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Impurity control in pressureless reactive synthesis of pure Ti_3SiC_2 bulk from elemental powders

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Abstract

The impurity control in pressureless reactive synthesis of pure Ti_3SiC_2 from elemental powders is reported. Ti_3SiC_2 bulk samples were prepared by sintering compacts of ball-mixed elemental powders at 1500 °C for 2 h in lidded alumina crucibles under Ar atmosphere. Undesirable TiC impurity was successfully eliminated from the synthesized product. Product with desired phase constituent can be fabricated by preparing samples according to phase diagram data. Keeping away from the phase fields that involve TiC is a vital way to obtain pure Ti_3SiC_2 without containing the undesirable TiC. The key for successful impurity control in the sintering process is the conservation of mass in the reactants.

Keywords: A. Powders: solid state reaction; A. Sintering; B. Impurities; D. Carbides; Phase equilibria

1. Introduction

Since it was first synthesized by Jeitschko and Nowotny in 1967 [1], the ternary compound Ti_3SiC_2 has attracted great attention because of its unique properties. As a typical representative of the novel MAX phase material ($M_{n+1}AX_n$, where M is an early transition metal, A is an A-group element, X is either carbon or nitrogen), it has merits of both metals and ceramics [2]. Detailed descriptions of this material were given by Barsoum [3,4]. It has good machinability, excellent high temperature strength and fatigue-damage tolerance, high stiffness, high thermal and chemical resistance, high thermal shock resistance, high electrical conductivity and also self-lubricating properties. Therefore, it is a promising candidate for numerous applications such as commutating brushes for motors, armor, bearing, turbine blades, etc. [5]. Other than all these remarkable properties, Ti_3SiC_2 is a bioinert material as well. The combination of this inertness with high fracture toughness, excellent corrosion resistance, easy machinability and self-lubricating property make it a new class of potential biomaterials for orthopedic applications, dental implants, and fixation devices for the bone [6]. The purity of the implant material is a crucial safety concern in human body implants. However, the synthesis of pure bulk Ti_3SiC_2 on a large scale has proven to be difficult in practice.

Different methods with various starting materials have been used for the synthesis of this advanced ceramic material. Recently, preparation of high purity and/or dense Ti_3SiC_2 bulk by using reactive hot pressing (HP) [3,7,8], hot isostatic pressing (HIP) [5], spark plasma sintering (SPS) [9–12], and pulse discharge sintering (PDS) [13–16] were reported. However, the expensive equipment used in these methods and the limited size of the prepared product greatly hinder the large production and the application of these materials. The pressureless sintering method has two major advantages over other processing techniques: high efficiency and easy availability. Furthermore, pressureless sintering offers more freedom in shaping the sample by powder compaction in a selected mold with the desired shape. The drawback is that the prepared product contains a significant amount of porosity (usually 10 vol.% or higher). However, for synthetic bone graft substitutes, porosity is usually required to develop large specific surfaces able to catch and absorb proteins and also allow for cells and tissue ingrowth into the core of the implant

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[17]. In this case, the porosity produced from the pressureless sintering is beneficial to the final product.

Due to the narrow homogeneity range of Ti_3SiC_2 and the readiness of Si loss through melting or evaporation at high temperature, the purity of synthesized Ti_3SiC_2 is very sensitive to the starting molar ratio of raw materials. Various powder mixtures with different combinations, including mixtures of elemental powders and carbides of Ti and Si, have been employed as the reactant materials. However, in most cases the as-synthesized Ti_3SiC_2 contains a usually undesirable impurity – TiC, which is hard to remove from the products [18–27]. In this paper, the authors report the preparation of Ti_3SiC_2 bulks, with controllable impurity, by the pressureless reactive sintering of Ti, Si, and graphite powders. Undesirable TiC impurity was successfully eliminated from the synthesized product.

2. Experimental procedures

Commercially available Ti (>99.9 wt.% purity, −300 mesh), Si (>99.9 wt.% purity, −300 mesh) and graphite (>99 wt.% purity, −500 mesh) powders were selected as starting materials. Nominal compositions of the prepared samples are listed in Table 1. The powder mixtures were ball-mixed under Ar for 24 h at a rotating speed of 60 r/min. Zirconia balls with diameter of 6 mm and ball to powder mass ratios of 5:1 were used. After drying at 60 °C for 24 h under vacuum, the ball-mixed powders were pressed to form disc-shaped compacts in a steel mold by using a pressure of 500 MPa. The green compacts are 20 mm in diameter and approximately 5 mm in thickness.

Differential scanning calorimetry (DSC) experiments were performed by using a NETZSCH STA449C Thermal Analysis Instrument under high purity Ar (99.999%) with a flow rate of 40 ml/min. Specimens for DSC analysis were cut from green compacts of Samples 1–5. The specimens were heated from ambient to 1500 °C at a heating rate of 5 °C per minute. The analyzed DSC specimens (Samples 1 and 3) were ground separately in an agate mortar and the obtained powders were then studied by a PANalytical X'Pert PRO X-ray diffractometer (XRD), with Cu K_α radiation, operating at 40 kV and 40 mA. The scanning rate used was 0.02°/s.

The green compacts were placed into lidded alumina crucibles and pre-heated at 400 °C for 2 h under vacuum. After that, high purity Ar (99.999%) was passed into the tube furnace and the furnace was raised to higher temperatures. When the furnace reached 750 °C, a heating rate of 5 °C/min was used to heat the samples up to 1500 °C. Sintering was carried out at 1500 °C for 2 h under Ar. Microstructure of the sintered bulk samples were studied by a LEO 1530 VP field-emission scanning electron microscope. Powder samples for XRD analysis were obtained by drilling the as-sintered bulk materials and then ground in an agate mortar.

3. Results and discussion

Nominal composition of Samples 1–5 was selected so as to avoid the formation of the undesirable TiC by-product. Locations of Samples 1–5 in the Ti–Si–C ternary phase diagram [28] are illustrated in Fig. 1. From Fig. 1, it can be seen that the stoichiometric Ti_3SiC_2 is the only ternary phase; it is surrounded by 4 three-phase fields, namely Ti_3SiC_2–$Ti_5Si_3C_x$–$TiSi_2$, Ti_3SiC_2–$TiSi_2$–SiC, Ti_3SiC_2–$Ti_5Si_3C_x$–TiC and Ti_3SiC_2–TiC–SiC. In order to avoid the formation of TiC, sample compositions should neither be selected from the Ti_3SiC_2–TiC–SiC and Ti_3SiC_2–$Ti_5Si_3C_x$–TiC three-phase fields nor from the Ti_3SiC_2–TiC two-phase field.

Due to the narrow homogeneity of Ti_3SiC_2 and the readiness of Si loss through melting or evaporation at high temperatures, the purity of reactive synthesized Ti_3SiC_2 is very sensitive to the starting molar ratio of the raw materials. As shown in the T–Si–C phase diagram at 1500 K [28] (Fig. 1), if a nominal composition of exact stoichiometry was selected (a molar ratio of Ti:Si:C = 3:1:2), the loss of Si during synthesis at high temperatures will definitely push the final reactant composition into a phase field that involves TiC and thus favor the formation of TiC as a by-product. Therefore, keeping away from the phase fields that involve TiC and minimizing the Si lost during sintering are the two vital steps in obtaining pure Ti_3SiC_2 without containing the undesirable TiC. In order to compensate the Si lost, some researchers added excess Si into the stoichiometric composition [18,19,21,24,25] but, as a result, the impurities in their final products can hardly be controlled.

As shown in Fig. 1 and Table 1, Samples 1–3 are specimens with a fixed Ti to C molar ratio of 3:2, but with an increasing Si content. These samples and also Sample 5 are located in the Ti_3SiC_2–$TiSi_2$–SiC three-phase equilibrium zone, while Sample 4 was prepared to be located in the Ti_3SiC_2–$Ti_5Si_3C_x$–$TiSi_2$ three-phase field. Unlike TiC and SiC, which are difficult to be removed from the synthesized Ti_3SiC_2, silicides of Ti can easily be removed by dissolving in HF acid; therefore, the selected Sample 4 in this study is a good candidate for high purity Ti_3SiC_2 fabrication.

Table 1
Nominal composition of the samples and characteristics of the synthesized Ti_3SiC_2.

Sample	Molar ratio Ti:Si:C	Composition (at.%)			Ti_3SiC_2 formation temperature (°C)	Impurity phases
		Ti	Si	C		
1	3:1.1:2	49.2	18.0	32.8	>1475	$TiSi_2$, SiC
2	3:1.2:2	48.4	19.4	32.2	1473	$TiSi_2$, SiC
3	3:1.5:2	46.2	23.1	30.7	1439	$TiSi_2$, SiC
4	3:1.2:1.8	50.0	20.0	30.0	>1475	$TiSi_2$
5	0.42:0.23:0.35	42.0	23.0	35.0	1405	$TiSi_2$, SiC

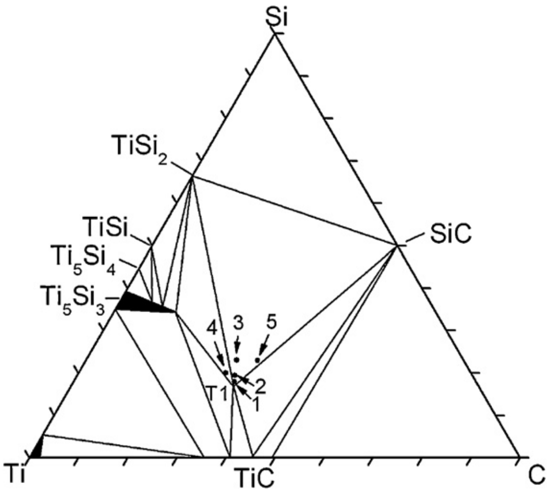

Fig. 1. Locations of Samples 1–5, as marked in a Ti–Si–C ternary phase diagram at 1500 K [27], T1 represents Ti_3SiC_2.

Fig. 2 illustrates DSC curves of the green powder compacts of Samples 1–5. From these curves, it can be seen that no new phase was formed below 700 °C and sharp exothermic peaks appeared at 1473 °C, 1439 °C and 1405 °C in Samples 2, 3 and 5, respectively. However, no such sharp exothermic peak appeared in Samples 1 and 4. In order to verify the phase formed at these sharp exothermic peaks, XRD experiments were carried out on the tested DSC samples. Fig. 3 shows XRD results on the tested DSC Sample 1 and Sample 3. The results indicate that the main product in Sample 3 is Ti_3SiC_2, while the main phases in Sample 1 are TiC and Ti_5Si_3, with some Ti_3SiC_2 and graphite as coexisting phases. It is clear that TiC and Ti_5Si_3 are intermediate phases that formed during the reactive synthesis of Ti_3SiC_2, yet graphite is the unreacted carbon. Thus, it can be concluded that the reaction mechanism of forming Ti_3SiC_2 in the final stage of sintering is:

$$4TiC + Ti_5Si_3 + 2C \rightarrow 3Ti_3SiC_2 \quad (1)$$

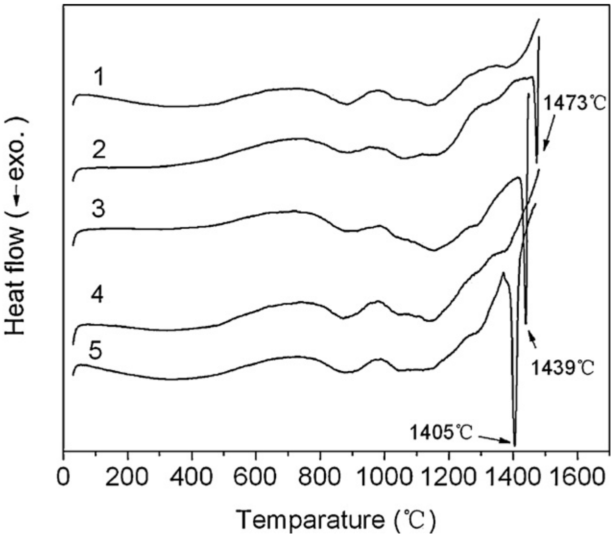

Fig. 2. DSC curves of the green compacts of Samples 1–5.

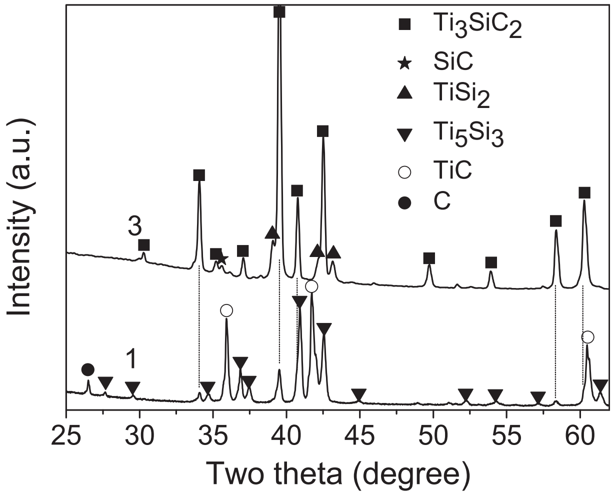

Fig. 3. X-ray diffraction patterns of the DSC tested Samples 1 and 3.

There is no doubt that the massive forming of Ti_3SiC_2 in Sample 3 caused the sharp exothermic peak at 1439 °C. On the other hand, results obtained from Sample 1 showed that there is neither massive Ti_3SiC_2 phase forming nor sharp exothermic heat evolution during sintering. Therefore, it can be concluded that the sharp exothermic peaks in Fig. 2 were due to the massive formation of Ti_3SiC_2. Combining the XRD and DSC results, we know that Ti_3SiC_2 can be formed rapidly when 1405 °C was reached and that the forming temperature increased noticeably with the decrease of initial Si content. Table 1 shows the nominal composition of the samples and characteristics of the synthesized Ti_3SiC.

Fig. 4 depicts the X-ray diffraction patterns of sintered Samples 1–5. From Fig. 4, it can be seen that TiC peaks were not present at all. Fig. 5 shows the relative diffraction peak intensities of various impurity phases in the sintered samples (relative to the major peak of Ti_3SiC_2 (1 0 4) at $2\theta = 39.5°$, impurity peaks of TiC (2 0 0) at $2\theta = 41.7°$, $TiSi_2$ (0 2 2) at

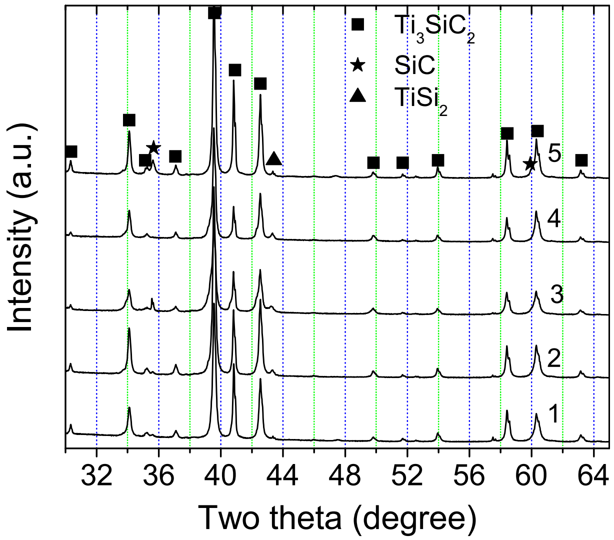

Fig. 4. X-ray diffraction patterns of Samples 1–5, sintered at 1500 °C for 120 min.

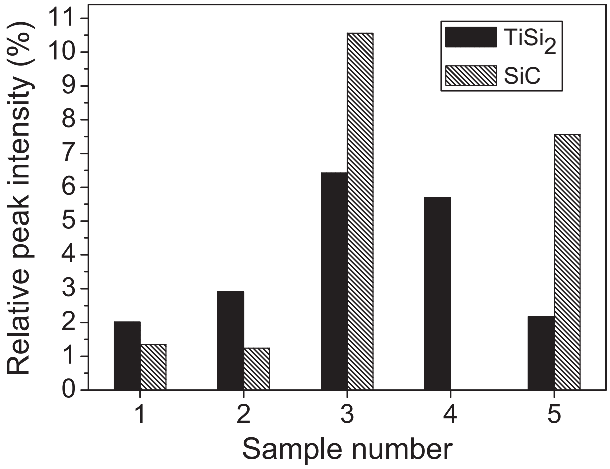

Fig. 5. Relative XRD intensities of various impurity phases in the as-synthesized Ti_3SiC_2 bulks (relative to the major peak of Ti_3SiC_2 at $2\theta = 39.5°$).

$2\theta = 43.2°$, Ti_5Si_3 (2 1 1) at $2\theta = 41.2°$ and SiC (1 1 1) at $2\theta = 35.6°$ were used). From Fig. 5 it can be seen that $TiSi_2$ was the only impurity that can be found in Sample 4. $TiSi_2$ was removed by immersing the sintered Sample 4 into HF acid for about 1 h and stirring from time to time, then draining the reacted acid and repeating the process by using fresh HF acid. Pure Ti_3SiC_2 bulk sample was obtained after rinsing the sample with deionised water to eliminate the residual acid. Fig. 6(a) is a SEM micrograph showing the surface morphology of the pure Ti_3SiC_2 bulk sample. In Fig. 6(a), the dark spots are pores. Fig. 6(b) shows the secondary electron images of the fracture surface of the pure Ti_3SiC_2 bulk sample. From Fig. 6(b), the hexagonal structure of Ti_3SiC_2 can be seen clearly and the lamellar structure of Ti_3SiC_2 can also be seen on the fractured grains. The pure Ti_3SiC_2 bulk sample has a density of 3.02 g/cm^3 (a relative density of 66.7%) and a compressive strength of 182 MPa.

From Fig. 5 it can also be seen that by using an initial composition of Ti:Si:C = 3:1.1:2 (Sample 1), Ti_3SiC_2 with the lowest level of impurity can be obtained. Moreover, the trend showed by Samples 1–3 in Fig. 5 indicated that Ti_3SiC_2 with higher purity can be obtained by decreasing the excess Si content. However, further experimental work is needed to find out what the optimal excess Si content is. Results obtained from Samples 1–3 also revealed that higher excess Si content will lower the Ti_3SiC_2 formation temperature but is harmful to the purity of the synthesized product. As the excess Si content increases, the total amount of impurities increases, although the impurity constitution remains unchanged. When an initial composition of Ti:Si:C = 3:1.5:2 was used (Sample 3), there was a sharp decrease in Ti_3SiC_2 purity. Unlike results in previous reports [18–27], TiC-free Ti_3SiC_2 bulk samples were successfully prepared in this study.

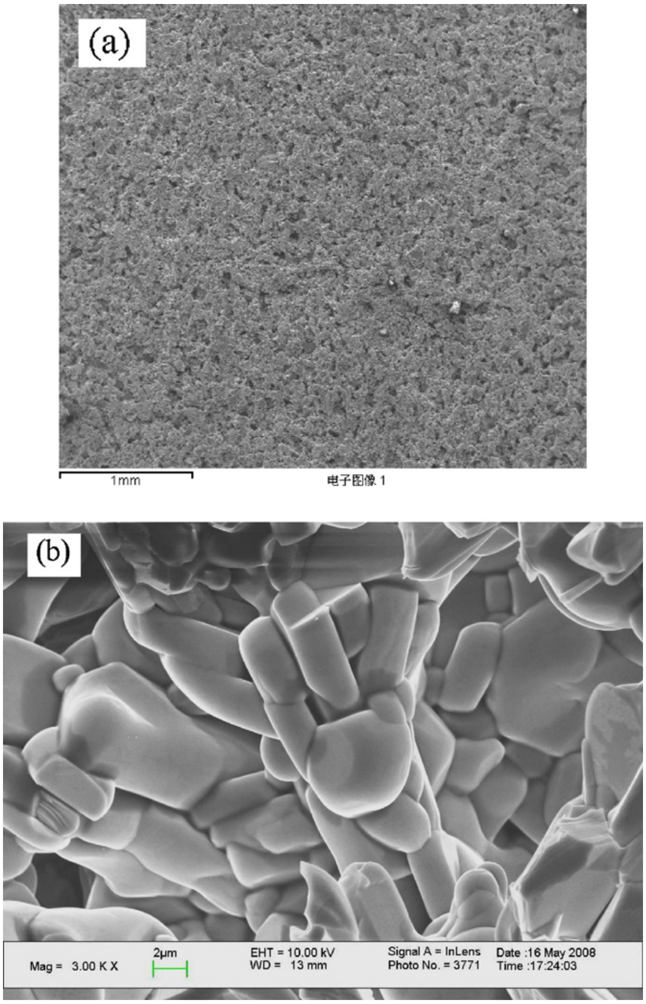

Fig. 6. SEM micrographs of the pure Ti_3SiC_2 bulk sample: (a) surface morphology and (b) Ti_3SiC_2 grains on the fracture surface.

By reactive sintering of blended elemental reactants with excess Si (with nominal compositions of Ti:Si:C = 3:1.1:2 and 3:1.2:2 in molar ratio) at 1350 °C under flowing Ar, Radhakrishnan et al. [19] fabricated Ti_3SiC_2 bulks with relative density of 50% and purity better than 96 vol.% (with TiC, $TiSi_2$ and Ti_5Si_3 as impurities). They obtained dense Ti_3SiC_2 samples through hot pressing the reactively synthesized compacts in graphite die under vacuum at 1350 °C and 40 MPa for 1 h. S.B. Li et al. [24] adopted a mechanically activated sintering process to fabricate Ti_3SiC_2 by using elemental powder mixtures with a stoichiometric composition and also with nominal compositions of Ti:Si:C = 3:1.2:2. Their mechanically alloyed powders consisted of TiC, Ti_3SiC_2 and silicides. After pressureless sintering at 1250 °C for 1 h under vacuum, their mechanically alloyed powder compact was composed of Ti_3SiC_2 with TiC and Ti_5Si_3 as major impurities. They found that the purity of the sintered Ti_3SiC_2 bulks was not improved with the addition of excess Si. By adding 4 wt.% of NaF into the Ti, Si and graphite powder mixtures (with a composition of Ti:Si:C = 0.42:0.23:0.35 in molar ratio), Sun et al. [21] used a solid–liquid synthesis method to fabricate Ti_3SiC_2 powder by annealing the mixtures at 1250 °C for 2 h under flowing Ar in BN crucibles. Their products contain TiC and $TiSi_2$ as impurities. It is interesting to note that although the sample compositions that Radhakrishnan et al. [19] used are equivalent to those of Sample 1 and Sample 2 in this study, and sample compositions that used by S.B. Li et al. [24] and Sun et al. [21] are the same as those of Sample 2 and Sample 5, respectively, in this study, TiC cannot be eliminated from their prepared

Ti_3SiC_2 samples, except for in Radhakrishnan's sample with nominal compositions of Ti:Si:C = 3:1.2:2 [19]. However, as mentioned in a later section, Orthner et al. [25] repeated Radhakrishnan's experiments and all their sintered samples contained TiC as an impurity. Furthermore, no XRD pattern was given in Radhakrishnan's paper; therefore it is doubtful whether there is really no TiC in Radhakrishnan's sample. Since the nominal composition of all these samples are located in the Ti_3SiC_2–$TiSi_2$–SiC three-phase field, if the sintering temperature and sintering time are correctly chosen and the mass of the reactants are conserved, SiC and $TiSi_2$ should be the only possible impurities that can be found in the synthesized Ti_3SiC_2, and that is what happened with Samples 1, 2, 3 and 5 of this study. The sintering temperature that S.B. Li et al. [24] and Sun et al. [21] have chosen was 1250 °C, which is about 150 °C lower than that of the required temperature for massive Ti_3SiC_2 formation (1405 °C); Therefore, reactions for forming Ti_3SiC_2 were not completed (i.e. phase equilibrium was not reached) and intermediate phases such as TiC and Ti_5Si_3 remained as impurities in the synthesized products. While the sintering temperature that Radhakrishnan et al. [19] used was 1350 °C, their relatively long sintering time of 5 h leaves open the possibility of a thorough reaction during the Ti_3SiC_2 synthesizing process. They reported that $TiSi_2$ was the only impurity that can be detected in their high Si content sample (Ti:Si:C = 3:1.2:2). This implies that their final reactant composition entered into the Ti_3SiC_2–$TiSi_2$ two-phase field, which is very unlikely to happen under their experimental conditions. Meanwhile, for their sample with a lower Si content (Ti:Si:C = 3:1.1:2), both TiC and Ti_5Si_3 impurities can be found, which seems like the loss of Si had pushed the reactant composition from the Ti_3SiC_2–$TiSi_2$–SiC three-phase field into the Ti_3SiC_2–$Ti_5Si_3C_x$–TiC three-phase field. From their reported results, it can be concluded that Radhakrishnan et al. encountered a serious Si loss situation. On the contrary, in this study, due to the proper control of Si loss by using lidded crucibles, products obtained from Samples 1 and 2, which have the same nominal compositions as those of Radhakrishnan's samples, showed that Ti_3SiC_2–$TiSi_2$–SiC three-phase equilibrium was reached after reactive sintering and that as the Si content decreases the amount of $TiSi_2$ and SiC impurities decreases, as shown in Fig. 5. Although the total amount of impurities in Sample 5 are much higher than those in Samples 1 and 2, the final reactant composition after sintering remained in the Ti_3SiC_2–$TiSi_2$–SiC three-phase field, indicating that the Si loss in this sample is not significant at all since the sample is located at the vicinity that is very close to the Ti_3SiC_2–TiC–SiC three-phase field, as shown in Fig. 1.

H. Li et al. [18] obtained 93 vol.% pure Ti_3SiC_2 by pressureless sintering of compacts of ball-milled elemental powders, with stoichiometric composition and excess Si (with nominal compositions of Ti:Si:C = 3:1.5:2 and 3:1.75:2 in molar ratio), under vacuum at 1450 °C for different soaking times in graphite crucibles. TiC was found in all of their sintered samples even after a long soaking time of 300 min was used. Impurities such as Ti_5Si_3 and/or $TiSi_2$ can also be found, especially in the samples that sintered at lower temperatures and/or for a shorter sintering time. Their results showed that sintering at 1380 °C for 20 min is not good enough to form pure Ti_3SiC_2. Although a high sintering temperature, long sintering time and a very high excess amount of Si were used, TiC persisted to stay in H. Li et al.'s samples. Their results indicated that TiC impurity cannot be eliminated from the synthesized product by simply adding excess Si into the initial reactants that composed of a stoichiometric composition of Ti_3SiC_2. Sample 3 prepared in this study has the same nominal composition as H. Li et al.'s sample that has a lower excess Si content (nominal composition of Ti:Si:C = 3:1.5:2). Again, due to the proper control of Si loss in this study, the result obtained from Sample 3 shows that Ti_3SiC_2–$TiSi_2$–SiC three-phase equilibrium was reached after reactive sintering, although the amount of $TiSi_2$ and SiC impurities are quite high, as shown in Fig. 5.

Zou et al. [22] prepared Ti_3SiC_2 by heating a non-stoichiometric powder mixture, which has a composition of Ti:Si:TiC = 2:2:3, at temperatures ranging from 1000 to 1400 °C for various soaking times in alumina crucibles under vacuum. They found that the XRD peak intensity of TiC impurity decreased as the heating temperature increases, which seems to imply that a high reaction temperature facilitates the conversion of TiC into Ti_3SiC_2. They obtained 99% pure Ti_3SiC_2 powder, with trace amount of TiC as the only detectable impurity, by heat treating the powder mixture at 1400 °C for 4 h under vacuum. The chemical composition of Zou et al.'s sample is the same as that of Sample 4 in this study even though they used Ti, Si and TiC powders instead of Ti, Si and graphite powders as the initial reactants. As shown in Fig. 1, Sample 4 is located in the Ti_3SiC_2–$Ti_5Si_3C_x$–$TiSi_2$ three-phase field, therefore no TiC should be found in the final sintered product. However, in Zou et al.'s sintered sample, even after a long annealing time of 4 h at 1400 °C, TiC remained as the only impurity that coexisted with the Ti_3SiC_2, indicating that the synthesizing reactions and also probably the loss of Si during the annealing pushed the reactant composition from the Ti_3SiC_2–$Ti_5Si_3C_x$–$TiSi_2$ three-phase field into the Ti_3SiC_2–TiC two-phase field. Yet, in this study, after 2 h of annealing at 1500 °C in a lidded alumina crucible under Ar, the final reactant composition of Sample 4 was pushed into the Ti_3SiC_2–$TiSi_2$ two-phase field, leaving $TiSi_2$ as the only impurity that can be detected in the sintered product. Reasons for this is may be due to the simultaneous loss of Si and Ti during sintering since there are Ti–Si eutectics at around 1330 °C, or because the amount of $Ti_5Si_3C_x$ formed is too small to be detected.

Orthner et al. [25] repeated Radhakrishnan et al.'s experiments [19] and all their samples contained TiC as an impurity. They confirmed that the addition of excess silicon may increase the yield of Ti_3SiC_2, but it cannot prevent the formation of the TiC impurity in the reaction synthesis of Ti_3SiC_2 from elemental powders. They employed a high-energy ball-milling plus reaction sintering method to prepare pure Ti_3SiC_2. The milling of Ti, Si and carbon black powders initiated an exothermic reaction and the starting material was completely converted into a mixture composed mainly of TiC with minor amounts of $TiSi_2$, $Ti_5Si_3C_x$ and Ti_3SiC_2. TiC existed in all of their milled samples, no matter what stoichiometric composition or how much excess Si was used. Compacts of their as-milled powder were then annealed at 1350 °C for 2 h in a vacuum furnace equipped with a tungsten heating element. A slight percentage of weight loss was detected in their compacts after sintering. They attributed this effect to the vaporization of elemental silicon or titanium silicides. They found that pure Ti_3SiC_2 can be obtained by sintering the milled powders that have a nominal composition of Ti:Si:C = 3:1.3:2 (although not mentioned in their paper, trace amount of TiC remained in that particular sample since a tiny TiC peak can be seen in Fig. 5 of their paper [25]). In Orthner et al.' experiments, the formation of TiC, $TiSi_2$, $Ti_5Si_3C_x$ and Ti_3SiC_2 after milling lowered the possibility of Si loss during the sintering process and also lowered the Ti_3SiC_2 forming temperature, which made possible for the yielding of pure Ti_3SiC_2 with only trace amounts of TiC. It is worth mentioning that Orthner et al.'s experimental results, both for the repeats of Radhakrishnan et al.'s [19] experiments and for the ball-milled plus reaction sintering experiments, showed the existence of TiC impurity. Compared to Orthner et al.'s results and Radhakrishnan et al.'s results, no TiC was found in all the synthesized samples of this study, although the initial reactant compositions are the same as those of Orthner et al.'s and Radhakrishnan et al.'s. The reason for this is because the Si loss was controlled by using lidded crucibles in the present study, while, in the other studies, their samples were open to the sintering atmosphere. As a result, phase equilibrium can hardly be reached because of the continuous loss of Si during sintering.

From above results, it can be seen that sintering conditions exerted significant effects on the purity of the synthesized Ti_3SiC_2. Other than the conservation of mass in the reactants (by using lidded crucibles in this case), the material of the crucible is important too. The use of graphite dies may have led to an extra supply of carbon and thus complicated the experimental conditions. Lastly, the proper selection of initial composition and the acquisition of phase equilibrium by the proper selection of sintering parameters, especially for the synthesizing temperature and time, are crucial in obtaining the synthesized product with controlled impurity.

4. Summary

This paper reported the preparation of Ti_3SiC_2 bulks with controllable impurity by the pressureless reactive sintering of Ti, Si and graphite powder compacts at 1500 °C for 2 h in lidded alumina crucibles under Ar atmosphere. Undesirable TiC impurity was successfully eliminated from the synthesized product. DSC results indicated that no new phase was formed at the temperature ranging from ambient to 700 °C, while a sharp exothermic peak corresponding to the massive formation of Ti_3SiC_2 appeared when 1405 °C was reached. This formation temperature increased noticeably as the initial Si content of the sample decreased. TiC and Ti_5Si_3 are the intermediate phases that formed during the reactive synthesis of Ti_3SiC_2, from elemental powders.

Product with desired phase constituent can be fabricated by preparing the samples according to phase diagram data. TiC, which is a commonly found impurity that is difficult to remove, can be avoided in the synthesized Ti_3SiC_2 by the proper selection of nominal composition and the appropriate addition of excess Si content. High purity porous Ti_3SiC_2 bulk, which has potential applications in synthetic bone graft substitutes and a density of 3.02 g/cm^3 and a compressive strength of 182 MPa, was prepared.

The key for successful impurity control in reactive sintering is the conservation of mass in the reactants. The encapsulation of the green powder compacts in lidded alumina crucibles is a crucial step to limit Si loss during sintering. Experimental results indicated that the adaptation of this method can allow a more controllable sintering process. Lastly, the acquisition of phase equilibrium by the proper selection of sintering parameters, especially for the synthesizing temperature and time, is also crucial in obtaining the synthesized product with controlled impurity.

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