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Sintering of Ti_3SiC_2 with B_2O_3 additions

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Abstract

Titanium silicon carbide (Ti_3SiC_2) is a remarkable material for it combines the best properties of metals and ceramics. When Ti_3SiC_2 is synthesized by normal sintering, the self-combustion reaction usually takes place. In this work, self-combustion reaction is avoided by adding B_2O_3 sintering aids, obtaining 83 vol.% Ti_3SiC_2. Morphology and preferred orientation of Ti_3SiC_2 grains are also studied and compared with those without B_2O_3 aid. © 2002 Published by Elsevier Science Ltd and Techna S.r.l.

Keywords: A. Pressing; A. Sintering; B. X-ray method; B. Microstructure-final; Ti_3SiC_2

1. Introduction

Titanium silicon carbide (Ti_3SiC_2) is a promising structural/functional material, and it has received considerable attention by both material scientists and physicists for its unusual combination of metallic and ceramic properties. Like metals, it is an excellent electrical and thermal conductor, and is very readily machinable. Like ceramics, it is elastically rigid with a Young modulus of 320 GPa, and stable to at least 1700 °C under an inert atmosphere or vacuum [1]. HP and HIP with Ti, Si and graphite powders at 1600 °C are the main ways to synthesize bulk Ti_3SiC_2 material [2,3]. However, these methods are too complex to use in the industry. In the synthesis of bulk Ti_3SiC_2, nearly no normal sintering method is used, because a slightly higher heating rate will result in a combustion reaction. In this case, the as-derived sample will have a great volume expansion, which creates the Al_2O_3 crubicle to break, and the volume percentage of Ti_3SiC_2 is not very high. To solve the problems mentioned above, this work focuses on avoiding the combustion reaction of Ti_3SiC_2 by adding some B_2O_3 sintering aids. By comparing to the synthesis of Ti_3SiC_2 without sintering aid, B_2O_3 has large influences on the purity, preferred orientation and grain morphology of Ti_3SiC_2.

2. Experimental procedure

Ti_3SiC_2 was fabricated in two different groups.

For group A, Ti, Si and graphite powders were mixed in a stoichiometric molar ratio of 3:1:2. The green bodies of samples 1–6 were put into Al_2O_3 crubicles and normal sintered in flowing argon gas, at 1250, 1300, 1350, 1400, 1450 and 1500 °C, respectively, for 2 h.

For group B, Ti, Si and graphite powders were mixed in a stoichiometric molar ratio of 3:1:2 with 5 wt.% B_2O_3 sintering aid. The green bodies of samples 7–12 were directly put into Al_2O_3 crubicles and normal sintered in flowing argon gas, at 1250, 1300, 1350, 1400, 1450 and 1500 °C, respectively, for 2 h.

Powder X-ray diffraction (XRD) samples were made by milling the former bulk samples (1–12) with the particle size less than 20 μm. In order to get more precise data, the background scattering was eliminated and $K_{\alpha,1}$, $K_{\alpha,\ 2}$ diffraction was separated. The bulk samples 2 and 8 were also observed by scanning electron microscope (SEM). Sample 8 was used to obtain the Ti_3SiC_2 powders with a higher purity. We used the method following to eliminate the remaining B_2O_3 sintering aid and TiC second phase.

Since the oxidization rate of Ti_3SiC_2 was much lower than that of TiC, a controlled oxidation at 400 °C in air for about 3 h was performed to improve the purity of Ti_3SiC_2. The products were TiO_2, SiO_2, Ti_3SiC_2, a little TiC, and the remaining B_2O_3 sintering aid. After dissolving SiO_2, TiO_2 and B_2O_3 by hydrofluoric acid,

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H_2SO_4 and $(NH)_4SO_4$, the final products contained about 93 vol.% Ti_3SiC_2.

3. Results and discussions

3.1. Purity analysis

In the study of XRD, the $\{hkl\}$ peaks for substance i can be written as:

$$I_i^{hkl} = k_i^{hkl} v_i \tag{1}$$

where I_i^{hkl} is the intensity for $\{hkl\}$ peak of a certain substance i; v_i is the volume percentage for substance i, and k_i^{hkl} is a constant. Since at high temperature, only TiC and Ti_3SiC_2 coexist in Ti–Si–C system [4], if we ignore the existence of B_2O_3 sintering aid, we can use Eqs. (2) and (3) [5] to determine the volume percentage of Ti_3SiC_2.

$$\frac{v_{\mathrm{TSC}}}{v_{\mathrm{TiC}}} = \frac{(I_{\mathrm{TSC}}^{104} + I_{\mathrm{TSC}}^{105})}{(I_{\mathrm{TiC}}^{200} + I_{\mathrm{TiC}}^{111})} \times \frac{(k_{\mathrm{TiC}}^{200} + k_{\mathrm{TiC}}^{111})}{(k_{\mathrm{TSC}}^{104} + k_{\mathrm{TSC}}^{105})} \tag{2}$$

$$v_{\mathrm{TSC}} + v_{\mathrm{TiC}} = 1 \tag{3}$$

The volume percentages of each Ti_3SiC_2 sample are listed in Table 1.

According to Table 1, at 1250 °C in Group A, 57 vol.% Ti_3SiC_2 is obtained, while in Group B no Ti_3SiC_2 is developed (mainly $Ti_5Si_3C_x$ and TiC), which is mainly caused by the reaction mechanism of Ti_3SiC_2 material. Because Ti_3SiC_2 is a ternary compound, and also because Si and Ti atoms are relative large, the diffusion rate of Ti and Si atoms is quite important to the formation of Ti_3SiC_2. Only if the liquid and gas phase of Ti and Si exist, the diffusion rate of Ti and Si atoms can reach a value large enough. According to the Si–Ti–C phase diagram, the Ti_3SiC_2 will be formed by the following reaction [6].

$$\mathrm{L} + Ti_5Si_3C_x \rightarrow Ti_3SiC_2 + TiSi_2 (0<x<1) \tag{4}$$

Ti and Si alloy will form a liquid phase at about 1300 °C [7], which will speed up the diffusion of Ti and Si atoms. In Group A, since combustion reaction takes place [8], a great mount of heat will be released. Hence, in some local areas, the temperature will be higher than 1300 °C, and some Ti_3SiC_2 will be formed in the products. Since B_2O_3 exists as liquid phase at about 300 °C, which will impede the heat transmission in the reaction, thus avoiding the outset of combustion reaction. Therefore, in Group B, Ti_3SiC_2 will not appear until 1300 °C. In Group A, the crucibles are usually broken for the existence of combustion reaction, while in Group B, this dose not occur. Since it is very difficult to control the combustion reaction, the volume percentage of Ti_3SiC_2 is usually unpredictable in Group A. In Group B, when the synthesis temperature is 1300 °C, the purity of Ti_3SiC_2 reaches to the maximum value (83%), which is significantly higher than the purity of Group A. This occurs also because the B_2O_3 liquid enhances the diffusion rate of Ti and Si atoms. When the sintering temperature is higher than 1300 °C, the purity of Ti_3SiC_2 decreases as the synthesis temperature increases. This is mainly because, at high temperature, the Si atoms in the Ti–Si alloy are inclined to escape from the green body and also because the following reaction [9] will take place because the furnace in our experiment is mainly made from graphite.

Table 1
The volume percentages of each Ti_3SiC_2 sample

Purity	1250 °C	1300 °C	1350 °C	1400 °C	1450 °C	1500 °C
Group A (%)	57	67	46	63	55	–
Group B (%)	–	83	65	55	28	23

$$Ti_3SiC_2 + \mathrm{C} \rightarrow 3\mathrm{TiC} + \mathrm{Si}\uparrow \tag{5}$$

In Group B, the relationship between the Ti_3SiC_2 purity and synthesis temperature is shown in Fig. 1. At 1500 °C, all the Ti_3SiC_2 is decomposed to TiC [Eq. (5)] in Group A; while in Group B, there still are 23 vol.% Ti_3SiC_2 left, and this case is mainly because, in high temperature, the B_2O_3 liquid phase will enwrap the Ti_3SiC_2 grains, thus restricting the C gas contact with Ti_3SiC_2 and also making more difficult the escape of Si gas from Ti_3SiC_2 grains.

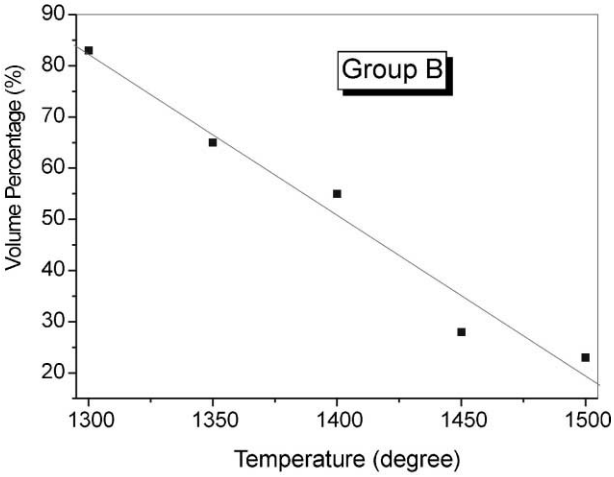

Fig. 1. Relationship between volume percentage and temperature of Ti_3SiC_2.

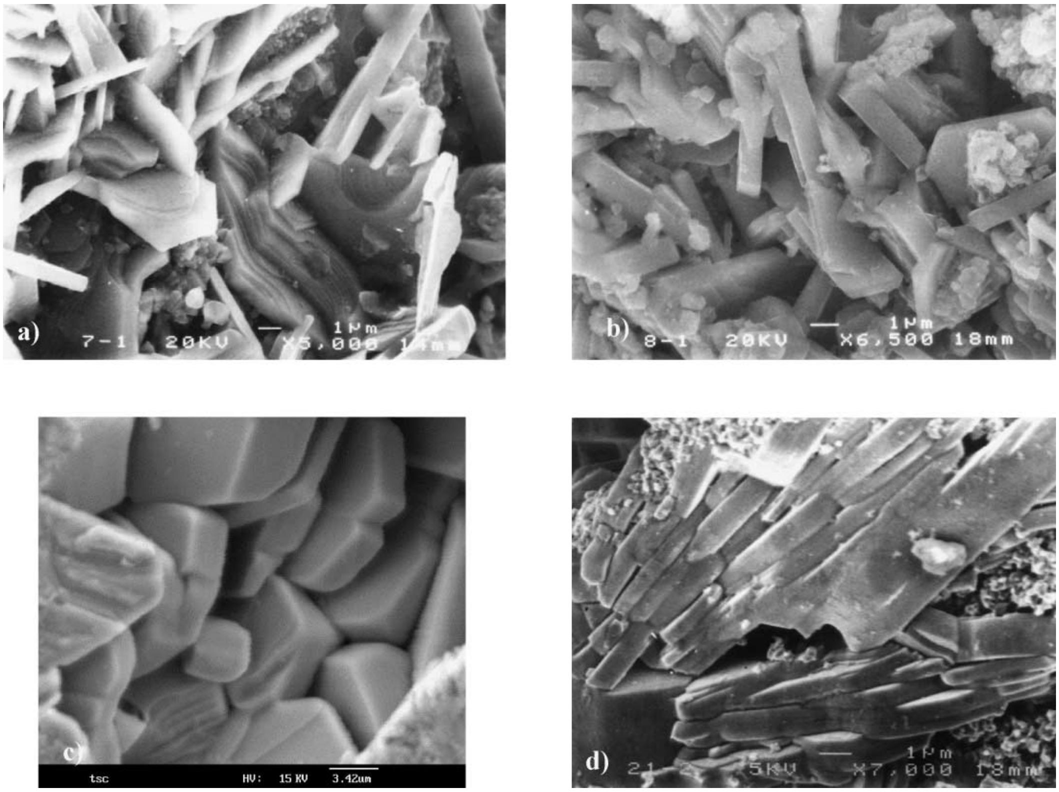

Fig. 2. Morphology of Ti_3SiC_2 grains: (a) in Group A; (b) in Group B; (c) ideal morphology by HP sintering; (d) intergrowth phenomenon in Group A.

3.2. Grain morphology of Ti_3SiC_2

According to the specific structure of Ti_3SiC_2, the present authors put forward a growth model of Ti_3SiC_2 grains [10]. The ideal morphology of Ti_3SiC_2 is a flat hexagonal prism with eight faces of $\{11\bar{2}0\}$ (side face) and $\{0001\}$ (basal face) planes, which was observed directly in Viala's work [11]. Fig. 2 (a, b) show the grain morphologies of Group A and B respectively. In Group A, the Ti_3SiC_2 grains mainly show plate-like morphology. When, compared to the grain morphology synthesized by hot-pressing (as shown in Fig. 2c), they do not show completely flat hexagonal prisms (ideal morphology of Ti_3SiC_2), which might be because in normal sintering the Ti_3SiC_2 grains will grow more freely. According to Fig. 2(d) (Group A), several Ti_3SiC_2 grains are found to form a larger "cluster", which is so-called intergrowth phenomenon. It seems contradictory to the *principle of maximum entropy*; which tells us that all the Ti_3SiC_2 grains should be distributed as randomly as possible. There might be three reasons to explain this case: If two grains grow together with their basal plane as boundary, they can easily form a coherent interface, where the boundary energy is much lower than those without a coherent interface. (2) Since the basal face of Ti_3SiC_2 grain is the close-packed plane, the free energy of basal plane is lower than that of all other planes in the crystal. If one Ti_3SiC_2 grain is formed, the nuclei of other Ti_3SiC_2 can easily be formed on its basal plane with lower nucleation energy. (3) In a local area, non-equilibrium procedures in combustion reaction, such as large temperature gradients, can commonly exist, which will help the intergrowth of Ti_3SiC_2 grains [12]. The intergrowth of neighboring grains could result in "local ordering" of Ti_3SiC_2 grains, and make polycrystal Ti_3SiC_2 anisotropic in a local area. In Group B the Ti_3SiC_2 grains do not usually show a plate-like but a rod-like morphology (as shown in Fig. 2b). Since B_2O_3 has a low melting point (about 500 °C), some B_2O_3 liquid droplets will attach to Ti_3SiC_2 nuclei. This attachment will impede the growth units (Ti_6C and Si atom) to link to some certain faces and impede the growth of those faces of Ti_3SiC_2 nuclei, which will prevent the formation of ideal morphology (flat hexagonal prism) of Ti_3SiC_2 grains.

The morphology of Ti_3SiC_2 grains will influence the *powder* XRD of Ti_3SiC_2 quite largely.

3.3. Preferred orientation of powder XRD

In general, when we prepare the powder XRD sample, we usually press the powders to make a relative flat face and obtain a relatively high intensity of $\{hkl\}$ plane. According to the plate-like morphology of Ti_3SiC_2, a

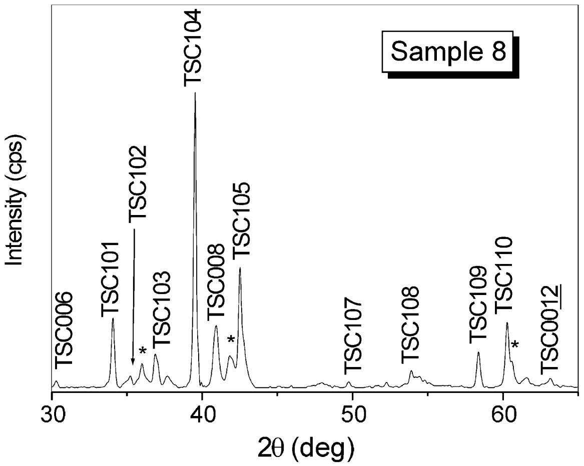

Fig. 3. XRD pattern of sample 8, * points to TiC peaks.

slight pressing force will rotate the basal plane of Ti_3SiC_2 to parallel to the surface of the powder carrier. That is, if a pressure is brought on the powders, a *{000l}* planar texture will be developed. Traditionally, the degree of *{000l}* texture is usually determined by the *f* factor method [13]. Since the {104} peak is the strongest peak in the calculated XRD data of Ti_3SiC_2, to determine the textural extent more conveniently, W_m is used in our work, which is defined as:

$$W_m = \frac{I^{008}_{\mathrm{TSC}}}{I^{104}_{\mathrm{TSC}}} \tag{6}$$

We can obtain the W_m value of Ti_3SiC_2 synthesized by CVD and HP methods from Ref. [14] and [5]. We use the powder XRD data of sample 2 and sample 8 to represent the preferred orientation of Group A and B, respectively. Table 2 lists the W_m value of CVD, HP, Group A, Group B, and calculated value, respectively.

According to Table 2, we can find that $W_{\mathrm{CVD}} > W_{\mathrm{HP}} > W_{\mathrm{A}} > W_{\mathrm{B}} \approx 4W_{\mathrm{cal}}$.

As we know, larger and more are the ideal Ti_3SiC_2 grains (with the morphology of flat hexagonal prism), stronger is the *{000l}* texture of Ti_3SiC_2 powders. According to Ref. [5] and [14], the Ti_3SiC_2 grains are quite large (in Ref. [14], it reaches to 100 μm) and show a plate-like morphology; while in Group A and B the grains are relatively small, the morphologies of Ti_3SiC_2 grains are relatively complex. In Group B, the existence of both rod-like and plate-like grains makes the crystal plane of Ti_3SiC_2 distributed more randomly, hence, the W_m value is almost equal to the calculated one [15]. The XRD pattern and data of sample 8 (Group B) are shown in Fig. 3 and Table 3.

Table 2
W_m values of different fabricated methods

	CVD	HP	Group A	Group B	Calculated value
W_m (%)	133	75	42	21	19.3

Table 3
Observed and calculated data of Ti_3SiC_2 powder XRD

hkl	I/I_0 in JCPDS card [16] (%)	Observed I/I_0 in sample 8 (%)	Calculated I/I_0 in Ref. [15] (%)
101	16	24	30.6
104	75	100	100
008	100	21	19.3
105	37	41	40.2
108	5	6	4.4
109	19	12	13.4
110	13	24	26.7

In powder XRD of Ti_3SiC_2, it is a big problem that the observed intensity of {0008} peak diverges greatly from the calculated one [15], even in the JCPDS card [16]. This case is mainly caused by the grain morphology, which will result in a *{000l}* planar texture very easily. Therefore, it is quite difficult to obtain the XRD sample without a *{000l}* planar texture. As mentioned above, the B_2O_3 aid will change the ideal morphology of Ti_3SiC_2 and make the crystal planes distribute more randomly. Therefore, the XRD data with B_2O_3 sintering aid can be considered as a standard data, when we study the anisotropy property and preferred orientation of Ti_3SiC_2 material.

4. Conclusions

In this work, the self-combustion reaction of Ti, Si and C powders is avoided by adding B_2O_3 sintering aid. The volume purity of Ti_3SiC_2 can reach to 83% when the sintering temperature is 1300 °C. The morphology and preferred orientation are also investigated comparing to those without sintering aid. The morphology of Ti_3SiC_2 grains with B_2O_3 aid mainly shows a rod-like morphology, which will not result in the commonly existed *{000l}* planar texture.

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