at high temperatures, in order to reveal the possibility for the synthesis of single phase Ti_3SiC_2 powder.

2. Experimental

High-purity powder of titanium (10 μm in average size, 99.9% in purity), silicon (2–3 μm in average size, 99% in purity), TiC (2–5 μm in average size, 99% in purity) with the molar ratios of 2:2:3 were used as starting powders and mixed using a Tubular shaker mixer in argon atmosphere for 24 h. Mixed powders were put into alumina crucible. The following synthesis process was performed in a vacuum furnace at temperature between 1100–1400 °C. The heating rate was 15 °C/min. The as-synthesized powders were analyzed by XRD with $\text{CuK}\alpha$ radiation at 30 KV and 40 mA. For the XRD analysis, the scan speed was 0.01° per second. Morphologies of powders were analyzed by scanning electron microscopy (SEM) equipped with energy-dispersive spectroscopy (EDS) system.

3. Results and discussion

Fig. 1 shows the XRD patterns for 2Ti/2Si/3TiC powders after heating at 1100–1400 °C for 2 h in vacuum. Except those peaks from Ti_3SiC_2 , only peaks

of TiC and Ti_5Si_3 can be detected at temperature above 1200 °C, while after heating at 1100 °C, weak peak of silicon can also be detected. During the reactive HIPing of titanium, SiC, and graphite powders, El-Raghy and Barsoum¹⁴ reported the appearance of intermediate phases including TiC_x and $\text{Ti}_5\text{Si}_3\text{C}_x$. Similarly, the in situ neutron diffraction on a pressureless reactive sintering of Ti/SiC/C mixtures under an argon atmosphere by Wu and co-workers²⁵ showed that the intermediate phase TiC_x and $\text{Ti}_5\text{Si}_3\text{C}_x$ ($x \leq 1$) formed firstly at ~800 to 1400 °C. Here, the corresponding peaks for $\text{Ti}_5\text{Si}_3\text{C}_x$ was identified as Ti_5Si_3 , because in the present Ti/Si/TiC system, the high stability of TiC ensures that its decomposition is unlikely to occur at low temperatures, in other words, no free carbon/graphite will appear in the system below 1200 °C based on the thermal dynamic, which is different from those references mentioned earlier.^{14,25} Therefore, it is reasonable to believe that the first compound to appear was Ti_5Si_3 instead of $\text{Ti}_5\text{Si}_3\text{C}_x$.²⁴ Compared with the reported results,^{10,20,21} it can be concluded that the formation rate for Ti_3SiC_2 powder from the present 2Ti/2Si/3TiC powders should be higher.

Fig. 2 shows the temperature dependence of the relative intensity for representative peak of Ti_3SiC_2 (I_{TSC}/I), with I_{TSC} being the integrated intensity for the representative peak of Ti_3SiC_2 , and I is the sum of the integrated intensity for representative peaks of Ti_3SiC_2 , TiC and Ti_5Si_3 . For Ti_3SiC_2 and TiC, Ti_3SiC_2 (1 0 4) and TiC (2 0 0) at 2θ of 39.5 and 41.7°, respectively, was chosen as the corresponding representative peak. The locations for main peak of Ti_5Si_3 , Ti_5Si_3 (2 1 1) at 2θ of 40.95° and Ti_3SiC_2 (0 0 8) at 2θ of 40.82° are too close to be distinguished from each other in the XRD patterns, therefore, Ti_5Si_3 (3 0 0) at 2θ of 42° was chosen as the representative peak. The increase of relative intensity of Ti_3SiC_2 is obvious at temperature below 1210 °C. In the temperature range of 1210 °C to 1250 °C, that change is slight, and reached the apex at 1250 °C, being about 95% in the present study. At temperature above 1250 °C, it decreased with temperature. It implied that the optimal temperature for the formation of Ti_3SiC_2 powder from 2Ti/2Si/3TiC mixture is in the range of 1210–1250 °C. Calculations based on the assumption of $\text{Ti}_3\text{SiC}_2/\text{TiC}$ two-phase system²² showed that for treated 2Ti/2Si/3TiC mixture the highest content of Ti_3SiC_2 was about 99.3% after heating in vacuum at 1250 °C for 2 h.

Fig. 3 is the micrograph for powders after heating at 1200 °C in vacuum for 2 h. At least 3 kinds of particles appeared, a layered and the predominant one with particle size of 2–4 μm, a nub-like one with grain size about 5 μm, and one with irregular appearance with some small nodules. According to the EDS results as well as the XRD profiles, the corresponding particles are identified to be Ti_3SiC_2 , TiC, and Ti_5Si_3 , respectively, as marked in Fig. 3. It was reported that, the nucleation

Table 1
Reported synthesis of Ti_3SiC_2 powders

System	Method	Treatment	Environment	Purity of Ti_3SiC_2	Reference
Ti/Si/C + NaF	S-L	1200 °C-2 h	Flowing argon	Less than 10wt.%	20
		1250 °C-2 h		81wt.%	
		1300 °C-2 h		48wt.%	
Ti/Si/C	FS		Flowing argon	82.5 wt.%	21
Ti/Si/C	SHS	Initialed by tungsten resistance coil	Vacuum	58 wt.%	10

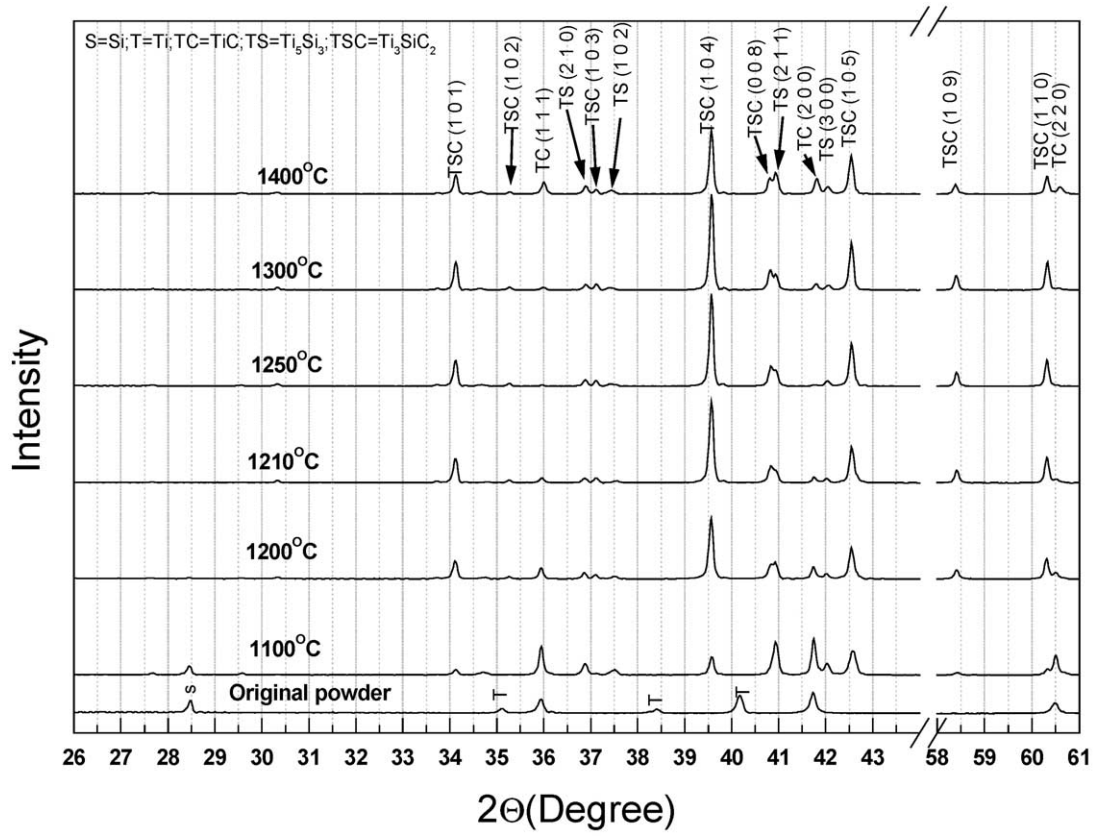


Fig. 1. XRD profiles of 2Ti/2Si/3TiC powders after heating at 1100–1400 °C for 2 h in vacuum.

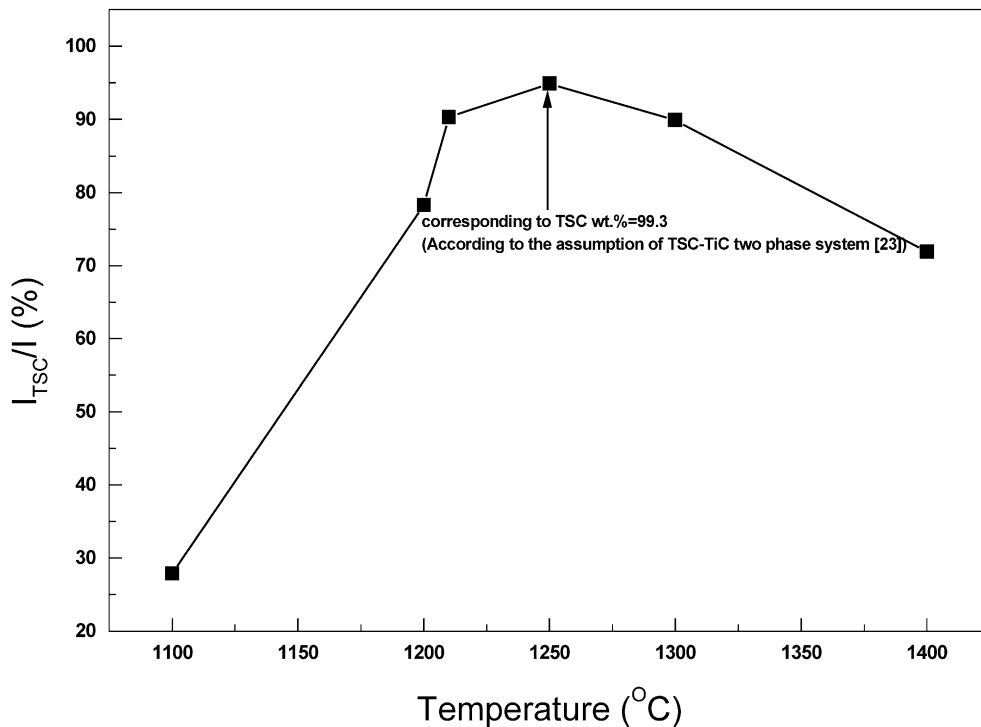


Fig. 2. Temperature dependence of the relative intensity for Ti_3SiC_2 (1 0 4) (TSC = Ti_3SiC_2).

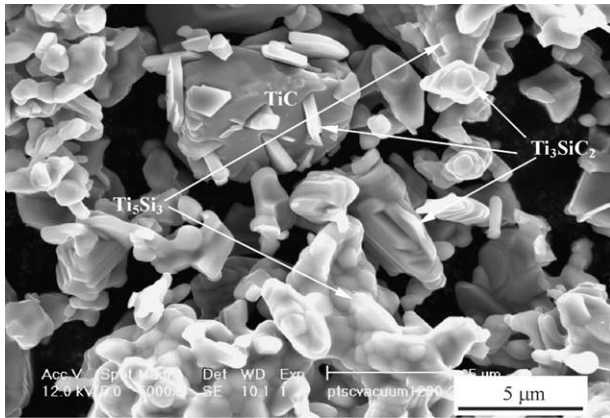


Fig. 3. SEM morphology of powders after heating in vacuum at 1200 °C for 2 h.

and growth of Ti_3SiC_2 within the Ti_5Si_3 grains is reasonable.^{14,24} Furthermore, it is evident that the formation of Ti_3SiC_2 within TiC particles is also possible. Up to now, the mechanism and the corresponding diffusion process for the formation of Ti_3SiC_2 in TiC particles are unclear and require further detailed experiments.

To understand the effect of heating time on the Ti_3SiC_2 content of the synthesized powders, 2Ti/2Si/3TiC powders were heated at 1210 °C for various times, and the corresponding XRD profiles are shown in Fig. 4. For those powders treated less than 1 h, weak peaks from silicon were detectable. With time increasing, the

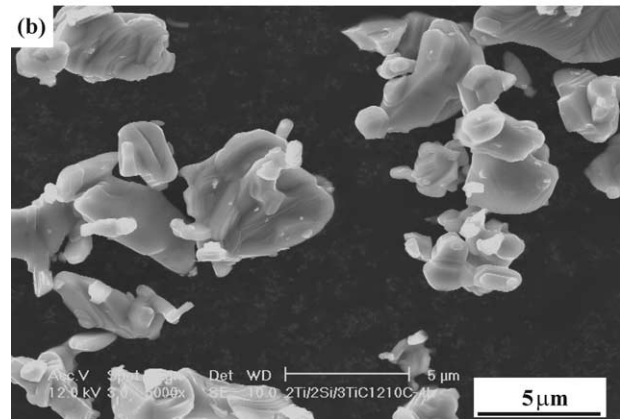
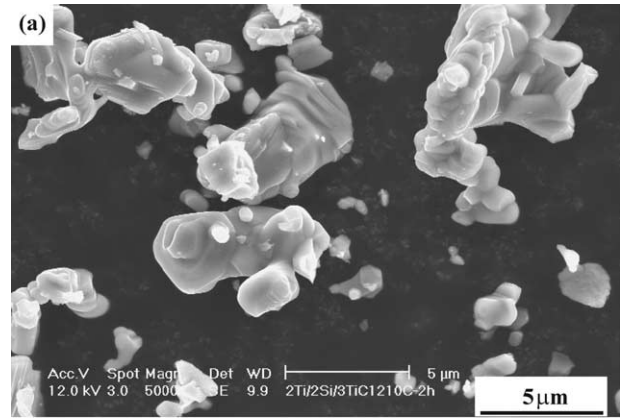


Fig. 5. SEM morphology of powders after heating in vacuum at 1210 °C for (a) 2 h and (b) 4 h.

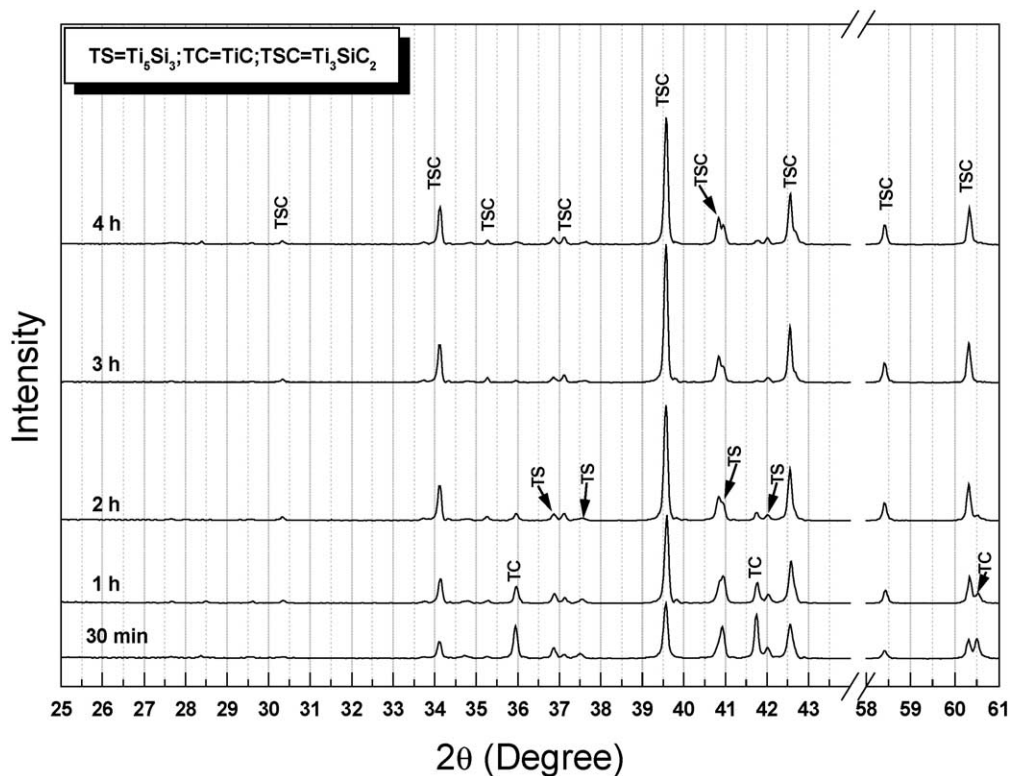


Fig. 4. XRD profiles of 2Ti/2Si/3TiC powders after heating at 1210 °C for various times in vacuum.

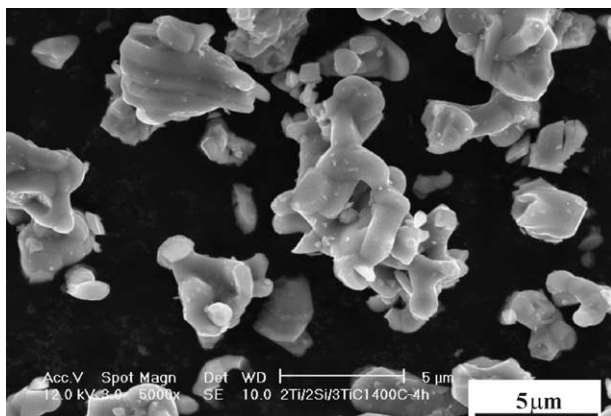


Fig. 6. Ti_3SiC_2 particles formed after heating in vacuum at 1400 °C for 2 h.

relative intensity for TiC and Ti_5Si_3 decreased obviously. After 3 h treatment, it is difficult to detect the existence of TiC. In fact, the XRD profiles for powders after heating at 1210 °C for 3 h are similar to that of the reported pure Ti_3SiC_2 in literature, which was synthesized and the secondary phase of TiC was removed by chemical dissolution.²⁰ But according to the XRD results, there should be some Ti_5Si_3 in the final powders, which was ignored in Ref. 20. It indicates that high Ti_3SiC_2 content powder can be synthesized by vacuum heating at 1210 °C for about 3 h.

Fig. 5 shows the morphology of powders after heating in vacuum at 1210 °C for 2 h [Fig. 5(a)] and 4 h [Fig. 5(b)], respectively. The typical appearance for the formed Ti_3SiC_2 is equiaxed with particle size of 2–4 μm regardless of the heating time, similar to the results after heating at 1200 °C for 2 h. The particle size of the formed Ti_3SiC_2 after heating at 1400 °C for 2 h was also found to be 2–4 μm (Fig. 6). Therefore, it can be concluded that, in the temperature range of 1200–1400 °C and heating time of 2–4 h the particle size for the formed Ti_3SiC_2 powders is independent of the heating temperature and time.

4. Conclusions

1. Almost single phase Ti_3SiC_2 powder (99.3 wt.%) can be synthesized by heating free 2Ti/2Si/3TiC powder mixture at 1210 °C for about 3 h in vacuum.
2. The experimental observation indicates the nucleation and growth of Ti_3SiC_2 within TiC particles.
3. The typical appearance for the formed Ti_3SiC_2 is equiaxed with particle size of 2–4 μm. When synthesized at 1200–1400 °C for 2–4 h, the particle size for the formed Ti_3SiC_2 powders is independent of the heating temperature and time.

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