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Short communication

Fabrication of Ti_3SiC_2 powders using TiH_2 as the source of Ti

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Abstract

High purity titanium silicon carbide powders were prepared by pyrolysis and heat treatment of polycarbosilane and TiH_2 powders. The results showed that high purity Ti_3SiC_2 could be obtained when the temperature of pyrolysis is 700 °C. The purity of the products is about 96%, which is calculated by RIR method. The atomic ratio (Ti:Si:C) of the products is about 3.06:1:1.96, which exactly conforms to the stoichiometric ratio of Ti_3SiC_2.

Keywords: B. Electron microscopy; B. X-ray methods; Chemical preparation

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1. Introduction

As a layered compound, titanium silicon carbide (Ti_3SiC_2) belongs to the ternary $M_{N+1}AX_N$ group, where M is an early transition metal, A usually groups IIIA and IVA, and X is either carbon or nitrogen [1].

It was firstly synthesized via chemical reaction in 1967 [2]. Due to its unusual combination of metallic and ceramic properties, such as low density, high Young's modulus, chemical resistance with low hardness, high electrical and thermal conductivity, Ti_3SiC_2 has attracted much attention from both material scientist and physicist [3–11].

In recent years, many attempts have been made to fabricate Ti_3SiC_2 bulk materials and powders, such as hot pressing (HP) [4], spark plasma sintering (SPS) [5,6], hot isostatic pressing (HIP) [7], mechanical alloying (MA) [8], self-propagating high-temperature synthesis (SHS) [9], and pressless sintering [10]. Recently, Luo et al. [12] has tried to make Ti_3SiC_2 materials by in situ reaction of polycarbosilane (PCS) and Ti metal powders firstly.

Nevertheless, it is difficult to find the best method for preparing high purity Ti_3SiC_2 or Ti_3SiC_2-based powders. Furthermore, Ti metal powders are chosen as the source of Ti to fabricate Ti_3SiC_2 materials in most of methods mentioned above. Ti metal is in the form of a finely dispersed powder, and it is even explosive in air, which is a great disadvantage for up scaled industrial production [13]. It has been shown that Ti_3SiC_2 can be prepared from a TiC/Si powder mixture [13,14], and few studies using TiH_2 as one of the starting reagents have been reported [15]. Comparing to Ti metal powders, TiH_2 is safe to handle at room temperature and could be more reactive at high temperature.

The purpose of this study was to fabricate high purity Ti_3SiC_2 powders by pyrolysis and heat treatment of PCS and TiH_2 powders at lower temperature of pyrolysis. In this work, the purity of the final powders have been obtained by relative intensity ratio (RIR) method.

2. Experimental procedure

Commercial TiH_2 (average particle size: 200 mesh, >99% purity) and polycarbosilane (average molecular weight: 1580, empirical formula: $SiC_{2.5}H_7$, Changsha, China) were chosen as the two main starting reagents.

Firstly, PCS was dissolved in solvent gasoline, and TiH_2 was put into the PCS solutions. Then, they were blended by ultrasonification and dried in vacuum.

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The mixtures were placed in alumina crucibles and pyrolyzed in argon (Ar) atmosphere at 700 °C at 5 °C/min for 30 min. The as-received powders were then put into alumina crucibles again and heat treated in Ar atmosphere at 1500 °C at 5 °C/min for 30 min. After the heat treatment, we could get the final powders.

The purity of Ti_3SiC_2 powders were mainly estimated from the relative intensity of representative X-ray diffraction (XRD) peaks of the different phases present in the final products, which were obtained with a Rigaku D/MAX-rC instrument (Japan). The diffraction patterns were scanned from 10° to 80° (2θ). RIR method was used to determine the quantitative mineralogy of the powders that were analyzed by XRD, which is a semi-quantitative XRD analysis. This method allows quantitative calculations without the presence of an internal standard. Microstructure characterizations and compositions of the powders were carried out by scanning electron microscopy (SEM) and Energy Dispersive Spectrometer (EDS).

3. Results and discussion

TiH_2 and PCS with different atomic ratios of Ti:Si (3:1, 3:1.2, 3:1.5, 3:1.7) are chosen as the starting reagents in the process. Firstly, the samples are pyrolyzed at 700 °C for 30 min, and then heat treated at 1500 °C for 30 min.

Effect of the starting reagents on the purity of Ti_3SiC_2 is discussed firstly. Fig. 1(a) and (b) shows the X-ray diffraction patterns of the powders with various atomic ratios of Ti:Si (3:1, 3:1.2, 3:1.5, 3:1.7) pyrolyzed at 700 °C and heat treated at 1500 °C, respectively.

Fig. 1(a) illustrates that the XRD patterns of all the pyrolyzed powders are similar and the main crystal phase is Ti, although the atomic ratios of the starting reagents are different. The reason is that as the starting reagents, hydrogen desorption of TiH_2 will occur at about 500 °C, which is lower than the temperatures of pyrolysis [16]. The possible reaction is

$$TiH_2 \rightarrow Ti + H_2\uparrow.$$

The organic hydrocarbon groups of PCS could be decomposed at 500 °C. By 800 °C, this organic-to-inorganic transition was almost complete, leading to an amorphous SiC-based product [17]. The possible reaction is

$$PCS \rightarrow SiC + C.$$

In our previous work, Ti and TiC peaks can be clearly found in the XRD profiles after the starting reagents including metal Ti and PCS were pyrolyzed at 900 °C for 30 min. The reason is that SiC and C will be obtained after PCS were pyrolyzed, and some Ti will react with C [18].

After the pyrolyzed powders are heat treated at 1500 °C for 30 min, the final powders can be obtained. XRD patterns of the final powders are shown in Fig. 1(b). When the atomic ratio of Ti:Si is 3:1 and 3:1.2, we can find that TiC, Ti_5Si_3 and Ti_3SiC_2 are the main phases in the XRD patterns. As shown in some literature [19], because of the evaporation of Si at high temperature, high purity Ti_3SiC_2 cannot be obtained when the atomic ratio of Ti:Si exactly conforms to the stoichiometric ratio of Ti_3SiC_2.

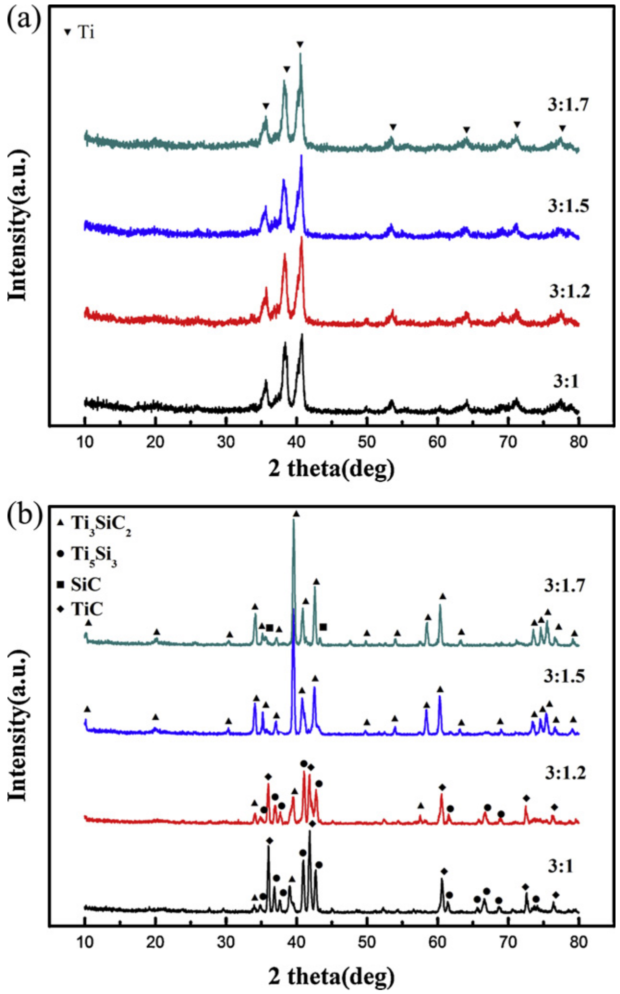

Fig. 1. X-ray diffraction patterns of the powders with various atomic ratios of Ti:Si (3:1, 3:1.2, 3:1.5, 3:1.7) (a) pyrolyzed at 700 °C and (b) heat treated at 1500 °C.

As the PCS content increases, the peaks of high purity Ti_3SiC_2 powders can be observed when the atomic ratio of Ti:Si is up to 3:1.5. There are few secondary phases in the XRD patterns, in which the peaks is weak remarkably. It is in accordance with the results of our previous work [18]. An initial mixture with a little excess of silicon is needed to fabricate high purity Ti_3SiC_2.

However, the peaks of SiC will be evidently found in the XRD pattern, when the atomic ratio of Ti:Si is 3:1.7. It means that when the PCS content increases to a high level, SiC phases, as one of pyrolysis products of PCS, will be left in the final powders.

The general reaction can be described as follows:

$$3Ti + SiC + C \rightarrow Ti_3SiC_2$$

According to the thermodynamic analysis, the ΔG^{θ} of the reaction is about −407.9 kJ/mol at 1500 °C, meaning that the reaction can proceed sufficiently on this condition. In addition, compared to our previous work, although effect of the starting

Table 1
Phases after heat treatment, mass fraction of Ti_3SiC_2 and conversion ratio to Ti_3SiC_2.

Composition (Ti:Si)	Phase identified in XRD	Mass fraction of Ti_3SiC_2	Conversion ratio to Ti_3SiC_2
3:1	TiC, Ti_5Si_3, Ti_3SiC_2	25%	23%
3:1.2	TiC, Ti_5Si_3, Ti_3SiC_2	21%	18%
3:1.5	Ti_3SiC_2	96%	97%
3:1.7	Ti_3SiC_2, SiC	81%	96%

reagents on the purity of the final products is similar, Ti_3SiC_2 powders could be obtained when the first step was carried out at 700 °C. The reason may be that hydrogen desorption of TiH_2 will occur at lower than 700 °C temperatures and the product of hydrogen desorption is more reactive than Ti metal powders, which will be favorable to in situ synthesis process.

The purity of the as-received Ti_3SiC_2 powders has been estimated in some studies [10,13]. In this work, RIR method is used to determine the quantitative mineralogy of the final powders obtained above. RIR is one of the simplest and quickest ways to quantify X-ray diffraction data, which is a semi-quantitative XRD analysis. In a two-phase system, the general definition of the RIR for phase β to reference phase α is given by [20]:

$$\mathrm{RIR}_{\alpha,\beta} = \left(\frac{I_\alpha}{I_\beta}\right)\left(\frac{X_\beta}{X_\alpha}\right) \tag{1}$$

$$X_\alpha + X_\beta = 1 \tag{2}$$

where I is the intensity and X is the mass fraction. The RIR value could be obtained by determination of the slope of the standard calibration plot or from other RIR values by:

$$\mathrm{RIR}_{\alpha,\beta} = \frac{\mathrm{RIR}_{\alpha,\gamma}}{\mathrm{RIR}_{\beta,\gamma}} \tag{3}$$

So we can get the mass fraction of phase α:

$$X_\alpha = \frac{I_\alpha}{I_\alpha + \mathrm{RIR}_{\alpha,\beta} I_\beta} \tag{4}$$

According to Eq. (4), the calculated purity of Ti_3SiC_2 powders are listed in Table 1. We can find from Table 1 that the purity of Ti_3SiC_2 is about 96% when the atomic ratio of Ti:Si is 3:1.5. In addition, the conversion ratio to Ti_3SiC_2 as a function of the reactant ratio is listed in Table 1, which is obtained according to the content of each component in the final powders. The conversion ratio to Ti_3SiC_2 is about 97% when the atomic ratio of Ti:Si is 3:1.5.

The microstructures and compositions of the Ti_3SiC_2 powders are studied by SEM and EDS, corresponding to the

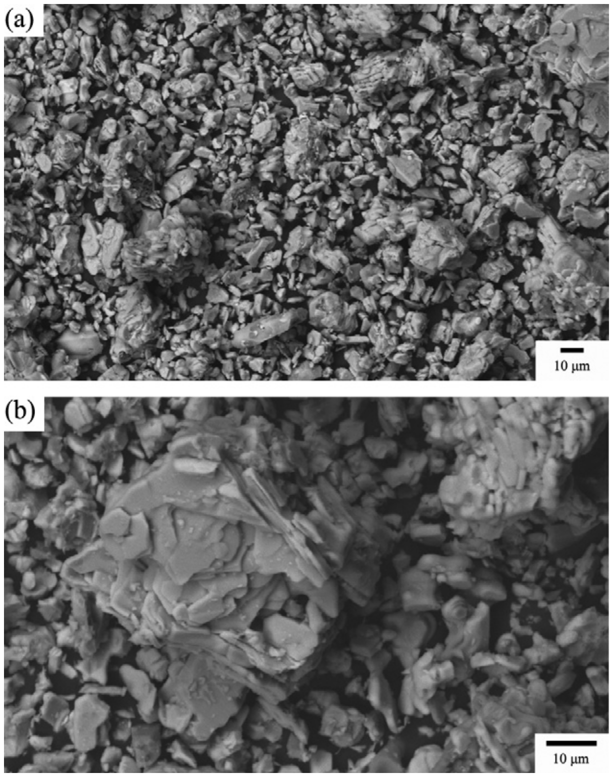

Fig. 2. SEM micrographs of Ti_3SiC_2 powders prepared with atomic ratio of Ti:Si of 3:1.5.

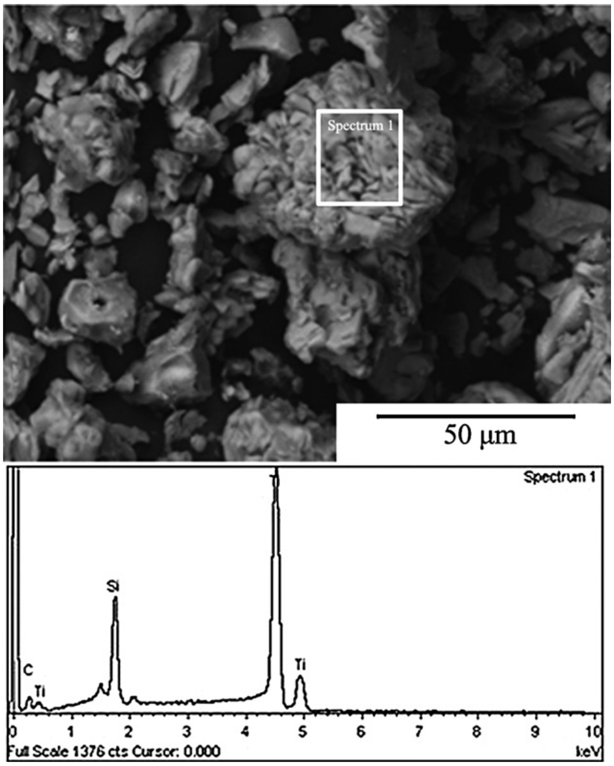

Fig. 3. EDS X-ray spectra of Ti_3SiC_2 powders prepared with atomic ratio of Ti:Si of 3:1.5.

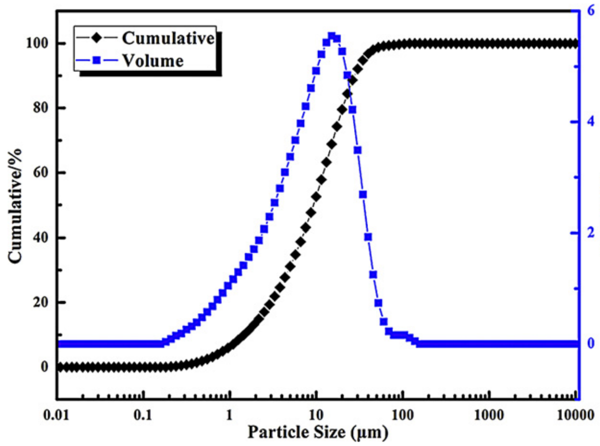

Fig. 4. Particle size distribution curve of Ti_3SiC_2 powders prepared with atomic ratio of Ti:Si of 3:1.5.

sample where the atomic ratio of Ti:Si is 3:1.5. Fig. 2(a) and (b) shows the SEM images with different enlargement factors respectively. From Fig. 2(a), we can find that the final powders become very small, which are about several or tens of microns. According to the particle size distribution curve, as shown in Fig. 4, D(50) is about 9.306 μm. The uniformity coefficient is 0.919, which means that particle size of Ti_3SiC_2 powders is very uniform and they have the same size nearly. Fig. 2(b) shows that the layer morphology characteristic of the Ti_3SiC_2, although it is not evident like our previous work. According to the results of EDS, as shown in Fig. 3, we can find that the atomic ratio of Ti:Si:C is about 3.06:1:1.96, which exactly conforms to the stoichiometric ratio of Ti_3SiC_2.

4. Conclusion

Preparation of high purity Ti_3SiC_2 powders was carried out using TiH_2 as the source of Ti when the temperature of pyrolysis is 700 °C. When the atomic ratio of Ti:Si is up to 3:1.5, high purity Ti_3SiC_2 powders can be obtained and there are few secondary phases in the XRD patterns, the purity of which is about 96%. The atomic ratio of Ti:Si:C of the high purity Ti_3SiC_2 is about 3.06:1:1.96, which exactly conforms to the stoichiometric ratio of Ti_3SiC_2.

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