Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 2027–2033

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Facile synthesis of Ti_3SiC_2 powder by high energy ball-milling and vacuum pressureless heat-treating process from Ti–TiC–SiC–Al powder mixtures

Meichao Peng [a], Xiaoliang Shi [a,b,*], Zhiwei Zhu [b], Mang Wang [b], Qiaoxin Zhang [a,b]

[a] *School of Materials Science and Engineering, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, China*
[b] *School of Mechanical and Electronic Engineering, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, China*

Received 19 April 2011; received in revised form 9 October 2011; accepted 12 October 2011
Available online 18 October 2011

Abstract

In this article, Ti/TiC/SiC/Al powder mixtures with molar ratios of 4:1:2:0.2 were high energy ball-milled, compacted, and heated in vacuum with various schedules, in order to reveal the effects of temperature, soaking time, thickness of the compacts, and carbon content on the purity of the sintered compacts. X-ray diffraction and scanning electron microscopy were employed to investigate the phase purity, particle size and morphology of the synthesized samples. It was found that the Ti_3SiC_2 content nearly reached 100 wt.% on the surface layer of the sintered compacts prepared in the temperature range from 1350 °C to 1400 °C for 1 h. Powder containing 91 wt.% Ti_3SiC_2 was successfully synthesized by heating 6 mm green compacts of 4Ti/1TiC/2SiC/0.2Al at 1380 °C for 1 h in vacuum. The excessive carbon content failed to improve the purity of Ti_3SiC_2 powder. TiC phase was the main impurity in the formation process of Ti_3SiC_2.

Keywords: A. Powders: solid state reaction; B. Grain size; B. Impurities; B. X-ray methods

1. Introduction

Ti_3SiC_2 is the most extensively studied MAX ternary compound (viz., $M_{n+1}AX_n$ where, M: early transition metal, A: group A element, X: C and/or N, $n = 1, 2, 3$) [1]. The crystal structure of Ti_3SiC_2 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. The layered structure of Ti_3SiC_2 that Ti–C bonds is exceptionally strong together with relatively weak Ti–Si bonds is the trace of unusual combination of properties [1,2]. Ti_3SiC_2 is a material with a unique combination of metallic and ceramic properties. With metal-like properties, it exhibits high electrical and thermal conductivity, and it is machinable. Moreover, with ceramic-like properties, it is extremely resistant to oxidation and thermal shock. Most importantly, it maintains the strength with elevated temperature at which the best available superalloy is unstable [3]. Ti_3SiC_2 possesses low density (4.52 g/cm^3), high melting point (≈3000 °C) and excellent thermostability (at least 1700 °C in insert atmosphere). At room temperature it has electrical and thermal conductivities of $4.5 \times 10^6\ \Omega^{-1}\ m^{-1}$ and $37\ W\ m^{-1}\ K^{-1}$, respectively. Its coefficient of thermal expansion is $9.2 \times 10^{-6}\ {}^\circ C^{-1}$. Ti_3SiC_2 has a hardness of 4 GPa, a Young's modulus of 325 GPa and a room temperature fracture toughness of 7 MPa m^{-2}. And it is remarkable damage-tolerant [1,4–10]. Ti_3SiC_2 exhibits a brittle-to-plastic transition around 1200 °C, and it is plastic with 'yield' point of 100 MPa and 500 MPa in flexure and compression at 1300 °C, respectively. When the samples with large oriented grains (2–4 mm) are tested under compression at room temperature, macro-plasticity is observed by formation of shear and kink bands. It shows parabolic oxidation behavior in air in the 900–1400 °C temperature range [4,5].

In the 1960s, Hans Nowotny's group in Vienna published a review article that they had synthesized a large number of carbides and nitrides. In 1967, they discovered Ti_3SiC_2 and Ti_3GeC_2 [1]. In the mid-1990s, Barsoum and El-Raghy made a breakthrough that they synthesized relatively phase-pure samples of Ti_3SiC_2. In recent years, Ti_3SiC_2 has been successfully developed by various techniques, such as chemical vapor deposition (CVD) [11], reactive hot-pressing

---

[*] Corresponding author at: School of Mechanical and Electronic Engineering, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, China. Tel.: +86 27 87651793; fax: +86 27 87651793.
E-mail address: sxl071932@126.com (X. Shi).

0272-8842/$36.00 © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2011.10.038

(HP) [12–14], hot-isostatic pressing (HIP) [15], pulse discharge sintering (PDS) [16–19], spark plasma sintering (SPS) [20–22], self-propagating high-temperature synthesis (SHS) [23], and mechanical alloying (MA) [24,25]. The rapid sintering techniques, such as SPS and PDS, have been employed for the synthesis of bulk Ti_3SiC_2 material. Liang et al. [21] fabricated the sintered compact of Ti_3SiC_2 with 96.5 wt.% by MA and SPS from a starting mixture composed of $n(Ti):n(Si):n(Al):n(C) = 3:1:0.2:2$, the experimental results showed that the additional proper amount of Al significantly increased the purity of Ti_3SiC_2 as well as reduced the sintering temperature of Ti_3SiC_2. Zhang et al. [9] firstly synthesized Ti_3SiC_2 through a PDS technique from mixtures of Ti, SiC, and C at 1200–1400 °C for 15–60 min under a pressure of 50 MPa. The results showed that when the molar ratio Ti/SiC/C was adjusted to 3/1.1/2 or 5/2/1, the purity of Ti_3SiC_2 was improved to about 91 wt.%, and TiC and $TiSi_2$ were the main impurities. The Ti_3SiC_2 bulk material could be rapidly fabricated by the SPS and PDS technique at a relative low temperature, however, TiC and $TiSi_x$ impurities always existed. Meanwhile, most of the methods could not synthesize Ti_3SiC_2 bulk material with high-yield, low cost and energy-consuming. Practically, the synthesis of Ti_3SiC_2 powder provides an available route for the development of bulk single-phase Ti_3SiC_2 as well as Ti_3SiC_2-based composite materials. Moreover, the application of some potential high temperature candidate materials, such as NiAl and $MoSi_2$, is restrained by their poor mechanical properties [8]. The synthesis of Ti_3SiC_2 powder enables the development of Ti_3SiC_2 dispersion-strengthened materials. In recent years, a simple process that the elemental powders are carried through heat treatment in vacuum has been employed to synthesize Ti_3SiC_2 powder. Sun et al. [8] successfully synthesized single phase Ti_3SiC_2 with little TiC phase by heat-treating the powder mixtures consisting of Ti, Si, and TiC. When heat-treated at temperature 1250 °C or higher for 2 h, high-purity Ti_3SiC_2 powder with more than 99 vol.% content is obtained. Li et al. [26] fabricated 81 vol.% Ti_3SiC_2 from Ti, Si, and C powder with the molar ratio of 3:1:2 through pressureless sintering at 1450 °C for 2 h, and found that TiC was the most impurity. However, if the compacts were sintered at excessively high or low temperatures, $TiSi_2$ and Ti_5Si_3 phase would appear, respectively. Sun et al. [27] reported that 3Ti/SiC/C powder mixture was compacted and heated in vacuum at 1773 K for 2 h, and the relative density of the Ti_3SiC_2 could reach 97%. As mentioned above, regardless of bulk or powder synthesis of Ti_3SiC_2, most of elemental powder mixtures are Ti/Si/C, Ti/Si/TiC or Ti/SiC/C. Using Ti/Si/C and Ti/SiC/C elemental powders, the high weight ratio of Ti increases production cost of Ti_3SiC_2 because titanium is a aeronautical metal, and expensive. During the heating process of Ti/Si/C and Ti/Si/TiC powder mixtures, evaporative silicon could adhere to heater block and damage heating equipment. Zhang et al. [28] provided a new route for fabricating 92 vol.% bulk Ti_3SiC_2 with TiC impurity phase by the PDS from 4Ti/TiC/2SiC powder mixtures at 1350 °C for 15–120 min. Compared to other chemical formulations, Ti/TiC/SiC powder mixtures possess lower Ti weight ratio and have not Si element. Few researchers synthesized Ti_3SiC_2 from Ti/TiC/SiC powder mixtures by solid state reaction technique in vacuum. In this study, in order to readily synthesize high-purity Ti_3SiC_2 powder, 4Ti/TiC/2SiC/0.2Al powders were mixed by high energy ball-milling and heated in vacuum. Effects of the temperature, soaking time, thickness of the compacts, and carbon content on the purity of Ti_3SiC_2 were investigated.

2. Experimental

Commercial powders of Ti (38 μm in average size, 99.9% in purity), TiC (38 μm in average size, 99.9% in purity), SiC (18 μm in average size, 99% in purity), and Al (99.9% in purity) with a molar ratio of Ti:TiC:SiC:Al = 4:1:2:0.2 were used as starting powders and mixed for 10 h by high energy ball-milling with vacuum degree of 10 Pa. Balls and vials were made of hard metal, the charge ratio (ball to powder mass ratio) employed was 10:1, the milling time and speed are 10 h and 200 rpm, respectively. Meanwhile, in order to investigate the effects of carbon content on the purity of the sintered compacts, the excess graphite powder (75 μm in average size, 99.9% in purity) was ball-milled with Ti/TiC/SiC/Al powder mixtures. In order to study if the C atmosphere in the carbon tube furnace permeated in the samples and affected the purity of the synthesis of Ti_3SiC_2, the appropriate graphite powder was added to the green mixtures. The graphite powder contents of the powder mixtures were 0 wt.%, 2 wt.%, 3 wt.%, and 4 wt.%, respectively. The powder mixtures with proper paraffin were compacted to billets with a diameter of 25 mm and thickness of 4–7 mm using automatic tablet press with a metallic mold under an axial pressure of 15 MPa. The green compacts were put in a graphite crucible with diameter of 70 mm and thickness of 22 mm and heated in a vacuum furnace (vacuum degree 10^{-2} Pa). Heating temperatures were selected to be from 1300 °C to 1500 °C with a heating rate of 15 °C/min, and the soaking time ranged from 10 to 120 min. The sintered compacts were milled to powders by high energy ball-milling in alcohol for 2 h, and then the ball-milled powders were dried at 80 °C under vacuum condition. The sintered compacts and corresponding powders were examined by XRD with Cu Kα radiation at 30 kV and 40 mA at a scanning speed of $0.01^\circ\ s^{-1}$ for the identification of the phase constitution, and observed by scanning electron microscope (SEM) for the microstructure. Energy dispersive spectrum analysis (EDS) for local composition was also carried out.

3. Results and discussion

Fig. 1 is the XRD patterns of the original 4Ti/2SiC/TiC/0.2Al mixed powders and the surfaces of the vacuum heat-treated green compacts at 1300–1500 °C temperature range for 1 h. Ti, TiC and SiC peaks can be clearly seen in the diffraction profile of the original powder mixtures. For the 1300 °C heated samples, unreacted TiC and SiC, newly formed $TiSi_2$ and Ti_3SiC_2 were detected. With the increasing of the synthesized temperature, TiC at $2\theta = 35.89^\circ$ (1 1 1), 41.8° (2 0 0), SiC at $2\theta = 41.38^\circ$ (1 0 4) and $TiSi_2$ at $2\theta = 43.2^\circ$ (0 2 2) peaks

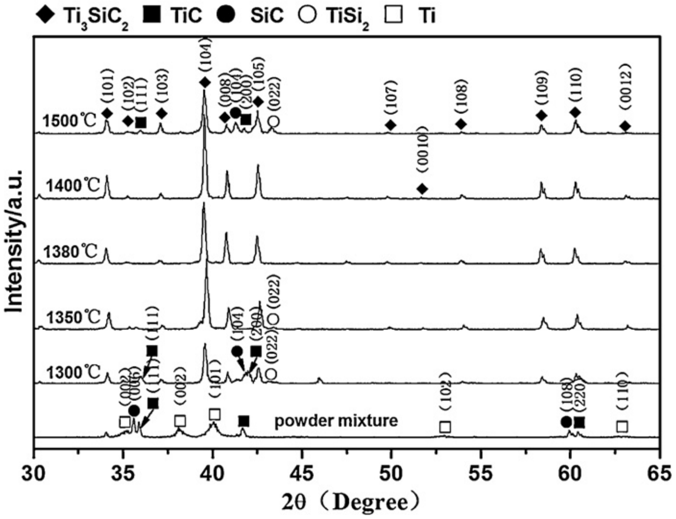

Fig. 1. XRD patterns of the original mixed 4Ti/2SiC/TiC/0.2Al powder and the surfaces of the vacuum heat-treated green compacts at different temperature for 1 h.

abruptly reduced. Except main crystalline phase, Ti_3SiC_2, only quite weak TiC peak (2 0 0) was detected in the sample reacted at 1380–1400 °C. The results indicated the single-phase Ti_3SiC_2 seemed to be easily synthesized by using high energy ball-milling and vacuum pressureless heat-treating process from Ti–SiC–TiC–Al powder mixtures. However, when the sintering temperature was as high as 1500 °C, TiC at $2\theta = 35.89°$, 41.8°, SiC at $2\theta = 41.38°$ and $TiSi_2$ at $2\theta = 43.2°$ peaks appeared again.

Fig. 2 shows the XRD patterns of the high energy ball-milled powders of the vacuum heat-treated green compacts prepared at 1300–1400 °C for 1 h. Except those peaks of Ti_3SiC_2, only peaks of TiC at $2\theta = 41.8°$ (2 0 0), 35.89° (1 1 1) can be detected in the sintered samples prepared at the temperature ranges from 1300 °C to 1400 °C for 1 h. With the increasing of the sintering temperature, the TiC peaks decreased. When the sintering temperature was 1380 °C, it reached to the minimum value. While the sintering temperature was 1400 °C, the TiC peaks started to go up. The results showed that the synthesized Ti_3SiC_2 could partly decompose when the temperature was over 1380 °C.

Assuming a Ti_3SiC_2–TiC two phase composite, the calibration for weight percentage of the two constitutive phases were performed based on the X-ray diffraction data and the weight percentage of Ti_3SiC_2 phase can be calculated according to the calibration [7]:

$$W_{\mathrm{TSC}} = \frac{1.8}{1.8 + I_{\mathrm{TC}}/I_{\mathrm{TSC}}} \tag{1}$$

where I_{TC} and I_{TSC} are the integrated intensity of representative diffraction peaks of TiC (2 0 0) and Ti_3SiC_2 (1 0 4), respectively. The weight percentage of Ti_3SiC_2 calculated from the X-ray diffraction data are summarized in Fig. 3. As shown in Fig. 3(a), in the temperature range from 1350 °C to 1380 °C, the Ti_3SiC_2 content of surface of the sintered compact was mostly 100 wt.%. As shown in Fig. 3(b), with the increasing of the sintering temperature, the Ti_3SiC_2 content of the powders increased as a whole. When the sintering temperature was 1380 °C, the Ti_3SiC_2 content of the powders could reach 91 wt.%. But the Ti_3SiC_2 content of powders was only 73.47 wt.%, while the sintering temperature was 1400 °C. It showed that the Ti_3SiC_2 content of the whole vacuum sintered compacts could not reach 100 wt.%. Sun et al. [27] found that the Ti_3SiC_2 content of the surface layer of the vacuum sintered specimens reached 100 wt.%. However, the internal components of the sintered compacts were not concretely analyzed. In our work, the same phenomenon also happened, the surface Ti_3SiC_2 content of the sintered compacts almost reached 100 wt.%. However, the highest Ti_3SiC_2 content after triturating the sintered compacts prepared at 1380 °C for 1 h was only 91 wt.%. Therefore, the green compacts should be further investigated at 1380 °C with different soaking time, compact thickness, and carbon content, in order to find if the whole Ti_3SiC_2 content of the sintered compacts was affected by these

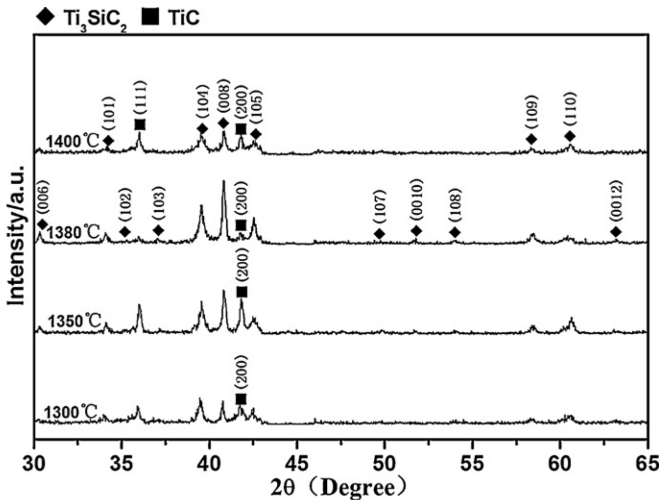

Fig. 2. XRD patterns of the high energy ball-milled powders of the vacuum heat-treated green compacts prepared at 1300–1400 °C for 1 h.

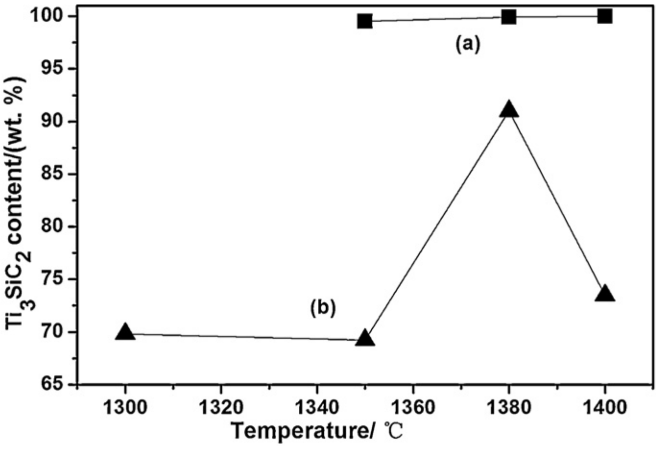

Fig. 3. Ti_3SiC_2 content of: (a) the surfaces of the vacuum heat-treated green compacts prepared at 1300–1400 °C for 1 h; (b) the high energy ball-milled powders of the vacuum heat-treated green compacts prepared at 1300–1400 °C for 1 h.

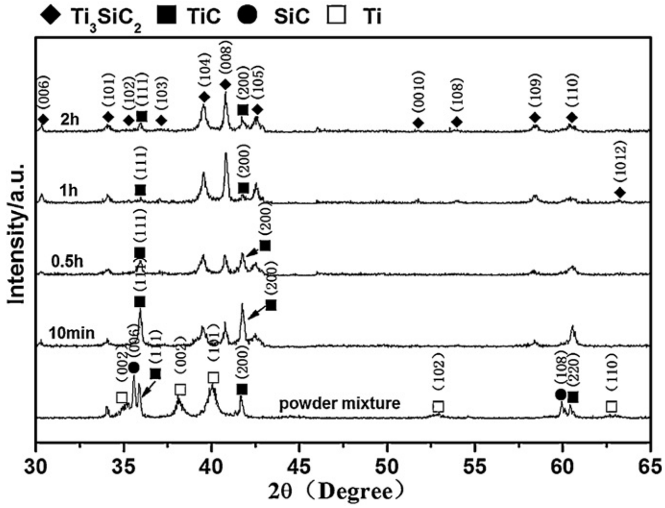

Fig. 4. XRD patterns of the original mixed 4Ti/2SiC/TiC/0.2Al powders and the high energy ball-milled powders of the 1380 °C vacuum heat-treated green compacts with different soaking time.

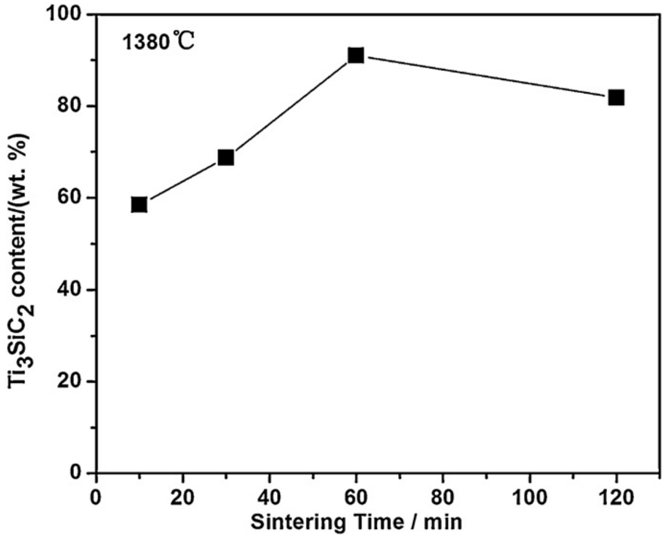

Fig. 5. Ti_3SiC_2 content of the powders after triturating the vacuum heat-treated 4Ti/2SiC/TiC/0.2Al compacts prepared at 1380 °C with different soaking time by high energy ball-milling.

factors. Meanwhile, we tried to investigate the reason that the surface content of the sintered compacts prepared at 1340–1400 °C for 1 h nearly reached 100 wt.%, but the whole content was lower than the surface content of the sintered compacts.

Fig. 4 shows the XRD patterns of the original 4Ti/2SiC/TiC/0.2Al powder mixtures and high energy ball-milled powders of the 1380 °C vacuum heat-treated green compacts with different soaking time. When the sintering temperature was 1380 °C, with the increasing of the soaking time, the peak intensity of TiC at $2\theta = 41.8°$ (2 0 0) gradually decreased. It reached the minimum value while the soaking time was 1 h. The experimental results showed that the 1380 °C–1 h sintered samples contained the most Ti_3SiC_2 peaks and the least impurity TiC peaks. It showed that the present 4Ti/TiC/2SiC/0.2Al powders could be regarded as a modified mixture for the synthesis of Ti_3SiC_2 using high energy ball-milling and vacuum heat-treated techniques.

The weight percentage of Ti_3SiC_2 calculated from the X-ray diffraction data are summarized in Fig. 5. Generally, with the increasing of the sintering time, the content of Ti_3SiC_2 remarkably increased. When the soaking time was 1 h, the content of Ti_3SiC_2 reached 91 wt.%. However, when the soaking time was higher than 1 h, the content of Ti_3SiC_2 began to decrease. According to Fig. 7, it showed that longer sintering time could lead to more C penetration and contribute to the decreasing of Ti_3SiC_2 purity.

Fig. 6 shows the XRD patterns of the powders after triturating the vacuum heat-treated green compacts with different compact thickness prepared at 1380 °C for 1 h by high energy ball-milling technique. It can be seen that the TiC peak decreased with the

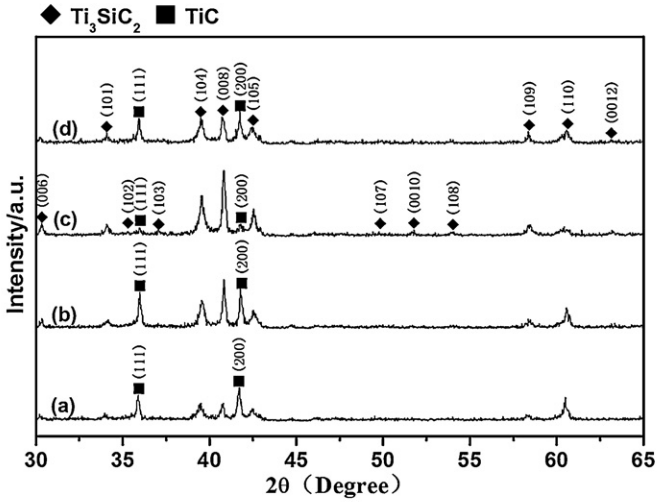

Fig. 6. XRD patterns of the powders after triturating the vacuum heat-treated green compacts prepared at 1380 °C for 1 h with different compact thickness of (a) 4 mm, (b) 5 mm, (c) 6 mm, and (d) 7 mm by high energy ball-milling.

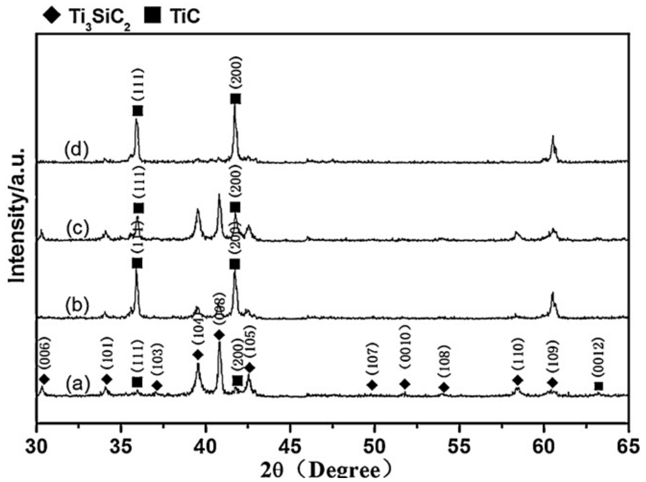

Fig. 7. XRD patterns of the powders after triturating the vacuum heat-treated green compacts prepared at 1380 °C for 1 h with various graphite contents of (a) 0 wt.%, (b) 2 wt.%, (c) 3 wt.%, and (d) 4 wt.% by high energy ball-milling.

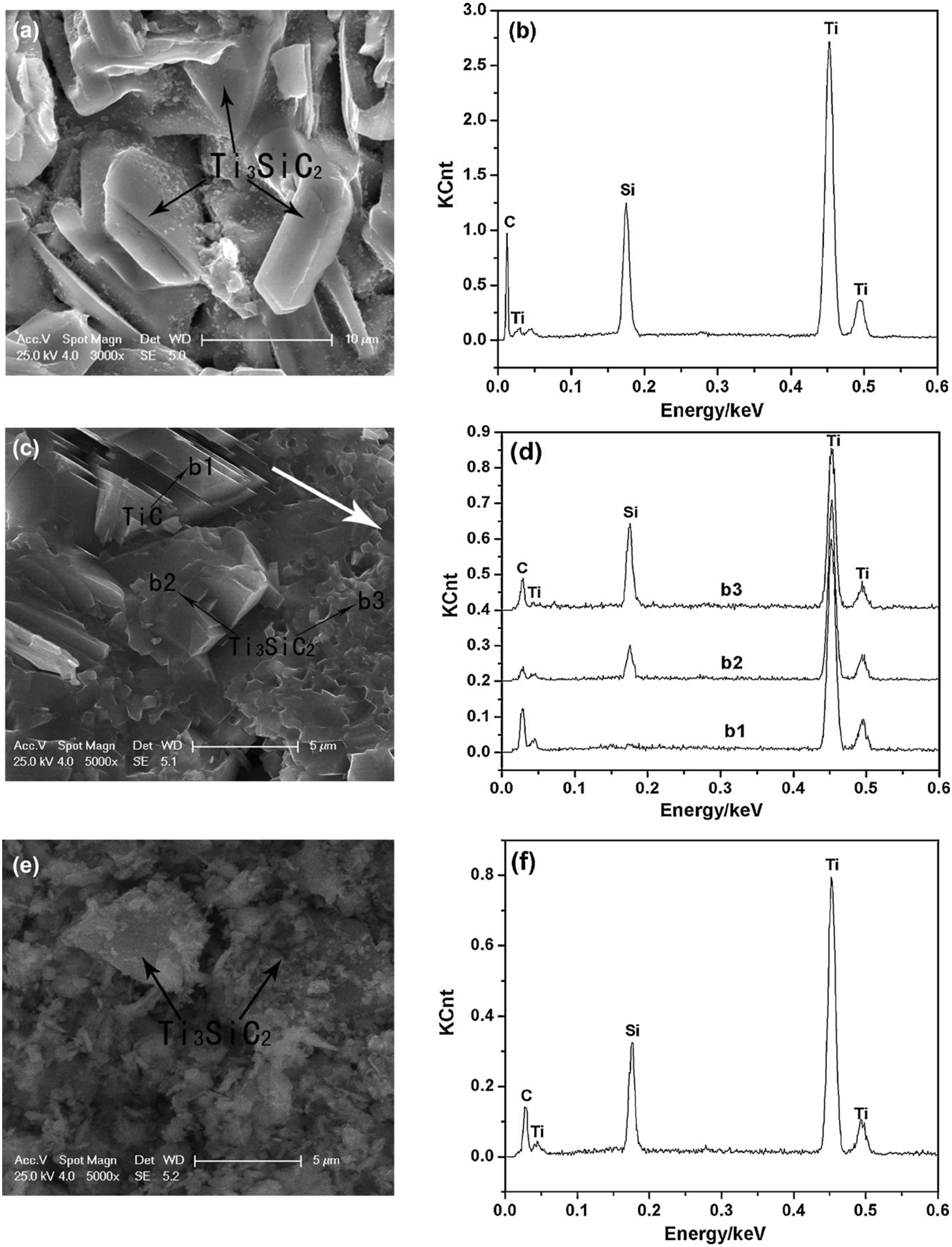

Fig. 8. SEM micrographs and EDS microanalysis of the surface (a, b) and inside (c, d) of the sintered compacts prepared at 1400 °C for 1 h, and powder (e, f) obtained after triturating the vacuum heat-treated green compact of 6 mm thickness prepared at 1380 °C for 1 h by high energy ball-milling.

increasing of the green compact thickness. When the green compact thickness was 6 mm, the TiC peak intensity reached the lowest value. However, the green compact thickness was larger than 6 mm, the TiC peak gradually increased. The experimental results could be explained by the next reasons. On the one hand, when the thickness of green compact was lower than 6 mm, the temperature field could easily penetrate in the whole green compact. However, the flow velocity of $TiSi_2$ (liquid) toward the green compact surface by capillary action might be too fast to completely react, thus the excrescent $TiSi_2$ (liquid) might happen to decomposite and generate TiC impurity. On the other hand, when the thickness of green compact was higher than 6 mm, the $TiSi_2$ (liquid) that flowed to the green compact surface by capillary action could be changed into Ti_3SiC_2 well. But the temperature field could not completely penetrate in the whole green compact, and it led to the temperature differences between the external and internal green compact existing in the vacuum heat-treating process and the increasing of TiC impurity. Therefore, the experimental result that 6 mm green compact thickness was the optimal could be reasonably explained.

Fig. 7 shows the XRD patterns of the powders after triturating the vacuum heat-treated green compacts prepared at 1380 °C for 1 h with various graphite contents. As shown in Fig. 7, the excess C cannot improve the Ti_3SiC_2 content of the sintered products, on the contrary, the excess C contributed to the emerge of more TiC. Especially, when the excess C were 2 wt.% and 4 wt.%, as shown in Fig. 7(b) and (d), the main phase was TiC, not Ti_3SiC_2. It showed that the Ti_3SiC_2 content of the sintered compacts was deteriorated by the excess C.

Fig. 8 shows the SEM micrographs and EDS microanalysis of the surface, inside of the 1400 °C–1 h sintered compacts, and high energy ball-milled powders from 1380 °C–1 h vacuum heat-treated green compacts with 6 mm thickness. As shown in Fig. 8(a) and (b), the surface Ti_3SiC_2 grain of the 1400 °C–1 h sintered sample is about 10 μm and plate-like, and possesses hexagonal structure. As shown in Fig. 8(c) and (d), the inside TiC grain of the 1400 °C–1 h sintered sample is relatively fine (about 2 μm) and possesses cuboid shape which could be formed by the growth of cubic TiC crystal particle along the white arrow. However, it is difficult to identify the grain size and shape of the Ti_3SiC_2 powders, as shown in Fig. 8(e). As shown in Fig. 8(f), according to the EDS of the high energy ball-milled powders of the 1380 °C–1 h vacuum heat-treated green compacts with 6 mm thickness, the powder is mainly comprised of Ti_3SiC_2 phase, which is consistent with the XRD analysis from Fig. 3. The b1, b2 and b3 for the EDS results are shown in Fig. 8(d), and the positive direction of the white arrow is near to the surface. Ti and C elements were detected by the EDS in the b1 area as shown in Fig. 8(d), revealing that the main phase of b1 area was TiC. Ti, Si and C elements were detected by the EDS in the b2 and b3 areas as shown in Fig. 8(d), revealing that the main phase of the b2 and b3 areas was Ti_3SiC_2. It is interesting that the surface of the sintered compact mostly is 100 wt.% Ti_3SiC_2 phase, but along the direction of the white arrow as shown in Fig. 8(c), the parts near to the surface of the sintered compact were continuous Ti_3SiC_2 phases, and big TiC particles started to appear in the central parts of the sintered compact.

It was reported by Zhang et al. [28] that Ti–Si system has two eutectic reactions for the Si–$TiSi_2$ and Ti–Ti_5Si_3 compositions both at the temperature of 1333 °C. When the sintering temperature reached this eutectic point, the $TiSi_2$, Ti_5Si_3 eutectic liquid appeared between Ti and Si particles. It supposed that the formation of Ti_3SiC_2 happened between the Ti–Si liquid phase and TiC particles, i.e. $2TiC + Ti–Si$ (liquid) → Ti_3SiC_2. As shown in Fig. 1, during the sintering process of the green compacts, TiC and $TiSi_2$ peaks repeatedly appeared on the surfaces of the sintered compacts. Therefore, the formation of Ti_3SiC_2 is suggested as follows:

$$Ti + SiC \rightarrow TiC + Si \tag{2}$$

$$Ti + 2Si \rightarrow TiSi_2(\text{liquid}) \tag{3}$$

$$Ti + TiSi_2 + 4TiC \rightarrow 2Ti_3SiC_2 \tag{4}$$

where Ti, SiC and TiC serve as reactants, Si and $TiSi_2$ are regarded as intermediate phase, and Ti_3SiC_2 is the final product. Moreover, It is necessary to explain that Zou et al. [29] also proposed similar reaction mechanism about the synthesis of Ti_3SiC_2 using PDS technique, and they still proposed a further reaction mechanism ($5Ti + 3Si \rightarrow Ti_5Si_3$, $Ti_5Si_3 + 10TiC + Si \rightarrow 5Ti_3SiC_2$) when the temperature was over 1200 °C. It is obvious that the disagreement between the article and article 29 was related to the reaction mechanism of the Ti_3SiC_2 synthesis. The reason of leading to this difference could be the different sintered techniques. In particular, the pressure of PDS in the sintering process readily resulted in different distribution field of liquid $TiSi_2$, and led to disagreement reaction mechanism.

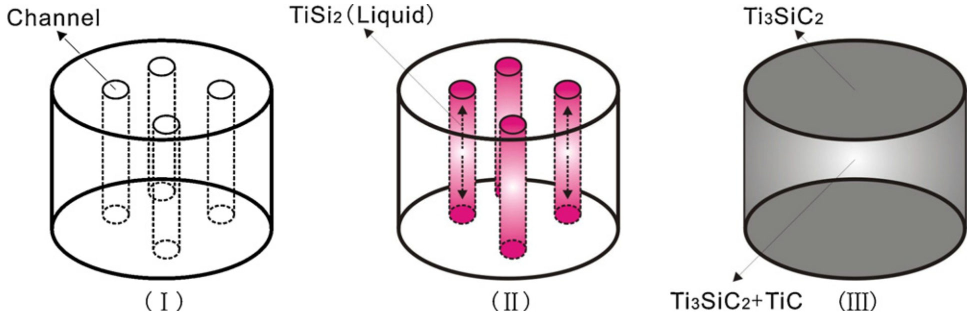

Fig. 9. Diagram of the difference of Ti_3SiC_2 purity between the surface and inner parts of the vacuum sintered compacts prepared at 1350–1400 °C for 1 h.

On the basis of the analytical results of Figs. 3 and 8(a) and (c), together with the above inference of the reaction process, the reason that the surface and whole Ti_3SiC_2 purity of the sintered compacts prepared at 1350–1400 °C for 1 h are nearly 100 wt.% and 91.0 wt.%, respectively, could be explained by the schematic diagram as shown in Fig. 9. It could be explained by the followed guesses: (I) at lower temperature, with the increasing of the temperature, the paraffin waxes started to volatile out from the green compact and generate through-hole until all paraffin waxed were debinded; (II) when the temperature reached 1333 °C [28], the liquid $TiSi_2$ phase appeared. It moved to the surface of the sample under the action of vacuum capillary function as well as linear shrinkage, and the content of $TiSi_2$ gradually decreased from the surface to the inside of the sintered compacts; (III) when the temperature was higher than 1350 °C, the reaction according to Eq. (4) began to work. The graded content of $TiSi_2$ caused 100 wt.% Ti_3SiC_2 content on the surfaces of the sintered samples, but the whole sintered samples possessed some TiC impurity.

4. Conclusion

(1) The surface Ti_3SiC_2 purity of the sintered compacts prepared at 1350–1400 °C for 1 h from 4Ti/1TiC/2SiC/0.2Al powder mixtures nearly reached 100 wt.%.
(2) When the sintering temperature, soaking time and thickness of the green compacts were 1380 °C, 1 h, and 6 mm, respectively, the highest Ti_3SiC_2 purity of the high energy ball-milled powders of the vacuum heat-treated green compacts reached 91 wt.%.
(3) The Ti_3SiC_2 content of the sintered compacts was deteriorated by the excess carbon.
(4) The differences of the Ti_3SiC_2 content between the surface and inside of the sintered compacts could be explained by the inference that the movement of the liquid $TiSi_2$ phase to the surfaces caused the reducing of the $TiSi_2$ phase of the sintered compact inside and the inside insufficient reaction, thus produced TiC surplus.

Acknowledgements

This work was supported by the Academic Leader Program of Wuhan City (201150530146); the Nature Science Foundation of Hubei Province (20101j0018); the Science Foundation of Wuhan University of Science and Technology (Grant No. 200910321092); and the Fundamental Research Funds for the Central Universities (2010-II-020).

References

[1] M.W. Barsoum, The $M_{N+1}AX_N$ phases: a new class of solids; thermodynamically stable nanolaminates, Prog. Solid State Chem. 28 (2000) 201–281.
[2] P. Eklund, M. Beckers, U. Jansson, H. Högberg, L. Hultman, The $M_{n+1}AX_n$ phases: materials science and thin-film processing, Thin Solid Films 518 (2010) 1–28.
[3] M.W. Barsoum, D. Brodkin, T. El-Raghy, Layered machinable ceramics for high temperature applications, Scripta Mater. 36 (1997) 535–541.
[4] T. El-Raghy, M.W. Barsoum, M. Sika, Reaction of Al with Ti_3SiC_2 in the 800–1000 °C temperature range, Mater. Sci. Eng. A 298 (2001) 174–178.
[5] T. El-Raghy, P. Blau, M.W. Barsoum, Effect of grain size on friction and wear behavior of Ti_3SiC_2, Wear 238 (2000) 125–130.
[6] S. Yang, Z.M. Sun, Q.Y.H. Hashimoto, Effect of Al addition on the synthesis of Ti_3SiC_2 bulk material by pulse discharge sintering process, J. Eur. Ceram. Soc. 27 (2007) 4807–4812.
[7] Z.M. Sun, S. Yang, H. Hashimoto, Effect of Al on the synthesis of Ti_3SiC_2 by reactively sintering Ti–SiC–C powder mixtures, J. Alloys Compd. 439 (2007) 321–325.
[8] Z.M. Sun, S. Yang, H. Hashimoto, Ti_3SiC_2 powder synthesis, Ceram. Int. 30 (2004) 1873–1877.
[9] Z.F. Zhang, Z.M. Sun, H. Hashimoto, Low temperature synthesis of Ti_3SiC_2 from Ti/SiC/C powders, Mater. Sci. Technol. 20 (2004) 1252–1256.
[10] S. Yang, Z.M. Sun, H. Hashimoto, T. Abe, Synthesis of single-phase Ti_3SiC_2 powder, J. Eur. Ceram. Soc. 23 (2003) 3147–3152.
[11] T.C. Lin, M.H. Hon, Synthesis and microstructure of the Ti_3SiC_2 in SiC matrix grown by chemical vapor deposition, Ceram. Int. 34 (2008) 631–638.
[12] Y.M. Luo, W. Pan, S. Li, J. Chen, Synthesis and mechanical properties of in-situ hot-pressed Ti_3SiC_2 polycrystals, Ceram. Int. 28 (2002) 227–230.
[13] H.B. Zhang, Y.C. Zhou, Y.W. Bao, M.S. Li, J.Y. Wang, Intermediate phases in synthesis of Ti_3SiC_2 and $Ti_3Si(Al)C_2$ solid solutions from elemental powders, J. Eur. Ceram. Soc. 26 (2006) 2373–2380.
[14] D.T. Wan, Y.C. Zhou, Y.W. Bao, C.K. Yan, In situ reaction synthesis and characterization of $Ti_3Si(Al)C_2$/SiC composites, Ceram. Int. 32 (2006) 883–890.
[15] A. Ganguly, T. Zhen, M.W. Barsoum, Synthesis and mechanical properties of Ti_3GeC_2 and $Ti_3(Si_xGe_{1-x})C_2$ ($x = 0.5$, 0. 75) solid solutions, J. Alloys Compd. 376 (2004) 287–295.
[16] Z.F. Zhang, Z.M. Sun, H. Hashimoto, T. Abe, A new synthesis reaction of Ti_3SiC_2 from Ti/$TiSi_2$/TiC powder mixtures through pulse discharge sintering (PDS) technique, Mater. Res. Innovat. 5 (2002) 185–189.
[17] Z.F. Zhang, Z.M. Sun, H. Hashimoto, T. Abe, Application of pulse discharge sintering (PDS) technique to rapid synthesis of Ti_3SiC_2 from Ti/Si/C powders, J. Eur. Ceram. Soc. 22 (2002) 2957–2961.
[18] Z.M. Sun, Z.F. Zhang, H. Hashimoto, T. Abe, Ternary compound Ti_3SiC_2. Part I. Pulse discharge sintering synthesis, Mater. Trans. 43 (2002) 428–431.
[19] S. Yang, Z.M. Sun, H. Hashimoto, Reaction in Ti_3SiC_2 powder synthesis from a Ti–Si–TiC powder mixture, J. Alloys Compd. 368 (2004) 312–317.
[20] J.Q. Zhu, B.C. Mei, L.P. He, Y.L. Chen, Synthesis of Ti_3SiC_2 by spark plasma sintering (SPS) of elemental powders, Trans. Nonferr. Met. Soc. China 13 (2003) 46–49.
[21] B.Y. Liang, S.Z. Jin, M.Z. Wang, Low-temperature fabrication of high purity Ti_3SiC_2, J. Alloys Compd. 460 (2008) 440–443.
[22] N.F. Gao, J.T. Li, D. Zhang, Y. Miyamoto, Rapid synthesis of dense Ti_3SiC_2 by spark plasma sintering, J. Eur. Ceram. Soc. 22 (2002) 2365–2370.
[23] P.R. Daniel, H.K. Erich, P. David, SHS of Ti_3SiC_2: ignition temperature depression by mechanical activation, J. Eur. Ceram. Soc. 26 (2006) 1051–1058.
[24] F. Meng, L. Chaffron, Y. Zhou, Synthesis of Ti_3SiC_2 by high energy ball milling and reactive sintering from Ti, Si, and C elements, J. Nucl. Mater. 386–388 (2009) 647–649.
[25] H.R. Orthner, R. Tomasi, F W.J. Botta, Reaction sintering of titanium carbide and titanium silicide prepared by high-energy milling, Mater. Sci. Eng. A 336 (2002) 202–208.
[26] H. Li, D. Chen, J. Zhou, J.H. Zhao, L.H. He, Synthesis of Ti_3SiC_2 by pressureless sintering of the elemental powders in vacuum, Mater. Lett. 58 (2004) 1741–1744.
[27] Z.M. Sun, S. Yang, H. Hashimoto, S. Tada, T. Abe, Synthesis and consolidation of ternary compound Ti_3SiC_2 from green compact of mixed powders, Mater. Trans. 45 (2004) 373–375.
[28] Z.F. Zhang, Z.M. Sun, H. Hashimoto, T. Abe, A new synthesis reaction of Ti_3SiC_2 through pulse discharge sintering Ti/SiC/TiC powder, Scripta Mater. 45 (2001) 1461–1467.
[29] Y. Zou, Z. Sun, S. Tada, et al., Synthesis of single-phase Ti_3SiC_2 with the assistance of liquid phase formation, J. Alloys Compd. 441 (1–2) (2007) 192–196.