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Intermediate phases in synthesis of Ti_3SiC_2 and $Ti_3Si(Al)C_2$ solid solutions from elemental powders

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Abstract

In this paper, we investigated the reaction path to synthesize Ti_3SiC_2 by the in situ hot pressing/solid–liquid reaction method. The effect of different content of Al addition on this process was also examined. Ti_3SiC_2 mainly formed from the reaction between $Ti_5Si_3C_x$, TiC_x, $TiSi_2$ and graphite at 1400–1500 °C. As an inescapable impurity in Ti_3SiC_2, TiC_x was removed by addition of small amounts of Al. This was owing to the fact that the addition of a minor quantity of Al increased the amount of "effective TiC_x" and relatively decreased that of "invalid TiC_x". Further increasing Al content, however, resulted in the presence of TiC_x again in the final product. This was due to the fact when significant amounts of Al was added, the stoichiometric ratio of silicon and graphite has been deviated from that for Ti_3SiC_2. More Si and less graphite were needed to prepare a monolithic $Ti_3Si(Al)C_2$ solid solution with high Al content.

Keyword: Ti_3SiC_2; Hot pressing; Impurities; X-ray methods

1. Introduction

Ti_3SiC_2 is a promising ceramic in many applications due to its unique combination of the merits of both metals and ceramics. It possesses many excellent properties, such as low density, high modulus, high strength, machinability, high ratio of fracture toughness to strength, damage tolerance at ambient temperature and good oxidation resistance below 1100 °C. So it attracts generous attentions and has been extensively investigated in recent years. Despite these efforts, there remain many unresolved basic issues related to this material. For example, the formation path of Ti_3SiC_2 in synthesizing process has not been fully understood.

In the last decade, various processes have been employed to synthesize Ti_3SiC_2 using different initial materials, such as the mixture powders of Ti/Si/C,[1–6] Ti/SiC/C,[7–11] Ti/Si/TiC,[12,13] Ti/SiC/TiC[14] and Ti/Si/C/SiC.[15] Each method may has a subtly (or even grossly) different reaction pathway that likely depends on the starting materials. The formation mechanism of Ti_3SiC_2 from Ti, SiC, and graphite powders has been widely investigated,[16–19] but those from other initial materials are rarely examined.

El-Raghy and Barsoum[16] proposed that the intermediate phases of $Ti_5Si_3C_x$ and TiC_x were intimately involved in the formation of Ti_3SiC_2 from Ti/SiC/C powders. Using the in situ neutron powder diffraction, Wu et al.[17,18] also investigated the reaction path of Ti_3SiC_2 and confirmed the results reported by El-Raghy and Barsoum. The reactions for synthesizing Ti_3SiC_2 from Ti/SiC/C powders were described by,

$$3\mathrm{Ti} + \mathrm{SiC} + \mathrm{C} = \frac{4}{3}\mathrm{TiC}_x + \frac{1}{3}\mathrm{Ti_5Si_3C}_y + \frac{6-4x-y}{3}\mathrm{C} \tag{1-1}$$

$$\frac{4}{3}\mathrm{TiC}_x + \frac{1}{3}\mathrm{Ti_5Si_3C}_y + \frac{6-4x-y}{3}\mathrm{C} = \mathrm{Ti_3SiC_2} \tag{1-2}$$

Riley and Kisi et al.[19] used the in situ neutron powder diffraction to capture the formation mechanism of Ti_3SiC_2 from Ti/SiC/C powders during the self-propagating high-temperature synthesis (SHS). The evolution of phases was

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consistent with those reported by Wu et al.[17,18] except that a intermediate phase, which was considered to be a solid solution of Si in TiC, was presented before the formation of Ti_3SiC_2.

Yang et al.[20] reported the reaction path for synthesizing Ti_3SiC_2 from Ti/Si/TiC powders. They stated that Ti_5Si_3 was the only intermediate phase during the heating process. The reaction could be presented as

$$Ti_5Si_3 + 10TiC + 2Si = 5Ti_3SiC_2 \tag{1-3}$$

Sato et al.[21] investigated the formation sequence of Ti_3SiC_2 from Ti/Si/C powders. The schematic sequence was as following: firstly, the reaction between Ti and graphite produced TiC; secondly, the Ti–Si eutectic liquid appeared near the eutectic temperature (1603 K); finally, Ti_3SiC_2 grew up between the eutectic liquid phase and the TiC particles.

In our previous work,[4] we reported a novel in situ hot pressing/solid–liquid reaction synthesis method for preparing fully dense Ti_3SiC_2 using Ti/Si/C as initial materials. This method displayed advantages of low processing temperature and short reaction time. However, the reaction mechanism of this process was not completely confirmed. Recently, using the same method, we prepared $Ti_3Si_xAl_{1-x}C_2$ solid solutions with different Al content in order to remove the impurity TiC_x in Ti_3SiC_2 and improve the oxidation resistance of this material.[22,23] When 3–10 at.% Si was substituted with Al, TiC_x was completely removed from Ti_3SiC_2. However, further increasing Al content in this system resulted in the presence of TiC_x again. These are intriguing and unknown problems, which are needed to be clarified.

Investigating the reaction path is a good way to understand the formation mechanism of a material, and provides valuable insight into the effect of elemental additive on the reaction process. So the formation mechanisms of three composition powders such as 3Ti/1Si/2C (denoted as TSC), 3Ti/0.9Si/0.1Al/2C (denoted as 10Al) and 3Ti/0.5Si/0.5Al/2C (denoted as 50Al) were studied in this work. By investigating the TSC, 10Al and 50Al systems, we tried to reveal the formation mechanism of Ti_3SiC_2 during the in situ hot pressing/solid–liquid reaction synthesis, to understand the elimination of TiC_x when small amounts of Si were substituted with Al and to explain the appearance of the TiC_x impurity again after the Al content exceeded the critical value, respectively. This work will benefit the full understanding of the formation mechanism of Ti_3SiC_2 during the in situ hot pressing/solid–liquid reaction synthesis and the effect of Al on this process.

2. Experimental

The starting materials were titanium powders and aluminum powders (40 μm, both from Institute of non-ferrous metals, Beijing, China), silicon powders and graphite powders (40 and 10 μm, respectively, both from China's No. 4 grinding wheel Inc., Shandong, China). Ti, Si, Al and graphite powders were weighted according to three different compositions and milled for 12 h in a polyurethane mill, using stainless steel balls coated with a layer of polyurethane as the mixing medium. Afterwards the mixed powders were dried and used in the later experiments.

Differential scanning calorimetry (DSC) experiments were performed in a Setsys 16/18 thermal analyzer (SETARM, France) to determine the onset of reaction temperatures. The powder samples were heated from ambient temperature to 1530 °C at a rate of 10 °C per minute in a flowing Ar atmosphere. The weight of mixed powders was about 10 mg, and Al_2O_3 crucibles were used in these tests.

Based on the results of DSC, bulk materials were prepared in the temperature range of 750–1500 °C to understand the phase evolution. The mixed powders were cold compacted into a disc of 25 mm in diameter in a graphite mold whose inner surface had been sprayed with a BN layer. Then the compacted discs were heated from room temperature to the requisite temperature and kept at that temperature for 5 min under a 30 MPa pressure.

Powder samples for XRD analysis were obtained by drilling the as-prepared bulk materials with a high-speed drill, and then ground in an agate mortar. Phase identification was conducted via a step-scanning X-ray diffractometer with Cu Kα radiation (Rigaku D/max-2400, Japan). The microstructures of the bulk samples were observed in a S-360 scanning electron microscope (Cambridge Instruments Ltd., UK) equipped with an energy-dispersive spectroscopy (EDS) system. Prior to the SEM examination, the samples were ground down to 1000 SiC papers and polished using diamond paste.

3. Results

3.1. Phase evolution in the formation of Ti_3SiC_2

Fig. 1 illustrates the DSC curves of Ti/Si/Al/C mixed powders with different compositions at a heating rate of 10 °C per minute under a flowing Ar atmosphere. In

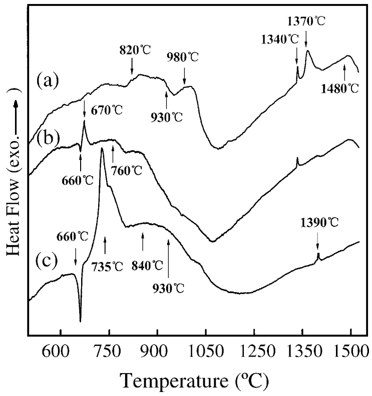

Fig. 1. DSC curves of (a) 3Ti/1Si/2C, (b) 3Ti/0.9Si/0.1Al/2C and (c) 3Ti/0.5Si/0.5Al/2C mixed powders heated from ambient temperature to 1530 °C under a flowing Ar atmosphere. The heating rate is 10 °C per min.

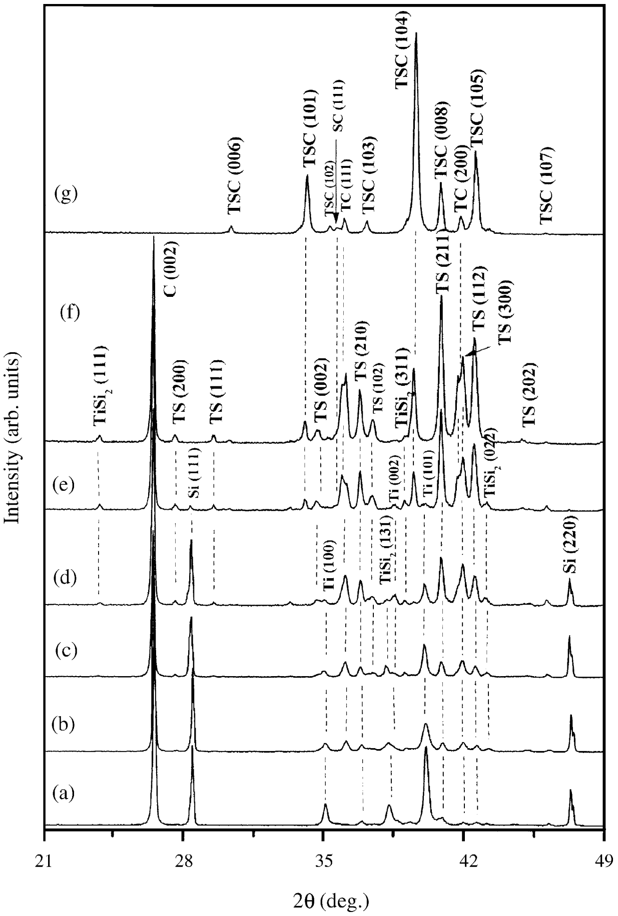

Fig. 2. XRD patterns of the 3Ti/1Si/2C mixed powders heated at (a) 900 °C, (b) 1000 °C, (c) 1100 °C, (d) 1200 °C, (e) 1300 °C, (f) 1400 °C, (g) 1500 °C (TSC = Ti_3SiC_2; TS = $Ti_5Si_3C_x$; TC = TiC_x; SC = SiC).

Fig. 1(a), there are several endothermic and exothermic peaks for the TSC sample. These peaks include exothermic ones at 820, 980, 1340, 1370 and 1480 °C, respectively, and a broad endothermic one starting at about 930 °C. Fig. 2 presents the XRD patterns of the 3Ti/1Si/2C powders heated at 900–1500 °C. For the sample heated at 750 °C, no newly formed phase is identified by XRD (not shown here). The newly formed phases are $Ti_5Si_3C_x$ at 900 °C, and TiC_x and $TiSi_2$ at 1000 °C, respectively (Fig. 2). We can observe different regions in the backscattered electron image of the sample treated at 1000 °C (Fig. 5(a)). The EDS analysis indicates that the white region is rich in Ti, the deep-gray one in Si, the black one in C, and the gray one in Ti, Si and graphite. Some interfaces between Ti and graphite are identified as TiC_x. Combined the results of DSC, XRD and EDS, the exothermic peak at 820 °C corresponds to the formation of $Ti_5Si_3C_x$ and the peak at 980 °C relates to the formation of TiC_x and $TiSi_2$. At 1000–1300 °C, the amounts of $Ti_5Si_3C_x$ and TiC_x increase with simultaneous consumption of titanium, silicon and graphite (Fig. 2). As can be seen in Fig. 5(b), the gray regions increase significantly, while other regions shrink greatly at 1200 °C, confirming the results of XRD. However, the occurrence of the large endothermic peak is not due to the development of $Ti_5Si_3C_x$ and TiC_x because this process generates substantial heat.[19,21,24,25] It can be seen from the Ti–Si binary phase diagram[26] that the phase transition from α-Ti to β-Ti begins at about 882 °C. This phase transition is an endothermic process because the thermal capacity of β-Ti is bigger than that of α-Ti. Through the in situ neutron diffraction, this phase transition was observed during heating a powder compact containing Ti, SiC and graphite.[17–19] So the endothermic peak partially derives from this phase transition. In the Ti–Si-C ternary phase diagram,[27] there exist two reactions related to the formation of liquid phases at about 1330 °C:

$$\text{Liquid} + \text{TiC} \rightarrow \text{bcc} - (\text{Ti}) + \text{Ti}_5\text{Si}_3\text{C}_x \tag{3-1}$$

$$\text{Liquid} \rightarrow \text{Si} + \text{SiC} + \text{TiSi}_2 \tag{3-2}$$

The sample treated at 1300 °C includes Ti, $Ti_5Si_3C_x$, $TiSi_2$, SiC and Si (Fig. 2). In this regard, it is reasonable to conclude that the Ti–Si liquid phase exist during the preparation process. The formation of this liquid phase also contributes to the occurrence of the endothermic peak. Small amount of desired Ti_3SiC_2 phase generates at 1300 °C (Fig. 2). As the temperature increased to 1400 °C, $Ti_5Si_3C_x$ and TiC_x become dominant phases (Fig. 2). In Fig. 5(c), the deep-gray regions are Ti_3SiC_2 and are presented within gray regions containing $Ti_5Si_3C_x$, and the black regions containing unreacted graphite shrink further at 1400 °C. Therefore, the exothermic peaks at 1340 and 1370 °C deduce from the formation of significant amounts of $Ti_5Si_3C_x$ and TiC_x phases. We can observe the phase transition from graphite, $Ti_5Si_3C_x$, TiC_x and $TiSi_2$ to Ti_3SiC_2 at 1400–1500 °C (Fig. 2). Therefore, it is reasonable to conclude that the reaction between graphite, $Ti_5Si_3C_x$, TiC_x and $TiSi_2$ produces Ti_3SiC_2 mainly within the temperature range of 1400–1500 °C. Moreover, the reaction to form Ti_3SiC_2 is exothermic.[5,25] This agrees with the observation of the exothermic peak at 1480 °C in DSC curve (Fig. 1).

3.2. Effect of Al on the phase evolution of Ti_3SiC_2 synthesis

3.2.1. Phase evolution in the formation of $Ti_3Si_{0.9}Al_{0.1}C_2$

In Fig. 1(b), a puniness endothermic peak at 660 °C is owing to the melting of Al. Subsequently, an exothermic peak is observed near 670 °C. It was reported that Ti and Al powders reacted intensively at about 700 °C, and this reaction generated a lot of heat.[28,29] But the XRD analysis reveals that only Ti, Si and graphite are presented in the sample heated up to 750 °C (not shown here). Thus, the exothermic peak at 670 °C may originate from the formation of a Ti–Al intermetallic phase, but its amount is too little to be identified by XRD. As temperature increases, another exothermic peak occurs at 760 °C (Fig. 1(b)). This peak corresponds to the formation of $Ti_5Si_3C_x$, TiC_x and $TiSi_2$ because these phases

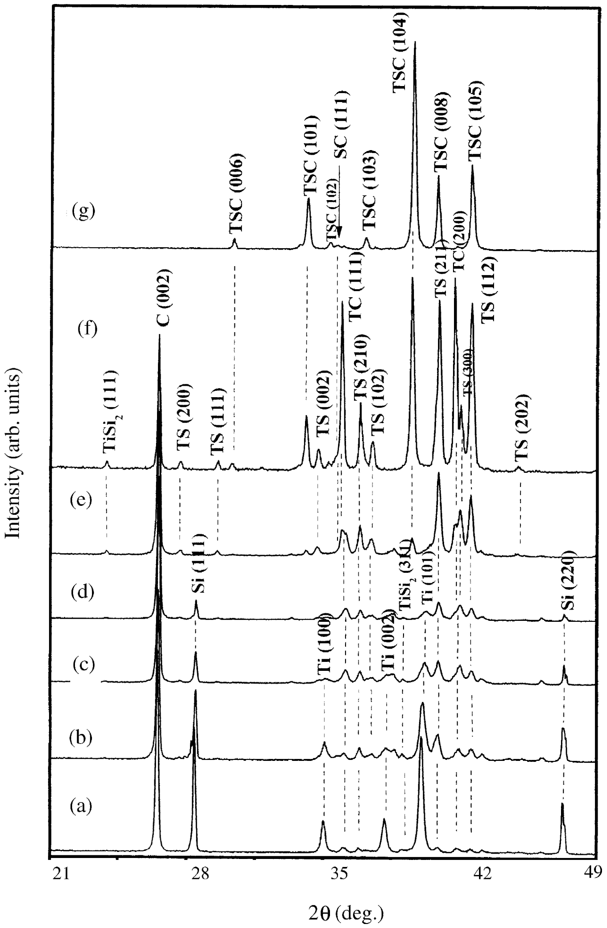

Fig. 3. XRD patterns of the 3Ti/0.9Si/0.1Al/2C mixed powders heated at (a) 900 °C, (b) 1000 °C, (c) 1100 °C, (d) 1200 °C, (e) 1300 °C, (f) 1400 °C, (g) 1500 °C (TSC = $Ti_3Si_{0.9}Al_{0.1}C_2$; TS = $Ti_5Si_3C_x$; TC = TiC_x; SC = SiC).

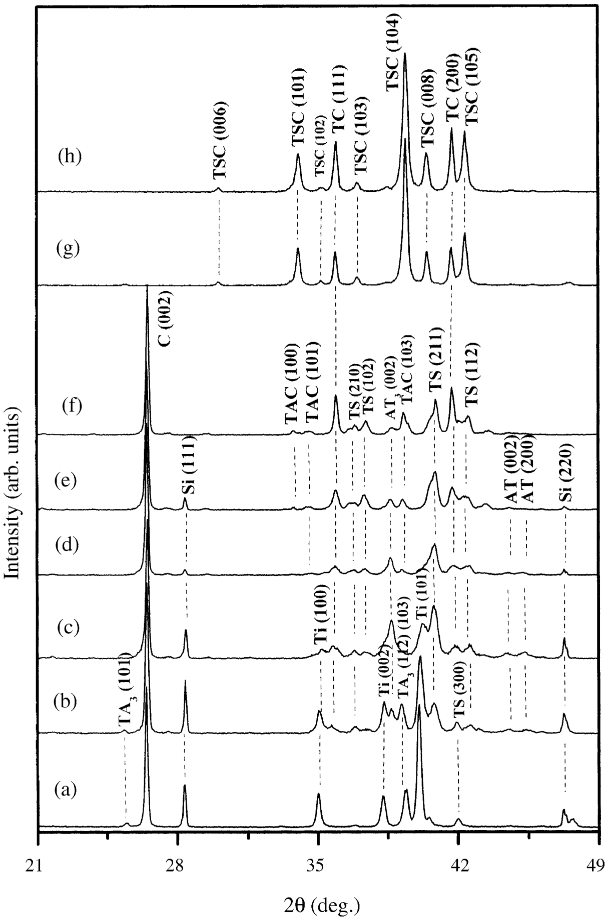

Fig. 4. XRD patterns of the 3Ti/0.5Si/0.5Al/2C mixed powders heated at (a) 750 °C, (b) 900 °C, (c) 1000 °C, (d) 1100 °C, (e) 1200 °C, (f) 1300 °C, (g) 1400 °C, (h) 1500 °C (TSC = $Ti_3Si(Al)C_2$; TS = $Ti_5Si_3C_x$; TC = TiC_x; AT = AlTi; TA3 = $TiAl_3$; AT3 = $AlTi_3$; TAC = Ti_2AlC).

are detected by XRD at 900 °C (Fig. 3). Thereafter, the phase evolution is akin to that of the TSC sample, so we will not describe the detailed results for briefness.

It should be noted that the phase evolution shows two different features compared to that of Ti_3SiC_2. One is that TiC_x forms at lower temperature, and the other is that the amount of TiC_x increases remarkably at 1400 °C (Fig. 3). We were also interested in the trace of Al during the reaction process, and found that Al existed in unreacted Ti, $Ti_5Si_3C_x$ and TiC_x by EDS analysis.

3.2.2. Phase evolution in the formation of $Ti_3Si_{0.5}Al_{0.5}C_2$

For the 50Al sample, the DSC curve includes exothermic peaks at 735, 840 and 1390 °C, and endothermic ones at 660 and 930 °C, respectively (Fig. 1(c)). The endothermic peak at 660 °C corresponds to the melting of Al. The exothermic peak at 735 °C is related to the formation of $TiAl_3$ because this phase is observed in the sample heated at 750 °C by XRD (Fig. 4). As the temperature increased to 900 °C, XRD analysis indicates the presence of the newly formed phases Ti_3Al, TiAl and TiC_x (Fig. 4). Hence the exothermic peak at 840 °C originates from the formation of these phases. As the temperature increased to 1000 °C, $TiAl_3$ is consumed and the amounts of Ti_3Al and TiAl increase (Fig. 4), indicating that $TiAl_3$ tends to dissociate into Ti_3Al and TiAl. The existence of liquid phases is not completely confirmed because the Ti–Si–Al–C phase diagram is too limited. Viala et al.[30] observed that the Al–Si based liquid was formed at 1000 °C in the Ti–Si–Al–C system. Ti_2AlC is identified at 1100 °C. The sample heated to 1300 °C includes graphite, $Ti_5Si_3C_x$, TiC_x, Ti_3Al, TiAl, Ti_2AlC in addition to $Ti_3Si(Al)C_2$. However, when the sample is heated to 1400 °C, only $Ti_3Si(Al)C_2$ solid solution and TiC_x presents (Fig. 4). The results of XRD and DSC suggest that $Ti_3Si(Al)C_2$ solid solution is the product of the reaction between these intermediate phases and mainly forms at 1390 °C. The quantity of TiC_x increases when the sample is heated in the range of 1400–1500 °C. This phenomenon demonstrates that the thermal stability of $Ti_3Si(Al)C_2$ solid solution with high Al content is decreased with increasing temperature. The corresponding microstructure changes are illustrated in Fig. 5(d) and (e).

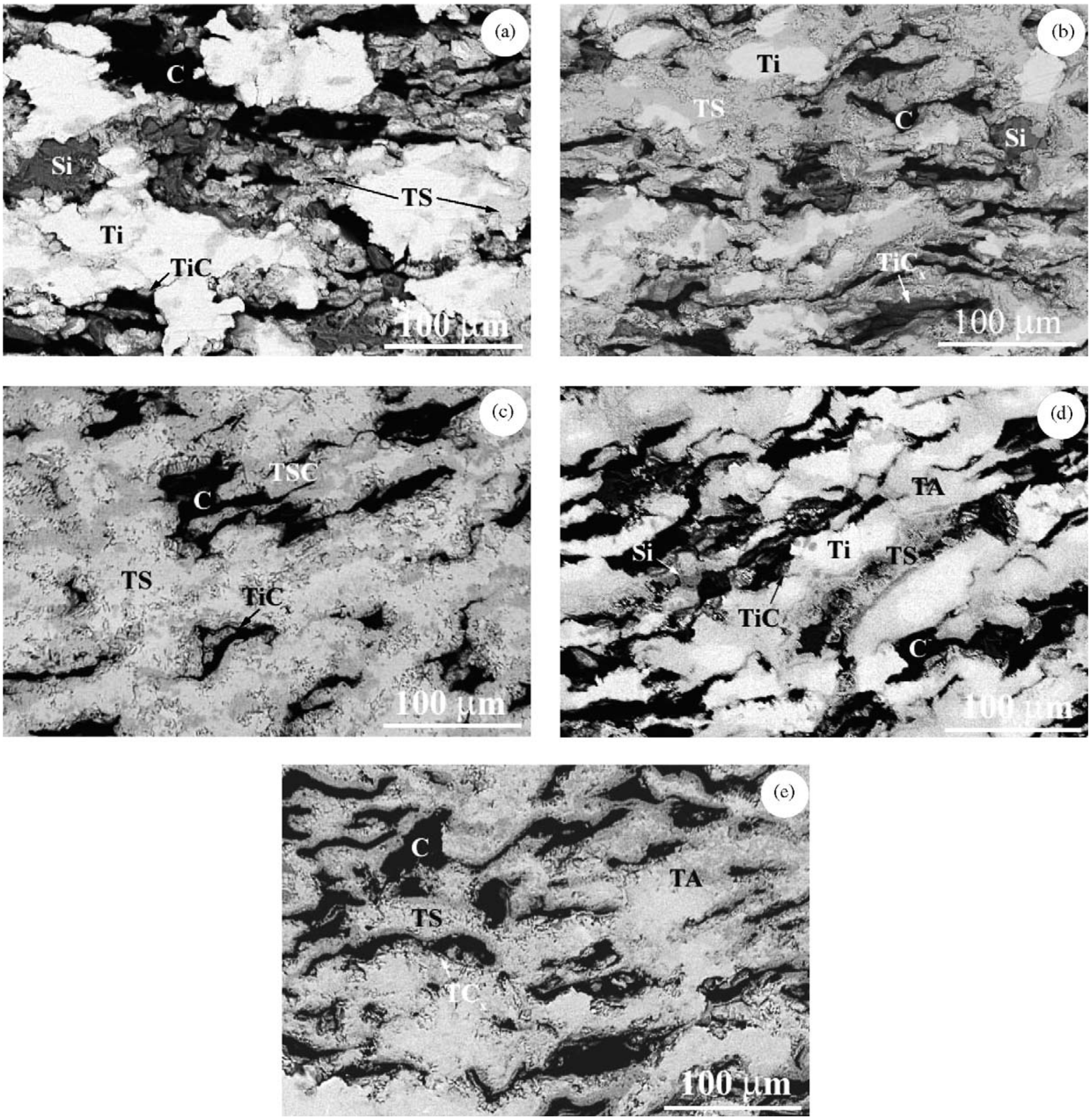

Fig. 5. Backscattered electron images of the TSC samples annealed at (a) 1000 °C, (b) 1200 °C, (c) 1400 °C and the 50Al samples at (d) 1000 °C (e) 1300 °C for 5 min (TS = $Ti_5Si_3C_x$; TSC = Ti_3SiC_2; TA = TiAl, Ti_3Al, Ti_2AlC).

4. Discussions

4.1. Reaction path of Ti_3SiC_2

Based on the above results, we propose the reaction process as follows. Firstly, $Ti_5Si_3C_x$ forms at about 820 °C through the reaction of Ti, Si and graphite. Subsequently, the reaction between Ti, Si and graphite produce TiC_x and $TiSi_2$ near 980 °C. Finally, Ti_3SiC_2 starts to form at about 1300 °C through the reaction between $Ti_5Si_3C_x$, TiC_x, $TiSi_2$ and graphite, and this phase is mainly formed at 1480 °C. The whole reaction process can be depicted as

$$5\mathrm{Ti} + 3\mathrm{Si} + x\mathrm{C} = \mathrm{Ti_5Si_3C}_x \quad (820\,^{\circ}\mathrm{C}) \tag{4-1}$$

$$2\mathrm{Ti} + 2\mathrm{Si} + x\mathrm{C} = \mathrm{TiC}_x + \mathrm{TiSi_2} \quad (980\,^{\circ}\mathrm{C}) \tag{4-2}$$

$$\frac{3}{10}\mathrm{Ti_5Si_3C}_x + \frac{29}{20}\mathrm{TiC}_y + \frac{1}{20}\mathrm{TiSi_2} + \left(2 - \frac{3}{10}x - \frac{29}{20}y\right)\mathrm{C} = \mathrm{Ti_3SiC_2} \quad (1300\text{–}1500\,^{\circ}\mathrm{C}) \tag{4-3}$$

Regardless of the details of reaction process, two nucleate mechanisms of Ti_3SiC_2 have been proposed. One was on $Ti_5Si_3C_x$[16–18,31–33] and the other on TiC_x.[20,34–36] The two mechanisms seemed equally reasonable because both $Ti_5Si_3C_x$ and TiC_x contained C–Ti octahedra, which were similar to those in Ti_3SiC_2 and provided a skeletal structure for the formation of Ti_3SiC_2. In this work, the growth of Ti_3SiC_2 occurs within the $Ti_5Si_3C_x$ phase (Fig. 5(c)), supporting the first mechanism.

Previous work[2] revealed that it was difficult to synthesize Ti_3SiC_2 through the solid–solid reaction in the Ti–Si–C system. For forming a liquid phase during preparation of Ti_3SiC_2, Sun et al.[37] added NaF to this system because NaF was melted at elevated temperature. Consequently, high content Ti_3SiC_2 was prepared only at 1250 °C.

In this experiment, Ti_3SiC_2 was formed at about 1300 °C, which was in good agreement with the reaction temperature related to the formation of liquid phases in the Ti–Si–C system.[28]

$$\text{Liquid} + \text{TiC} \rightarrow \text{bcc} - (\text{Ti}) + Ti_5Si_3C_x \tag{4-4}$$

$$\text{Liquid} \rightarrow \text{Si} + \text{SiC} + TiSi_2 \tag{4-5}$$

We observed the presence of Ti, $Ti_5Si_3C_x$, $TiSi_2$, SiC and Si in the sample heated at 1300 °C and the endothermic peak in DSC curve. All the facts further confirmed the existence of the Ti–Si liquid phases during the preparation.

The existences of liquid phases in the formation of Ti_3SiC_2 were mentioned in literatures from different aspects.[4,12,21,38–40] Many attempts have been made to prove the existence of a liquid phase during preparation of Ti_3SiC_2. Sato et al.[21] investigated the composition of samples prepared from different mixing ways: hand mixing with a mortar and pestle, wet ball milling in ethanol for 100 h and dry ball milling in argon atmosphere for 500 h. The results demonstrated that the reaction products for the three different methods were similar. Tang et al.[33] examined the thermal shrinkage curve during synthesizing Ti_3SiC_2, and found the shrinkage rate increased greatly at 1000–1480 °C. This contract of the sample was due to the appearance of a liquid phase. Zhang et al.[40] observed the growth morphology of Ti_3SiC_2 grain, and concluded that Ti_3SiC_2 crystallites grew from melt under low supersaturation condition.

4.2. *Effect of Al addition on the reaction path of Ti_3SiC_2*

4.2.1. *Reaction path of $Ti_3Si_{0.9}Al_{0.1}C_2$*

The reaction process to form $Ti_3Si_{0.9}Al_{0.1}C_2$ is similar to that of Ti_3SiC_2. This process can be described by the following reactions,

$$\text{Al(solid)} = \text{Al(liquid)} \quad (660\,^\circ\text{C}) \tag{4-6}$$

$$7\text{Ti} + 5\text{Si} + (x + y)\text{C} = Ti_5Si_3C_x + TiC_y + TiSi_2 \quad (760\,^\circ\text{C}) \tag{4-7}$$

$$\frac{27}{100}Ti_5Si_3C_x + \frac{321}{200}TiC_y + \frac{9}{200}TiSi_2 + \frac{1}{10}\text{Al} + \left(2 - \frac{27}{20}x - \frac{321}{200}y\right)\text{C} = Ti_3Si_{0.9}Al_{0.1}C_2 \quad (1300 - 1500\,^\circ\text{C}) \tag{4-8}$$

Reaction (4-3) shows that Ti_3SiC_2 is formed through the reaction between $Ti_5Si_3C_x$, TiC_x and C mainly at 1400–1500 °C. Therefore, at 1400 °C, $Ti_5Si_3C_x$, TiC_x and C can be considered as the "real initial materials" to synthesize Ti_3SiC_2. The relative amounts of these phases significantly affect the composition of final products. For preparing Ti_3SiC_2, TiC_x acts as a "real initial material" at 1400 °C, but as an impurity phase in the sample at 1500 °C because Ti_3SiC_2 mainly forms in the temperature range of 1400–1500 °C. From this point of view, we can describe the TiC_x into two separate ways, the "effective TiC_x" and "invalid TiC_x". TiC_x present at 1400 °C is "effective" and at 1500 °C is "invalid". By the addition of Al, the amount of "effective TiC_x" is increased greatly compared to that in the TSC sample at 1400 °C. This relatively decreases the amount of "invalid TiC_x". As a result, the impurity phase of TiC_x is eliminated from Ti_3SiC_2 by the addition of Al in small amount.

4.2.2. *Reaction path of $Ti_3Si_{0.5}Al_{0.5}C_2$*

Based on the results of DSC and XRD, we describe the reaction mechanism as follows. Firstly, Al melts at 660 °C. Subsequently, the reactions between elemental powders produce $TiAl_3$ and $Ti_5Si_3C_x$ at about 735 °C. In the vicinity of 840 °C, $TiAl_3$ reacts with Ti to produce Ti_3Al and TiAl. TiC_x is also formed at this temperature. Ti_2AlC is present near 1100 °C. Finally, $Ti_3Si(Al)C_2$ starts to form at about 1300 °C and yields largest quantity at about 1400 °C. However, when the sample is heated to 1500 °C, the solid solution trends to dissociate into TiC_x. Thus, these processes can be depicted as

$$\text{Al(solid)} = \text{Al(liquid)} \quad (660\,^\circ\text{C}) \tag{4-9}$$

$$6\text{Ti} + 3\text{Si} + 3\text{Al} + x\text{C} = Ti_5Si_3C_x + TiAl_3 \quad (735\,^\circ\text{C}) \tag{4-10}$$

$$TiAl_3 + 5\text{Ti} + x\text{C} = 2\text{TiAl} + Ti_3Al + TiC_x \quad (840\,^\circ\text{C}) \tag{4-11}$$

$$\text{TiAl} + Ti_3Al + 2\text{C} = 2Ti_2AlC \quad (1100\,^\circ\text{C}) \tag{4-12}$$

$$\frac{x}{3}Ti_5Si_3C + \frac{y}{4}\text{TiAl} + \frac{y}{4}Ti_3Al + \left(3 - \frac{5}{3}x - 2y\right)\text{TiC} + \left(z + \frac{4}{3}x + \frac{3}{2}y - 3\right) + \frac{y}{2}Ti_2AlC = Ti_3Si_xAl_yC_z \quad (1300 - 1400\,^\circ\text{C}) \tag{4-13}$$

(x in $Ti_5Si_3C_x$ and y in TiC_y in reaction 4-13 are assumed to be 1 for the sake of simplicity.)

The amount of TiC_x is increased with increasing the temperature from 1400 to 1500 °C, indicating that the high Al content solid solution is stable at low temperature. Based on our experience on preparing Ti_3SiC_2, the existence of TiC_x in the final product is caused by the deficiency of Si in initial materials. In order to prepare monolithic solid solution with high Al content, we should enhance the Si content in the initial materials and decrease the synthesizing temperature. Fig. 6 is the XRD pattern of 3Ti/0.6Si/0.5Al/1.84C

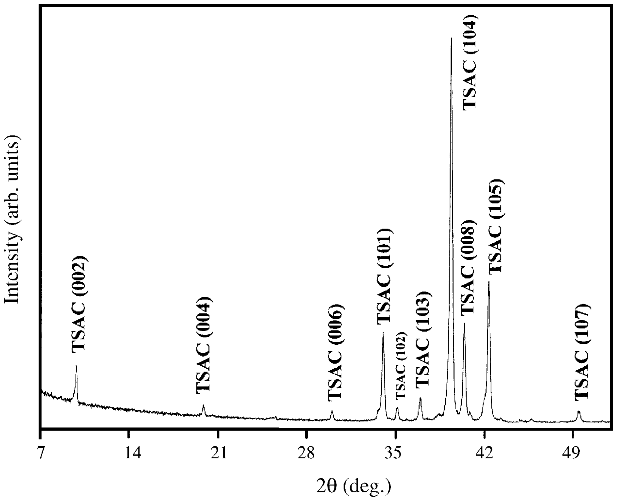

Fig. 6. XRD pattern of 3Ti/0.6Si/0.5Al/1.84C mixed powders heated at 1400 °C for 0.5 h.

mixed powders heated at 1400 °C for 0.5 h. It is found that increasing the amount of Si and simultaneously decreasing the amount of graphite remove TiC_x. This indicates that the stoichiometric ratio of silicon and graphite must be deviated from that of Ti_3SiC_2 in order to synthesize a monolithic solid solution with high Al content. So Si is deficient and C is surplus in terms of the composition of 3Ti/0.5Si/0.5Al/2C in present experiment, making for the formation of TiC_x in the final product easily. And it is clear why TiC_x exists in the final product for this composition.

5. Conclusions

In this work, we investigated the formation route of Ti_3SiC_2 during the in situ hot pressing/solid–liquid reaction synthesis and the effect of Al additive on this process. Ti_3SiC_2 mainly formed through the consumption of $Ti_5Si_3C_x$, TiC_x, $TiSi_2$ and graphite at 1400–1500 °C. The impurity TiC_x was removed from Ti_3SiC_2 by adding a small amount of Al during preparation. This was owing to the fact that the addition of a minor quantity of Al increased the amount of "effective TiC_x" and relatively decreased that of "invalid TiC_x". The addition of significant amounts of Al altered the original stoichiometric ratio of Si and C in Ti_3SiC_2. Monolithic $Ti_3Si(Al)C_2$ solid solution with high Al content could be synthesized by increasing the amount of Si and simultaneous decreasing the amount of C in the initial materials.

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