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Effect of liquid reaction on the synthesis of Ti_3SiC_2 powder

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Abstract

Synthesis of Ti_3SiC_2 powder was carried out by heat treating powder mixtures of Si, TiC and coarse Ti (−150 μm) in a temperature range of 1000–1400 °C. The phase content of Ti_3SiC_2 in the synthesized powder was improved to 99% when heat treated at 1400 °C for 4 h. Ti–Si liquid reaction was found to occur above the binary eutectic temperature, and this liquid reaction is believed to have assisted the synthesis reaction of Ti_3SiC_2.

Keywords: Titanium silicon carbide; Powder; Synthesis; Liquid reaction

1. Introduction

Recently, titanium silicon carbide (Ti_3SiC_2) has received considerable attention, because it is a remarkable material that combines many of the best attributes of metals and ceramics [1–13]. Its crystal structure is comprised of hexagonal nets of Si atoms separated by three nearly close-packed Ti layers that accommodate C atoms in the octahedral sites between them [14]. It possesses low density (4.52 g/cm^3), high melting point (~3000 °C) [15], good electrical and thermal conductivity (being about $4.5 \times 10^6\ \Omega^{-1}\ m^{-1}$ and 37 W/mK) [16,17], and excellent resistance to thermal shock [18]. Ti_3SiC_2 was first synthesized in 1967 by Jeitschko and Nowotny via chemical reaction [14]. In last decade, hot-isostatic-pressing (HIP) [3,19–22] and pulse discharge sintering (PDS) [6–11,23–25] were employed to synthesize bulk Ti_3SiC_2 material. But the size and purity of samples are limited by equipment. 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 [26]. In our previous work, almost single-phase Ti_3SiC_2 powder was synthesized through heat treating Ti/Si/TiC mixed powders at high temperature in vacuum [27–30]. In these work, fine Ti powder (−10 μm) was used for ensuring the reaction complete, where the heat treatment was conducted at temperatures below 1300 °C. This synthesis reaction is believed to be based on the diffusion among the solid reactants, considering that the temperatures are below the eutectics. However, it is not clear whether the single-phase Ti_3SiC_2 could be synthesized solely by diffusion among the solid reactants when coarse powders with large particle size are employed. There are two eutectic reactions in the Ti–Si binary system for the Si–$TiSi_2$ and Ti–Ti_5Si_3 compositions both at the temperature of 1330 °C, but the effect of liquid reaction on synthesis of Ti_3SiC_2 powder through heat treating Ti/Si/TiC mixed powders in vacuum is still unknown. In this study, coarse Ti powder (−150 μm) was employed to synthesize Ti_3SiC_2 in order to investigate the possibility of synthesizing Ti_3SiC_2 powder, where coarse Ti powder provides less specific surface area and larger diffusion distance for the reaction, provided the reaction are based on the diffusion mechanisms. On the other hand, fine Ti powder (−10 μm) is expensive, whose price is about eight times higher than that of coarse Ti powder (−150 μm). Therefore, to bring this fascinating ternary compound closer to application, the synthesis of Ti_3SiC_2 powder from coarse Ti powder is a practical attempt. Therefore, the main purpose of the present work is twofold, namely to study the possibility of synthesizing Ti_3SiC_2 powder by pressureless sintering Ti/Si/TiC mixture containing coarse Ti powder, as well as to understand the effect of the liquid reaction on the synthesis of Ti_3SiC_2 powder when sintering temperature is beyond Ti–Si eutectic temperature.

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2. Experimental procedures

Starting powders of coarse Ti (−150 μm, 99.9%), Si (−10 μm, 99.9%) and TiC (2–5 μm, 99%), were used in this study. The molar ratios of Ti:Si:TiC was selected to be 2:2:3, slightly off stoichiometric, according to our previous work [6–9,26–30], where single-phase Ti_3SiC_2 was synthesized from powder mixtures at this molar ratio. These powders were mixed in a Turbula shaker mixer in Ar atmosphere for 24 h. These powder mixtures were put into alumina crucibles and heated in a vacuum furnace at temperatures between 1000 and 1400 °C for various soaking times. The heating rate was controlled at 10 °C/min. The heated powders were analyzed by X-ray diffractometry (XRD) with Cu Kα radiation at 30 kV and 40 mA to identify the phase constitution. The microstructure of the synthesized samples were observed and analyzed by using scanning electron microscopy (SEM) equipped with an energy-dispersive spectroscopy (EDS) system.

3. Results and discussion

3.1. Synthesis reactions during the heating process

In order to understand the reaction route, powder mixtures were heated to various temperatures and the furnace was cooled down immediately when the preset temperature is reached. Fig. 1 shows the X-ray diffraction profiles of the powder mixture prior to heating and the samples heated to and immediately terminated at 1000, 1100, 1200, 1300 and 1400 °C, respectively. For the sample heated to 1000 °C, expect those peaks from Ti, Si and TiC peaks, the peaks of Ti_3SiC_2 also can be detected by XRD despite its weak intensity. This indicates that Ti_3SiC_2 starts to form when heated to around 1000 °C. With an increase in heating temperature, the intensity of Ti_3SiC_2 increased obviously and relative intensity of main peaks of Ti_3SiC_2 became higher than the peaks of TiC after being heated to 1300 °C.

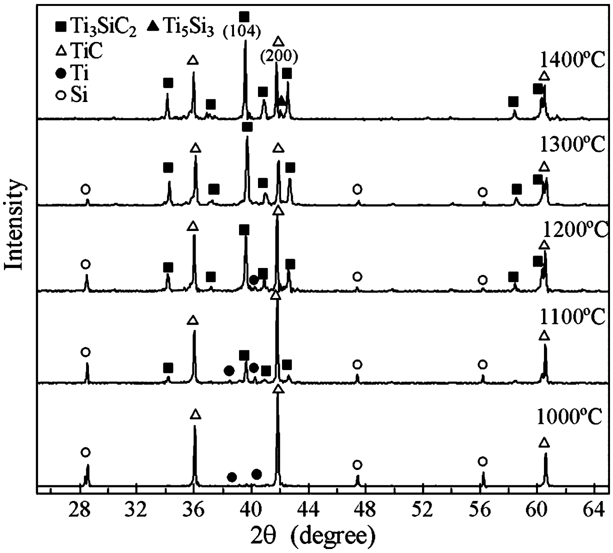

Fig. 1. X-ray diffraction patterns of 2Ti/2Si/3TiC mixed powders after being heated to various temperatures and cooled down immediately.

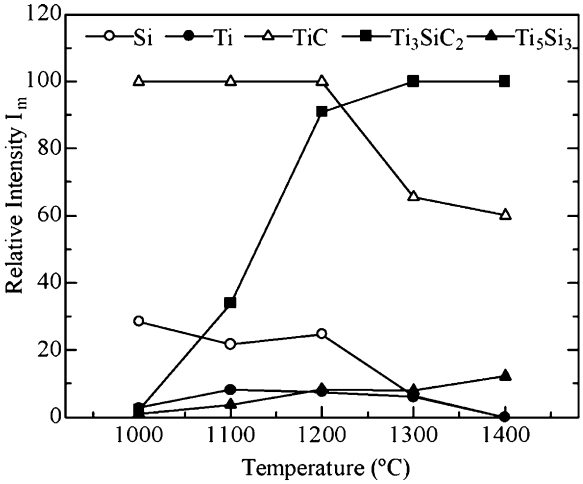

Fig. 2. Dependence of relative intensities of main peaks of various phases on heating temperature (the highest diffraction peak is defined as 100). The samples were heated to the respective temperatures and cooled down immediately for the investigation of intermediate phases.

Fig. 2 shows the variation of relative intensities of the main peaks of respective phases in the samples heated to various temperatures. The intensity of the highest diffraction peak is defined as 100, and I_m was the ratio of the integrated intensities of the main peaks of various phases to that of the main phase. Because the main peak (2 1 1) of Ti_5Si_3 overlaps with the peak (0 0 8) of Ti_3SiC_2 at 2θ around 40.85°, the intensity of peak (3 0 0) at 2θ of 41.91° was used as the relative intensity of the phase Ti_5Si_3. For the peak of TiC (2 0 0), the relative intensity maintains to be the highest at heating temperatures below 1200 °C. Ti_3SiC_2 peak appeared at 1000 °C and its relative intensity become the highest when heated to 1300 °C. When heated to temperatures from 1000 to 1400 °C, the relative intensity of Ti_5Si_3 was observed to be at a very low level in comparison with the intensity of highest peaks. It is noted that the relative intensity of Ti_5Si_3 is different from that reported in our previous work [30], where fine Ti powder (−10 μm) was used and mixed powders were heat treated at lower temperatures (700–1200 °C). In reference [30], the formation of Ti_5Si_3 is obvious when heat treated at 1000–1200 °C, and its relative intensity was higher than that of Ti_3SiC_2. One possible reason for this difference is the employment of coarse Ti powder in the starting material in this study. Ti powder with coarse particles has smaller specific surface area than fine Ti powder, so that the contact zone with Si surface is smaller, and therefore the amount of formed Ti_5Si_3 phase is less than that of fine Ti powder used at the same heating condition. The formed Ti_5Si_3 can react rapidly with the surrounding TiC to form Ti_3SiC_2. The reactions can be summarized as follows:

$$5Ti + 3Si = Ti_5Si_3 \tag{1}$$

$$Ti_5Si_3 + 2Si + 10TiC = 5Ti_3SiC_2 \tag{2}$$

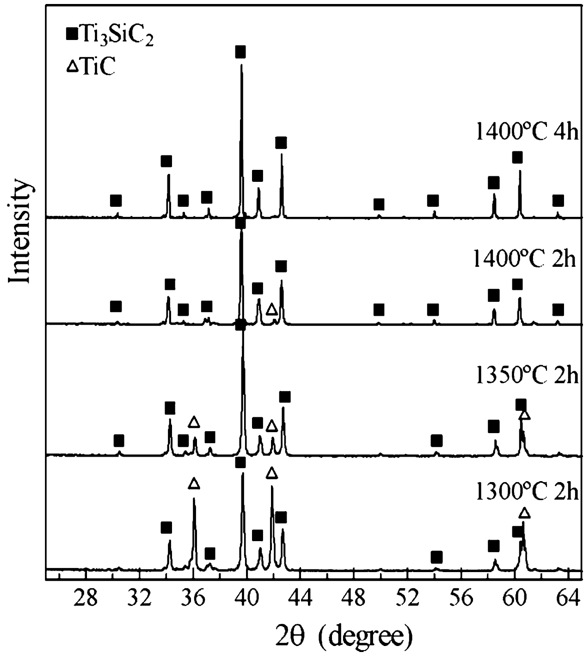

Fig. 3. X-ray diffraction patterns of 2Ti/2Si/3TiC mixed powders after heat treatment at 1300, 1350, 1400 °C for 2 h and 1400 °C for 4 h, respectively.

3.2. Synthesis of single-phase Ti_3SiC_2 powder

After investigation into the reaction routes of the Ti_3SiC_2 synthesis by heating the powder to various intermediate temperatures, further isothermal heat treatment was conducted to synthesize Ti_3SiC_2 powder. Fig. 3 shows the X-ray diffraction profiles of the powder mixture heat treated at 1300, 1350 and 1400 °C for 2 h, respectively. To investigate the effect of holding time at the heat treating temperature, another sample was heat treated at 1400 °C for 4 h. With an increase in heating temperature, the intensity of Ti_3SiC_2 peaks shows considerable increase while TiC peak intensities decreased. When heat treated at 1400 °C for 4 h, the TiC peaks became very weak and the primary diffraction peaks corresponded to Ti_3SiC_2 phase. To determine the content of Ti_3SiC_2 and TiC in the synthesized product, the TiC content can be calculated from the integrated XRD peak intensities according to our experimental calibration, assuming a (Ti_3SiC_2 + TiC) two-phase composition [8]:

$$W_{\mathrm{TiC}} = \frac{I_{\mathrm{TiC}}/I_{\mathrm{TSC}}}{1.8 + (I_{\mathrm{TiC}}/I_{\mathrm{TSC}})} \tag{3}$$

$$W_{\mathrm{TSC}} = \frac{1.8}{1.8 + (I_{\mathrm{TiC}}/I_{\mathrm{TSC}})} \tag{4}$$

where W_{TiC} and W_{TSC} represent the weight percentages of TiC and Ti_3SiC_2, respectively; I_{TiC} and I_{TSC} represent the integrated diffraction peak intensities of TiC (2 0 0) and Ti_3SiC_2 (1 0 4), respectively.

Fig. 4 shows the relative weight percentage of Ti_3SiC_2 and TiC. It can be seen that the relative content of TiC decreases with increasing heat treating temperature and time. When the sample is treated at 1400 °C for 2 h, the content of TiC is remarkably reduced and the content of Ti_3SiC_2 reached 96%. When the heat treating time is prolonged to 4 h at 1400 °C, Ti_3SiC_2 powder in purity of 99% was synthesized.

3.3. Effect of liquid reaction

Now, we wonder whether the availability of the almost single-phase Ti_3SiC_2 synthesis from powders with particles of as large as 150 μm is also attributed to a diffusion controlled reaction mechanism. In Ti–Si binary system, there are two eutectic reactions for the Si–$TiSi_2$ and Ti–Ti_5Si_3 compositions both at the temperature of 1330 °C. Evidence of Ti–Si liquid reaction above Ti–Ti_5Si_3 eutectic temperature was revealed by studying the shrinkage displacement curve in our recent research on the synthesis of bulk Ti_3SiC_2 through PDS process. The powder mixture used in this study for Ti_3SiC_2 powder synthesis is identical with the one used for bulk Ti_3SiC_2 synthesis. Therefore, it is not unreasonable to assume that similar liquid reaction occurred when Ti/Si/TiC mixed powders were heat treated at temperatures above eutectic temperature in vacuum. According to Ti–Si binary phase diagram, the α-Ti transited to β-Ti at 865 °C and this temperature is to some extent decreased by the solution of Si into Ti at particle interface. Enhanced diffusion of Si in Ti after the α-Ti → β-Ti transition is available. With increasing temperature, some Ti/Si interface formed Ti_5Si_3 phase. Above 1170 °C, some Si-rich zone is consisted of β-Ti + Ti_5Si_3. Once the local temperature is above 1330 °C, Ti–Si liquid phase will form among those reactant particles of the composition in Ti–Ti_5Si_3 eutectic range. Depending on chemistry fluctuation in the Si-rich zone, the possible reaction is

$$\mathrm{Ti} + \mathrm{Si} \rightarrow (\mathrm{Ti{-}Si})_{\mathrm{L}} + \beta\text{-}\mathrm{Ti}_{(\mathrm{s})}$$

or

$$\mathrm{Ti} + \mathrm{Si} \rightarrow (\mathrm{Ti{-}Si})_{\mathrm{L}} + \mathrm{Ti}_5\mathrm{Si}_{3(\mathrm{s})}.$$

Considering that some Ti_5Si_3 had been reacted to form Ti_3SiC_2 when the heating temperature was lower than the eutectic

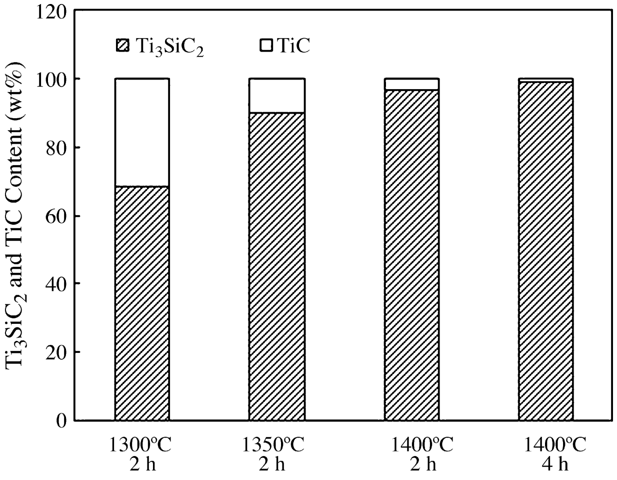

Fig. 4. Relative weight percentage of Ti_3SiC_2 and TiC in the samples after heat treatment at 1300, 1350, 1400 °C for 2 h and 1400 °C for 4 h, respectively.

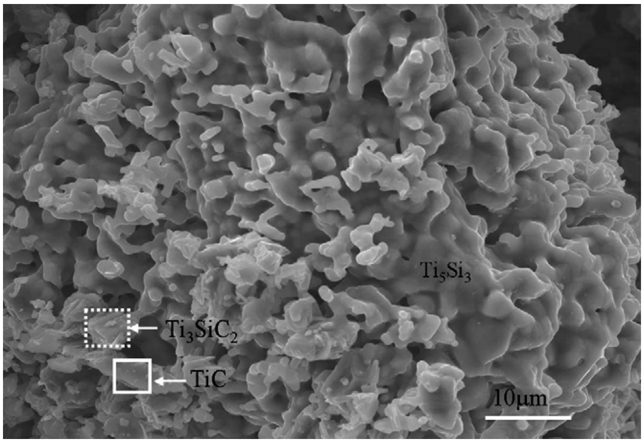

Fig. 5. SEM morphology of the powder after being heated in vacuum to 1400 °C and cooled down immediately.

temperature as expressed in Eq. (2), the amount of liquid phase is limited by the amount of those particles whose compositions are in Ti–Ti_5Si_3 eutectic range. When heat treated at temperatures above the eutectic, it was once a concern that too much liquid phase might form, which will result in the joining of the particles such that powder is not available as a final product. However, the heat treated samples were easily pulverized to fine powder, only showing slight adherence among the particles. This is an indication of the small amount of the formed liquid phase during the synthesis process, and that the Ti/Si/TiC is favorable for the synthesis of Ti_3SiC_2 powder than other powder mixtures such as Ti/SiC/C. As direct evidence of liquid reaction, Fig. 5 shows the morphology micrograph of the sample heated to 1400 °C and immediately cooled down, where the smooth shape of solidified liquid phase can be seen obviously. According to the EDS results, the Ti_3SiC_2, TiC and Ti_5Si_3 phases were marked in this figure.

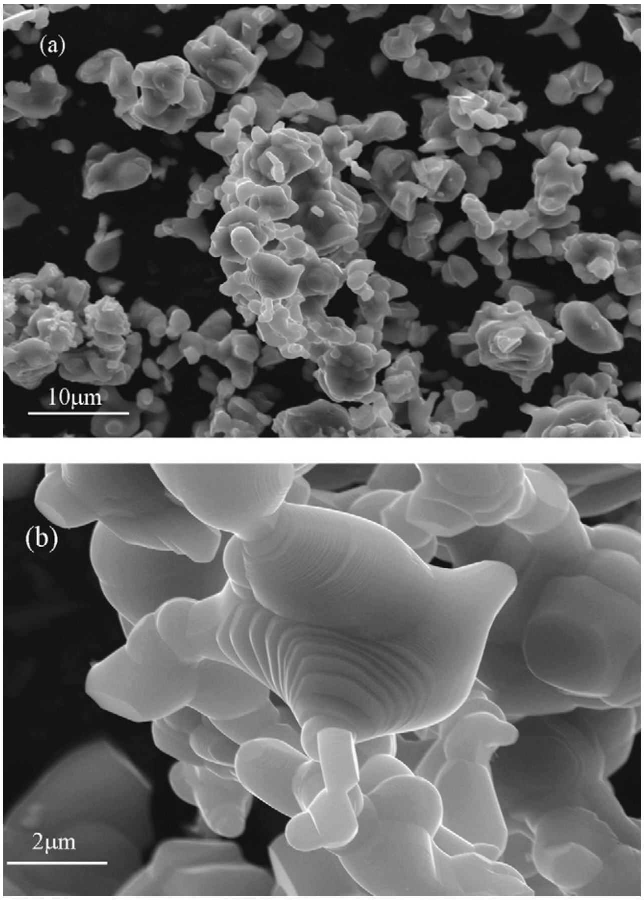

Fig. 6. (a) SEM morphology of powder after heat treatment in vacuum at 1400 °C for 4 h. (b) Crystallographic morphology of Ti_3SiC_2 powder that is synthesized by heat treatment in vacuum at 1400 °C for 4 h.

The role of liquid reaction in the synthesis of single-phase Ti_3SiC_2 powder is straightforward. The reaction process is greatly accelerated by the presence of liquid phase, which enables much rapider atom transport among the reactant particles.

3.4. Morphology of synthesized powders

Fig. 6(a) shows the morphology of powder synthesized in vacuum at 1400 °C for 4 h. The typical appearance for the formed Ti_3SiC_2 is equiaxed with particle size of 2–10 μm. Fig. 6(b) shows the crystallographic growth of Ti_3SiC_2 alone *c*-axes, the layer structure is observed obviously. It is intriguing that the synthesized product was easily pulverized to a powder with particle size one order of magnitude smaller than the starting Ti powder particles. This is indicating that during the synthesizing process, reactions lead to a porous structure of the compound even in single Ti particles. The detailed information is to be explored.

4. Conclusion

(1) Ti_3SiC_2 powder of 99% in content was successfully synthesized by heat treating powder mixture of Si, TiC and coarse Ti (-150 μm) at 1400 °C for 4 h in vacuum.
(2) Ti_5Si_3 as an intermediate phase appeared during the synthesis of Ti_3SiC_2 powder.
(3) Liquid reaction was found above the Ti–Si eutectic temperature, which enabled synthesis reaction of Ti_3SiC_2 from coarse Ti powder.

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