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Preparation and characterization of Ti_3SiC_2 powder

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Abstract

Pressureless sintering in vacuum was applied to synthesize Ti_3SiC_2 from elemental powders of Ti, Si and C. Based on the phase compositions and purities of the products obtained by X-ray diffraction, the elemental powders composition and sintering condition were optimized. It was found that the sample sintered at 1450 °C for 240 min from a mixture of 3Ti/1.75Si/2C (molar ratio) contained Ti_3SiC_2 with the volume fraction as high as 93%. It was proposed that loss of Si through gaseous vaporization and contamination of C might be the main obstacles against obtaining high-purity material by this way.

Keywords: Ti_3SiC_2; X-ray diffraction; Pressureless sintering in vacuum; Composition optimization

1. Introduction

Of the various reaction products within the Ti–Si–C system, titanium silicon carbide (Ti_3SiC_2) is the only stoichiometric ternary phase [1]. This hexagonal-structured compound is of technological interest due to its unique characteristics in that it exhibits a surprising combination of typical ceramic properties like high stiffness, thermal and chemical resistance with low hardness, high-fracture toughness, ductile behavior features, electrical conductivity and good machinability of metals [2–5]. This suggests that Ti_3SiC_2 possibly could be served as a new matrix materials, as well as second-phase reinforcement material resulting in Ti_3SiC_2-based composites such as Ti_3SiC_2–Cu [6], SiC–Ti_3SiC_2 and TiC–Ti_3SiC_2 [7] for high-temperature applications.

Consequently, over the past decade extensive investigations have been carried out on the processing–microstructure–property relationships of Ti_3SiC_2. Specifically, an understanding of the chemical reaction paths, kinetics, and high-temperature behavior of the Ti–Si–C system is important for the development of the processing technique, and will also provide some insights into the processing of non-oxide ceramics in general. To date, there have been several ways to synthesize bulk Ti_3SiC_2, among which chemical vapor deposition (CVD) was first proposed by Jeitschko and Nowotny [8] followed by hot isostatic pressing (HIP) [9], hot pressing (HP) [10], spark plasma sintering (SPS) [11], self-propagating high-temperature synthesis (SHS) [12], etc. In most cases, processing involved a two-step process where titanium, silicon carbide, and carbon mixtures [5,9,10] or titanium, silicon, and carbon powders [11,12] were first reacted together to form a powder compact that was subsequently pulverized, and then hot pressed to yield polycrystalline samples. The major barrier lies in the difficulty to obtain samples with high content of Ti_3SiC_2 since Ti_3SiC_2, TiC and $TiSi_2$, and sometimes, Ti_5Si_3 and/or SiC coexisted as the chemical reactive products during the aforementioned procedures except CVD.

However, so far there have been quite few reports on the synthesis of bulk polycrystalline Ti_3SiC_2 samples through pressureless sintering in vacuum. This method has at least two advantages over other processing techniques—relatively high efficiency and easy availability of porous sintered Ti_3SiC_2 compacts used as raw powders after pulverized for dense Ti_3SiC_2 samples and Ti_3SiC_2-based composites through HIP or HP procedures. Accordingly, the present investigation was focused on preparation of Ti_3SiC_2 powders through pressureless sintering in vacuum. Moreover, raw powders having a small excess of Si compared to the stoichiometric composition were used with the goal of limiting TiC crystallization by creating a more Si-rich liquid phase

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during reaction and maximizing the content of Ti_3SiC_2 in the products.

2. Experimental procedure

Commercial Ti (average particle size: 74 μm, >99% purity), Si (average particle size: 74 μm, >99.9% purity) and C (average particle size: 20 μm, >99% purity) were selected as the starting powders. As listed in Table 1, they were blended in a stoichiometric molar composition as $3Ti + Si + 2C$ and with other two levels of excess Si as $3Ti + 1.5Si + 2C$ and $3Ti + 1.75Si + 2C$ and are denoted, respectively, as TSC1, TSC2 and TSC3 in the following section. The mixtures were ball milled in ethanol for 48 h, then dried and ground with 10% polyvinyl alcohol ($C_{2n}H_{4n}O_n$, PVA) solution in order to improve the compactability and, finally, uniaxially die-pressed under 100 MPa into platelets with dimensions of 8 mm × 8 mm × 35 mm. The compacts were heated homogeneously up to 400 °C in vacuum (∼1 Pa) for 10 h with

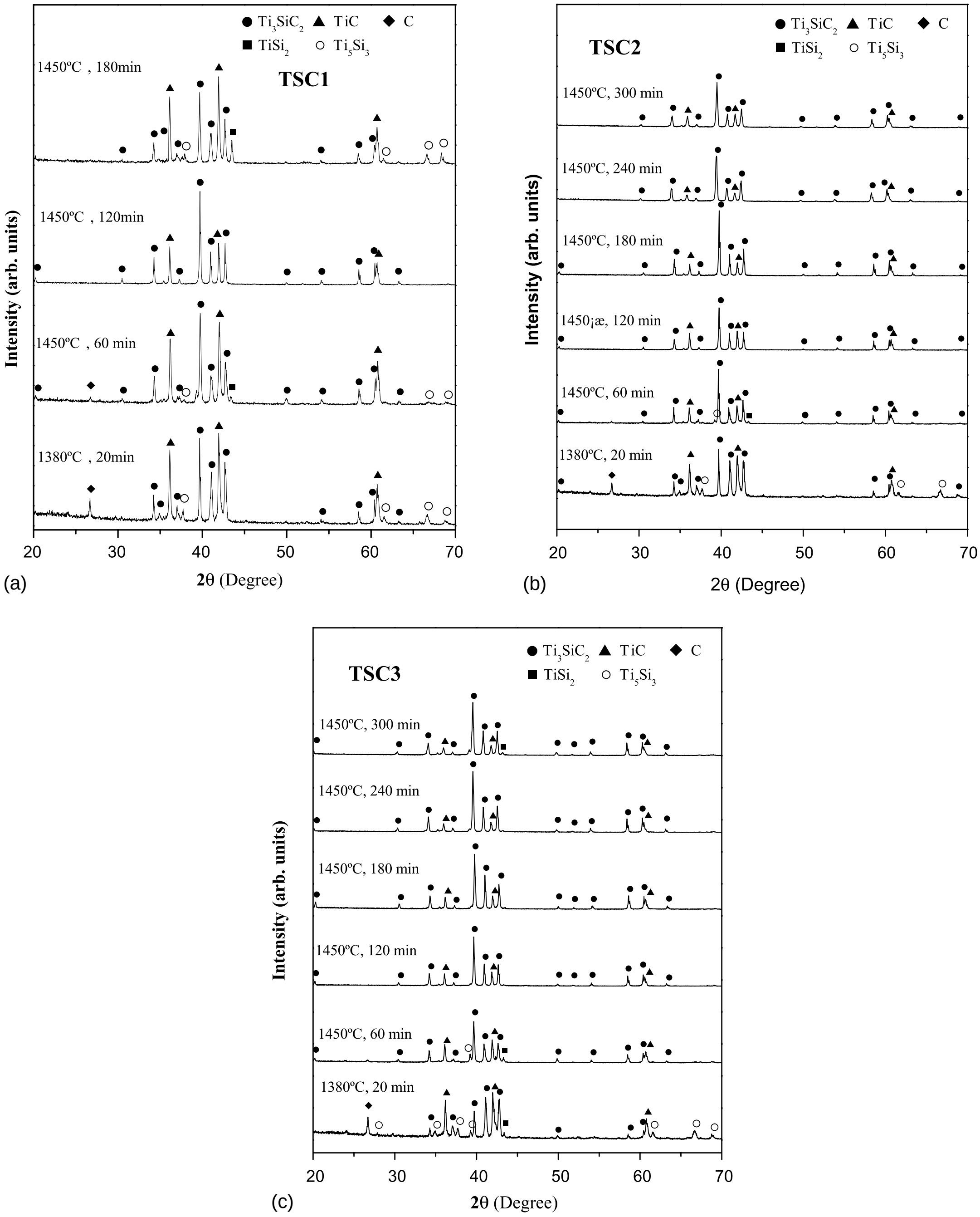

Fig. 1. X-ray diffraction (XRD) patterns of the products obtained by sintering the different mixed elemental powders at 1380–1450 °C for different times. (a) TSC1 (Ti:Si:C = 3:1:2), (b) TSC2 (Ti:Si:C = 3:1.5:2) and (c) TSC3 (Ti:Si:C = 3:1.75:2).

Table 1
Composition of raw powder mixture (in molar ratio), volume fraction of Ti_3SiC_2, and resulting phases after reactively sintered under different conditions

Sintering conditions		Volume fraction of Ti_3SiC_2 (%)			Resulting phases identified by XRD		
T (°C)	*t* (min)	TSC1 (3Ti + Si + 2C)	TSC2 (3Ti +1.5 Si + 2C)	TSC3 (3Ti + 1.75Si + 2C)	TSC1 (3Ti + Si + 2C)	TSC2 (3Ti +1.5 Si + 2C)	TSC3 (3Ti + 1.75Si + 2C)
1380	20	–	–	–	Ti_3SiC_2, TiC, Ti_5Si_3, C	Ti_3SiC_2, TiC, Ti_5Si_3, C	Ti_3SiC_2, TiC, Ti_5Si_3, $TiSi_2$, C
1450	60	–	–	–	Ti_3SiC_2, TiC, Ti_5Si_3, $TiSi_2$, C	Ti_3SiC_2, TiC, Ti_5Si_3	Ti_3SiC_2, TiC, Ti_5Si_3, $TiSi_2$
	120	81	82	87	Ti_3SiC_2, TiC	Ti_3SiC_2, TiC	Ti_3SiC_2, TiC
	180	–	91	89	Ti_3SiC_2, TiC, Ti_5Si_3, $TiSi_2$	Ti_3SiC_2, TiC	Ti_3SiC_2, TiC
	240	–	91	93	–	Ti_3SiC_2, TiC	Ti_3SiC_2, TiC
	300	–	87	90	–	Ti_3SiC_2, TiC	Ti_3SiC_2, TiC, $TiSi_2$

the purpose of removing PVA, moisture and absorbed gases. The green body was placed into a graphite crucible and sintering was conducted in vacuum (∼0.1 Pa) with two conditions: (1) at 1380 °C for 20 min, and (2) at 1450 °C for 60–300 min. After sintering, the surfaces of samples were ground to remove the graphite layer, then pulverized and ground into powders for X-ray diffraction (XRD, Philips, X'Perts PROSUPER) with Cu Kα radiation at 40 kV and 40 mA. The volume fraction of Ti_3SiC_2, V_{TSC} of some samples containing only Ti_3SiC_2 and TiC were calculated based on the following equation [11]:

$$V_{TSC} = 1 - V_{TC}, \qquad (1)$$

where V_{TC} is the volume fraction of TiC given by $V_{TC} = ((I_{TC}/I_{TSC})/(1.95 + I_{TC}/I_{TSC}))$ and I_{TC}/I_{TSC} is the integrated diffraction intensity ratio of TiC to Ti_3SiC_2 main peaks obtained from the XRD patterns. The microstructure evaluation of sintered compacts was performed on a scanning electron microscopy (SEM, XL30 ESEM) with an accelerating voltage of 20 kV.

3. Results and discussion

Fig. 1(a–c) represented the X-ray diffraction patterns of samples sintered from mixed elemental Ti–Si–C powders with different molar ratios at 1380–1450 °C for different times. After sintered at 1380 °C for 20 min, a little amount of TiC, free C and Ti_5Si_3 coexisted in all cases. For sample TSC3, a little amount of $TiSi_2$ also existed and the frac-

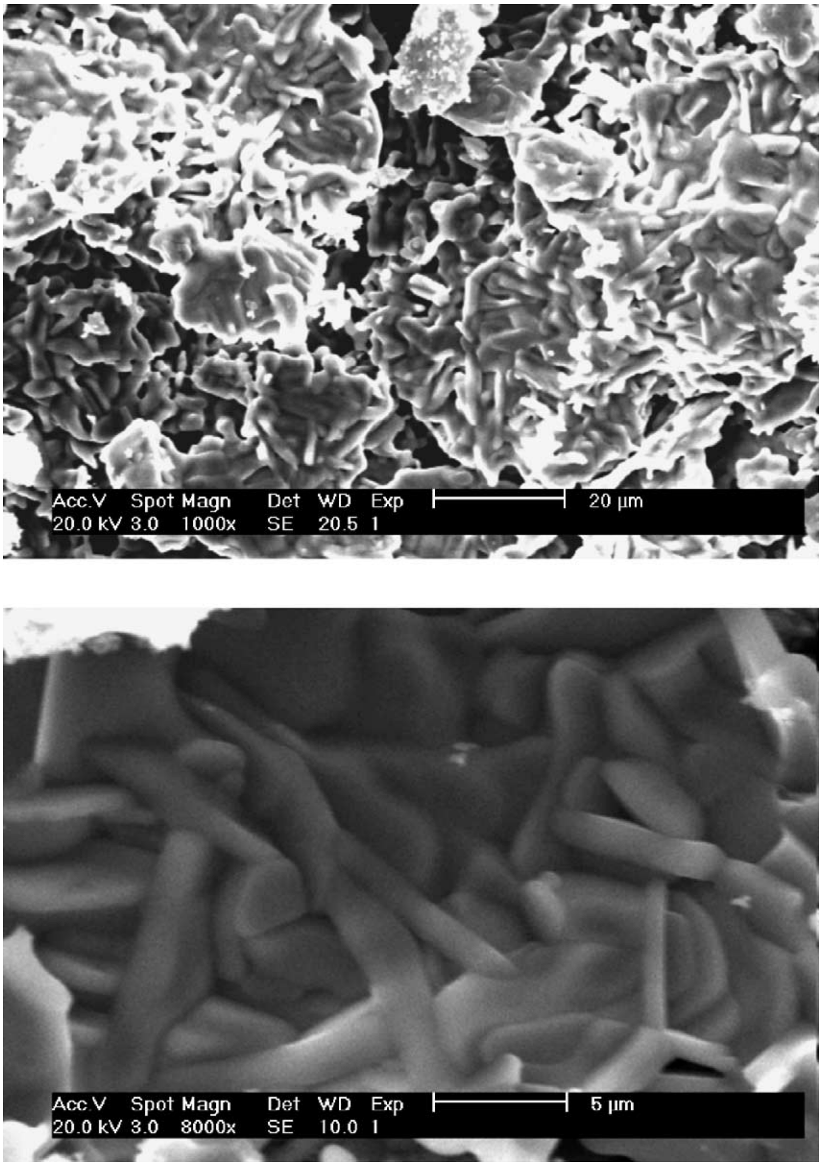

Fig. 2. SEM micrograph of the fractured surface of the highest-purity Ti_3SiC_2 sample fabricated in the present study (TSC3 sintered at 1450 °C for 4 h), where columnar grains and layered nature are apparent. (a) Low- and (b) high-magnification.

tions of impurities especially Ti_5Si_3 were higher than the other two samples. Unfortunately, some impurities still existed after sintered at 1450 °C for 60 min. However, free carbon was no more present except in TSC1 and the contents of TiC decreased remarkably in all the three samples since its corresponding integrated diffraction intensity of XRD patterns became weak. When sintering time increased, i.e., 120 min for sample TSC1, 120, 180 and 240 min for samples TSC2 and TSC3, only TiC accounted for the impurity. The content of Ti_3SiC_2 in these cases are calculated and presented in Table 1. It can be found that the sample TSC2 sintered at 1450 °C for 180 and 240 min had the same content of 91 vol.% Ti_3SiC_2, higher than that of the sample TSC1 with the highest volume fraction of Ti_3SiC_2 as 81%. The sample TSC3 sintered at 1450 °C for 240 min contained 93 vol.% Ti_3SiC_2, comparable to that of the samples fabricated through HP, HIP or plasma discharge sintering (PDS) technique routes and much higher than that of the sample sintered also from Ti/Si/C powder mixtures under similar conditions while in Ar atmosphere (0.1 MPa) [13]. Nevertheless, the purity of Ti_3SiC_2 decreased with increasing sintering time up to 240 min. For instance, after sintered at 1450 °C for 300 min the content of TiC in sample TSC2 increased significantly, and $TiSi_2$ in sample TSC3 appeared. For intuitive comparison, the resulting phases after reactively sintered under different conditions were also summarized in Table 1. Fig. 2 showed the SEM micrograph of the fractured surface of the highest-purity Ti_3SiC_2 sample fabricated in the present study (TSC3 sintered at 1450 °C for 240 min). It was evident that the microstructure was characterized by columnar grains as well as layered nature.

It was demonstrated from the previous study [14] that the chemical reactions occurred in the Ti–Si–C system during sintering by the following three steps:

$$Ti + C \rightarrow TiC \qquad (2)$$

$$Ti + Si \rightarrow Ti - Si(l) \qquad (3)$$

$$TiC + Ti - Si(l) \rightarrow Ti_3SiC_2 \qquad (4)$$

At first, TiC formed because reaction (2) has the highest thermodynamically reactivity and Ti has strong chemical affinity to C in low temperature solid-state reaction. Then the eutectic liquid appeared between the Ti and Si particles at the temperature near the eutectic point (1330 °C), followed by the reaction (4), during which Ti_3SiC_2 was formed at the interfaces between the eutectic liquid phases and the TiC particles. El-Raghy and Barsoum [15] proposed a mechanism operative during the last stage of sintering process as follows:

$$Ti_3SiC_2 + C \rightarrow 3TiC + Si(g) \qquad (5)$$

As demonstrated previously, TiC existed in all cases, independent of the elemental powder molar ratio and sintering conditions. This is quite consistent with the results of other reports where Ti_3SiC_2 was also synthesized from Ti–Si–C systems [11,12]. TiC may form through reactions (2) or (5). In case of low temperature and short time for sintering process, i.e., sintering at 1380 °C for 20 min in the present study, mechanism (2) led to the formation of TiC, whereas reaction (4) can not progress thoroughly, and thus TiC remained as impurities. Furthermore, loss of the eutectic liquid through partial vaporization of silicon, which it is not possible to quantify reliably, may prevent progress of reaction (4) to some extent and also increased the remaining content of TiC.

As the existence of TiC and unreacted free carbon in the sample TSC2 sintered at 1380 °C for 20 min was a persuasive evidence to the incompleteness of reactions (2–4), it is easy to understand the presence of Ti_5Si_3 as the main transformed phase from the unreacted eutectic liquid. Unlike the sample TSC2, the sample TSC3 sintered at 1380 °C for 20 min contained a little amount of $TiSi_2$ compound, which might be a phase separating out from the eutectic Si-abundant liquid phase. However, samples sintered at 1450 °C for 60 min still contained a little amount of Ti_5Si_3 and/or $TiSi_2$ since reaction (4) is a mass-diffusion and time-consuming process although free carbon disappeared except in TSC1, indicating the completeness of reaction (2). Ti_5Si_3 and $TiSi_2$ almost disappeared in samples TSC2 and TSC3 with extended sintering time, and therefore, only Ti_3SiC_2 and TiC coexisted in the products.

As evident from XRD patterns and results listed in Table 1, when the sintering time was extended from 120 to 240 min for sample TSC2 with 50% excess of Si, the volume fraction of Ti_3SiC_2 significantly increased from 82 to 91%. However, this value decreased to 87% when the sintering time was further extended to 300 min. The same trend was true for samples TSC1 and TSC3. The best sintering time was 120 min for TSC1 with the highest purity of 81 vol.% Ti_3SiC_2. In this case, it is reasonably concluded that reaction (5) might be attributed to the rising content of TiC. In another word, the generated Ti_3SiC_2 reacted with C deviated from graphite heater and graphite heat-insulating layer to form TiC and gaseous Si with excessively long sintering time. This indicated that Ti_3SiC_2 exhibited poor resistance to carbonization. For sample TSC3 with 75% excess of Si, the optimized sintering time was 240 min with the highest value of Ti_3SiC_2 purity as 93 vol.%. It has been illuminated that the loss of Si was the main obstacle against increasing the volume fraction of Ti_3SiC_2. Thus, with a small excess of silicon in raw material, an increase of Ti_3SiC_2 and decrease of TiC content in the product was observed as shown by the XRD patterns and results in Table 1. This suggested that the eutectic liquid phase in the Ti–Si system presumably enhanced the formation of Ti_3SiC_2. Additionally, sample TSC3 can counteract more loss of Si, and therefore, it can bear longer sintering time for the thorough progress of the reaction (4), which in turn contributed to the formation of Ti_3SiC_2. However, a little amount of $TiSi_2$ appeared again with sintering time extended to 300 min, probably due to the tendency of Ti_3SiC_2 to decompose into $TiSi_2$ at high temperature for longer holding time. This is consistent with the results of Gao et al. [16] where the content of $TiSi_2$ in the sintered samples increased with increasing temperature.

4. Conclusion

The way of synthesizing Ti_3SiC_2 from elemental powders of Ti, Si and C by pressureless sintering in vacuum was studied for its high productivity. The phase compositions of the sintered products were determined by XRD and purities of some samples were evaluated. It was found that Ti_3SiC_2 was obtained in all samples but impurities also coexisted under all circumstances. Besides TiC, the common impurity, Ti_5Si_3 and/or $TiSi_2$ would also occur, especially in those samples sintered at low temperature and/or for short time. It was demonstrated that the molar ratio among Ti–Si–C and the sintering conditions exerted significant effects on the purity of Ti_3SiC_2 in the products. The excessive Si added to the raw powders was considered as one of the effective ways to compensate for its loss through gaseous vaporization at the temperatures higher than the Ti–Si eutectic point (about 1330 °C). Thus, the green compact prepared from the powder mixture with 75 wt.% excessive Si could bear longer sintering time, i.e., at 1450 °C for 240 min, to form Ti_3SiC_2 with a volume fraction as high as 93%.

Acknowledgements

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