

Solid–liquid reaction synthesis of layered machinable Ti_3AlC_2 ceramic

Xiaohui Wang and Yanchun Zhou*

Shenyang National Laboratory for Materials Science, Institute of Metal Research,
Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, PR China.

E-mail: yczhou@imr.ac.cn; Fax: +86-24-23891320; Tel: +86-24-23843531 ext 55180

Received 26th September 2001, Accepted 16th November 2001

First published as an Advance Article on the web 24th January 2002

Fully dense polycrystalline Ti_3AlC_2 was fabricated by a solid–liquid reaction synthesis and simultaneous *in-situ* hot pressing of a mixture of Ti, Al and graphite powders at 1500 °C and 25 MPa for 5 minutes and subsequently annealing at 1200 °C for 20 minutes. The effects of various parameters including composition of the initial elemental powders, temperature as well as the hot pressing pressure on the purity, formation and densification of Ti_3AlC_2 were examined. In addition, the reaction path for the formation of Ti_3AlC_2 was investigated by DTA, XRD, SEM and EDS, suggesting that the reaction path during the heating process could be reasonably described as follows: Al powder melted at some 660 °C and coated the Ti particles; at about 740 °C the exothermic reactions between Al and Ti occurred and Ti–Al intermetallics like TiAl and Ti_3Al were formed; the diffusion of carbon in the Ti–Al intermetallics at elevated temperature resulted in the carbides Ti_2AlC , Ti_3AlC and TiC; and finally these carbides and the unreacted graphite reacted at about 1420 °C to yield Ti_3AlC_2 .

1 Introduction

Ti_3AlC_2 , a layered ternary carbide belonging to the ‘312’ family (*i.e.* Ti_3SiC_2 , Ti_3GeC_2 , Ti_3AlC_2), was identified in 1994 by Pietzka and Schuster¹ in the sample prepared by sintering of cold-compacted powder mixtures of titanium, TiAl, Al_4C_3 , and carbon under pure hydrogen for 20 hours. It has a crystal structure isotypic with Ti_3SiC_2 ² which possesses a unique combination of the properties of both metals and ceramics.^{3–7} Like Ti_3SiC_2 , Ti_3AlC_2 crystallizes in a hexagonal structure with a space group of $P6_3/mmc$. The structure of Ti_3AlC_2 can be described as two edge-shared layers of Ti_6C octahedra sandwiched between two-dimensional-close-packed sheets of Al atoms. Fig. 1 shows the crystal structure of Ti_3AlC_2 and because of this structural feature, Ti_3AlC_2 is expected to have properties similar to Ti_3SiC_2 . However, hitherto few methods for the fabrication of Ti_3AlC_2 have been reported. Tzenov *et al.*⁸ synthesized bulk Ti_3AlC_2 by reactive hot isostatic pressing of a mixture of titanium, Al_4C_3 and graphite powders at a pressure of 70 MPa and temperature of 1400 °C for 16 hours. They also investigated the mechanical, electrical and thermal properties of Ti_3AlC_2 . The results revealed that Ti_3AlC_2 combined an unusual set of properties. Like ceramics, it is light-weight, elastically stiff with a Young’s modulus of 297 GPa and a shear modulus of 124 GPa,⁹ and retains its strength to higher temperatures. Like metals, it is a good electrical and thermal conductor, readily machinable, damage-tolerant at room temperature and resistant to thermal shock. Meanwhile, Tzenov *et al.*⁸ also claimed that about 4 vol% Al_2O_3 was present in the final product of Ti_3AlC_2 synthesized by the reactive hot isostatic pressing process using titanium, Al_4C_3 and graphite as starting materials. They supposed that the reaction between Al_4C_3 and H_2O accounts for the formation of Al_2O_3 because Al_4C_3 is hygroscopic.⁸ There is no doubt that the presence of Al_2O_3 impurities in Ti_3AlC_2 is deleterious to the precise measurements of its intrinsic properties. In addition, the method proposed by Tzenov *et al.*⁸ is a time-consuming and high-cost process.

In the present work, we report a novel solid–liquid reaction synthesis and simultaneous *in-situ* hot pressing process for the fabrication of fully dense Ti_3AlC_2 with high purity utilizing commercially available elemental powders of Ti, Al and graphite as initial materials. This process provides the advantages of short synthesis time, simultaneous synthesis and densification, and high purity. The effects of various parameters including composition of the initial powders, temperature and hot pressing pressure on the purity, formation and densification of Ti_3AlC_2 have been systematically examined. Moreover, the reaction path for the formation of Ti_3AlC_2 from elemental powders was proposed.

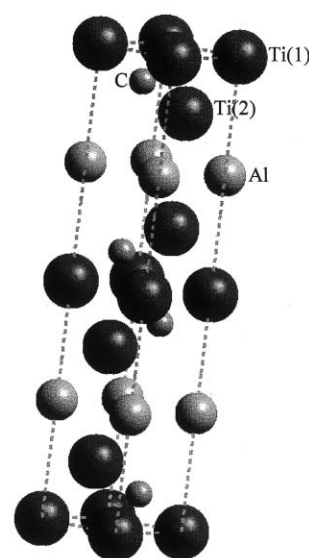


Fig. 1 Crystal structure of Ti_3AlC_2 .

2 Experimental

In our previous works, we have successfully synthesized Ti_3SiC_2 ,¹⁰ Ti_2AlC ¹¹ and Ti_2SnC ¹² utilizing the solid–liquid reactions between the elemental powders to significantly reduce the synthesis time. In the present work, we select commercially available elemental powders of Ti (99%, 300 mesh), Al (99.5%, 300 mesh) and graphite (98%, 200 mesh) as starting materials to develop a rapid and economical route for fabricating fully dense Ti_3AlC_2 . The starting Ti, Al and graphite powders were first weighed according to the Ti : Al : C molar ratio of 3 : 1 : 2 to synthesize stoichiometric Ti_3AlC_2 . Then they were mixed in a polyurethane jar, in which stainless steel balls coated with a layer of polyurethane were used as mixing balls, for 12 hours. The mixed powders were subsequently dried and compacted uniaxially under a pressure of 10 MPa in a graphite mold pre-sprayed with a layer of BN. The solid–liquid reaction synthesis and simultaneous *in-situ* hot pressing process were performed in a furnace using graphite as heating element in a flowing Ar atmosphere. Prior to heating the compacted mixture of elemental powders, the furnace was evacuated using an oil pump. The compacted mixture was first heated at a heating rate of $10^\circ\text{C min}^{-1}$ from ambient temperature to 1500°C and held at that temperature for 5 minutes, at which point a pressure of 25 MPa was applied. Then the mixture was cooled rapidly down to 1200°C and held at that temperature for 20 minutes. Finally, the sample was cooled down to room temperature. A slab of 50 mm in diameter and 10 mm in height was obtained after withdrawal from the graphite mold. The surface layers of the as-prepared slabs were machined off to avoid contamination from the graphite mold as well as the pre-sprayed BN layer. X-Ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) were used for phase identification, microstructure observation and elemental analysis, respectively. Microstructure observations were conducted in an S-360 scanning electron microscope (Cambridge Instruments, UK) equipped with a Link ISIS 300 energy dispersive spectroscopy system (Oxford Instruments, UK).

To study the effect of the composition of the elemental powders on the purity of Ti_3AlC_2 , three sets of starting elemental powders with slightly modified compositions according to the Ti : Al : C molar ratios of 3 : 1 : 2, 3 : 1.1 : 1.9 and 3 : 1.1 : 1.8, were subjected to the hot pressing runs. Elemental analyses were conducted on the prepared materials. The amounts of Ti and Al were determined by ICP-AES method in a 3410+ ICP-AES. The amount of C was obtained by IR adsorption of CO_2 formed from combustion in a CS-444LS carbon and sulfur analyzer (Leco. Corp., USA). The effects of temperature on the formation of Ti_3AlC_2 were investigated *via* parallel runs conducted in the temperature range of 1100°C to 1400°C for 1 hour. Pressureless sintering procedures on three sets of the starting elemental were also respectively conducted to evaluate the effect of the hot pressing pressure on the densification of Ti_3AlC_2 . To investigate the reaction path for the formation of Ti_3AlC_2 during the heating of the elemental powders, differential thermal analysis (DTA) was performed in a Pyris 7 DTA apparatus (Perkin-Elmer Instruments, USA), and parallel runs in the temperature range $800\text{--}1500^\circ\text{C}$ were also carried out.

3 Results and discussion

3.1 Effects of processing parameters on the fabrication of bulk Ti_3AlC_2

3.1.1 Effect of the composition of the starting elemental powders on the purity of Ti_3AlC_2 . Our initial interest is in the synthesis of stoichiometric Ti_3AlC_2 . Hot pressing the compacted mixture of the starting elemental powders with the

stoichiometric composition of Ti_3AlC_2 at 1500°C and 25 MPa for 5 minutes and subsequently annealing at 1200°C for 20 minutes resulted in the desired Ti_3AlC_2 phase and TiC as impurity phase. Attempts were then made by modifying the synthesis conditions to obtain monolithic Ti_3AlC_2 but TiC was always observed in the final product, as indicated by the powder XRD pattern shown in Fig. 2(a). In the previous report,⁸ Ti_3AlC_2 without TiC impurities was obtained by selecting the starting materials with a Ti : Al : C molar ratio of 3 : 1.1 : 1.8. The co-existence of TiC with Ti_3AlC_2 is attributed to the surplus of carbon in the starting powders. Therefore, we selected two other compositions with less carbon and richer in Al according to the Ti : Al : C molar ratios of 3 : 1.1 : 1.8 and 3 : 1.1 : 1.9, respectively. The powder XRD patterns of the samples obtained from the starting elemental powders with the Ti : Al : C molar ratios of 3 : 1.1 : 1.9 and 3 : 1.1 : 1.8 are shown in Fig. 2(b) and Fig. 2(c), respectively. It is seen that for the sample obtained from the starting elemental powders with the Ti : Al : C molar ratio of 3 : 1.1 : 1.8, no other phases but Ti_3AlC_2 were detected, which is consistent with the previous result.⁸ To examine if the final products retained the initial elemental compositions, elemental analyses were conducted on the samples prepared from the starting elemental powders with Ti : Al : C molar ratios of 3 : 1.1 : 1.8, 3 : 1.1 : 1.9 and 3 : 1 : 2, respectively. The amounts of Ti and Al were determined by the ICP-AES method. The amount of C was obtained by IR adsorption of CO_2 formed from combustion. For the final sample obtained from the starting elemental powders with a Ti : Al : C molar ratio of 3 : 1.1 : 1.8, the weight composition (wt%) determined by these two methods was 74.0 Ti, 14.9 Al and 11.1 C which is close to the initial composition of the raw material: 73.7 Ti, 15.2 Al and 11.1 C. For the final sample prepared from the starting elemental powders with a Ti : Al : C molar ratio of 3 : 1.1 : 1.9, the weight composition was 74.1 Ti, 14.0 Al and 11.7 C with respect to the starting composition of the raw material: 73.23 Ti, 15.13 Al and 11.63 C. For the final sample obtained from the starting elemental powders with a

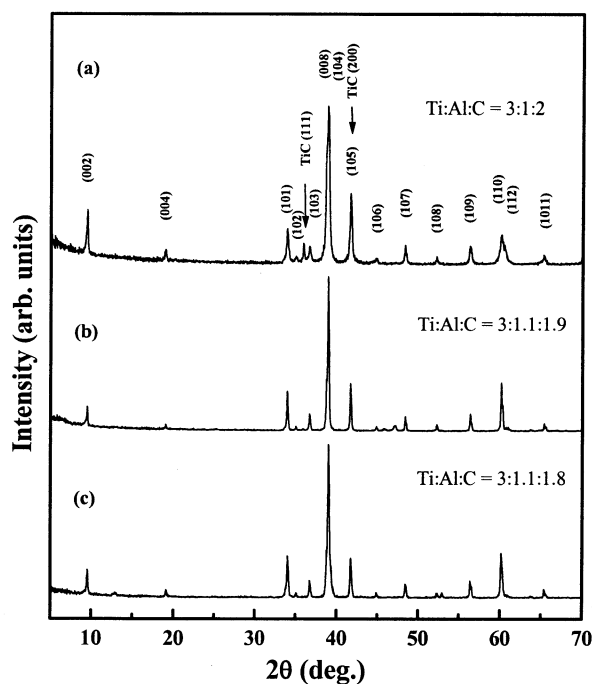


Fig. 2 Powder XRD patterns of the samples obtained from the starting elemental powders of Ti, Al and graphite with Ti : Al : C molar ratios of (a) 3 : 1 : 2, (b) 3:1.1 : 1.9 and (c) 3 : 1.1 : 1.8. Note the effect of the composition of starting materials on the purity of Ti_3AlC_2 .

Ti : Al : C molar ratio of 3 : 1 : 2, the weight composition was 74.2 Ti, 13.6 Al and 12.2 C compared to the starting composition of the raw material: 73.80 Ti, 13.86 Al and 12.34 C. These elemental analysis results suggest that the final materials prepared by the present solid-liquid reaction synthesis and simultaneous *in-situ* hot pressing process basically retained the initial elemental compositions. The Ti_3AlC_2 reported here is based on the sample obtained from the starting elemental powders with a Ti : Al : C molar ratio of 3 : 1.1 : 1.8, and $Ti_3Al_{1.1}C_{1.8}$ will henceforth be referred to as Ti_3AlC_2 unless otherwise specified.

The density of bulk Ti_3AlC_2 measured by the Archimedes method in water was 4.21 g cm^{-3} , which is quite close to the theoretical density of Ti_3AlC_2 (4.25 g cm^{-3}). Impurity phase like Al_2O_3 was not detected in the Ti_3AlC_2 prepared in this work by SEM and XRD within the limitation of the apparatus.

For comparison, Table 1 lists the fabrication details of the previous method⁸ and the present one for the fabrication of bulk Ti_3AlC_2 . It is obvious from Table 1 that the present method has a number of advantages over the previous one. These advantages mainly come from the solid-liquid reactions between the elemental powders of Ti, Al and graphite, and reaction path for the formation of Ti_3AlC_2 will be discussed in detail in section 3.2.

3.1.2 Effect of temperature on the formation of Ti_3AlC_2 . To understand the effect of temperature on the formation of Ti_3AlC_2 as well as to find the probability of decreasing the synthesis temperature without increasing the synthesis time profoundly, the compacted mixtures were heated in the temperature range 1100–1400 °C for 1 hour, respectively. The powder XRD patterns of the elemental powders heated at various temperatures are plotted in Fig. 3 and the corresponding results of phase analyses are summarized in Table 2. It is found from Fig. 3 and Table 2 that heating the compact of elemental powders of Ti, Al and graphite at 1100 °C resulted in the formation of Ti_2AlC , Ti_3Al , $TiAl$, TiC , and the sample contains unreacted graphite. For the sample heated at the higher temperature of 1200 °C, the amounts of Ti_3Al , $TiAl$ and graphite reduced (see Fig. 3). As the temperatures were further increased to 1300 °C or 1400 °C, the samples consisted of Ti_2AlC , Ti_3AlC , TiC and a small amount of graphite without the desired phase of Ti_3AlC_2 . However, once the heating temperature increased to 1500 °C, 5 minutes was enough to obtain the desired Ti_3AlC_2 (see Fig. 2(c)). So it is reasonable to conclude that a rapid reaction took place between 1400 °C and 1500 °C, which will be discussed in section 3.2.

3.1.3 Effect of applied pressure on the densification of Ti_3AlC_2

To investigate the effect of applied pressure on the densification of Ti_3AlC_2 , pressureless sintering procedures on compacted mixtures of the elemental powders with Ti : Al : C molar ratios of 3 : 1 : 2, 3 : 1.1 : 1.9 and 3 : 1.1 : 1.8, were carried out at 1500 °C, respectively. The pressureless sintering

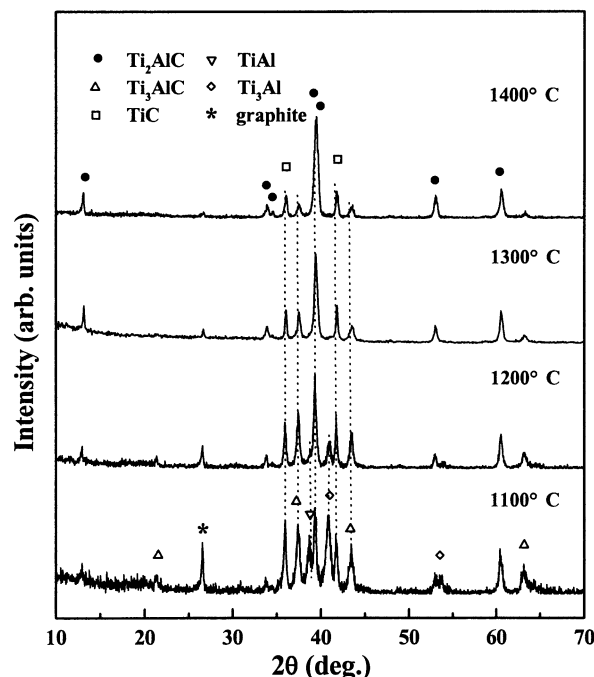


Fig. 3 Powder XRD patterns of the compacted mixtures of the starting elemental powders heated at various temperatures for 1 hour.

Table 2 Summary of phase analysis of the samples heated in the temperature range of 1100 °C–1400 °C for 1 hour

Temperature	Phases present in the samples
1100 °C	Ti_2AlC , Ti_3Al , Ti_3AlC , $TiAl$, TiC , graphite
1200 °C	Ti_2AlC , Ti_3AlC , TiC , graphite, Ti_3Al , $TiAl$
1300 °C	Ti_2AlC , TiC , Ti_3AlC , graphite
1400 °C	Ti_2AlC , TiC , Ti_3AlC , graphite

procedure is similar to the solid-liquid reaction synthesis and simultaneous *in-situ* hot pressing process. The difference between these two procedures is that no pressure was applied in the former. Phase analyses of the pressureless sintered products *via* XRD revealed that Ti_3AlC_2 was formed without the application of pressure at 1500 °C. However, the densities of the sintered compacts were only about 50% of the theoretical value of Ti_3AlC_2 . The application of hot pressing pressure resulted in a considerable increase in the density of Ti_3AlC_2 . For example, fully dense Ti_3AlC_2 was obtained at 1500 °C under a pressure of 25 MPa, demonstrating the significant effect of hot pressing pressure on the densification of bulk Ti_3AlC_2 . It should be noted that the pressure applied in the present work for the fabrication of fully dense polycrystalline Ti_3AlC_2 is much lower than that applied in the previous HIP process⁸ utilizing Ti, Al_4C_3 and graphite as initial powders.

Table 1 Comparison of fabrication details between the previous method⁸ and the present one for the preparation of bulk Ti_3AlC_2

Comparison items	Fabrication details and comments		
	The previous HIP ⁸	HP in the present work	Remarks
Fabrication method	Hot isostatic pressing (HIP)	Hot pressing (HP)	
Starting materials	Ti, Al_4C_3 and graphite	Ti, Al and graphite	Al_4C_3 is hygroscopic
Synthesis temperature	1400 °C	1500 °C	
Holding time	16 hours	5 minutes	
Applied pressure	70 MPa	25 MPa	
Impurity phase	Al_2O_3	None	$Al_4C_3 + 6H_2O \leftrightarrow 2Al_2O_3 + 3CH_4$
Procedure	Complicated	Simple	
Cost	High	Low	

3.2 Reaction path for the formation of Ti_3AlC_2 from elemental powders

In section 3.1.1, we have pointed out that the present solid-liquid reaction synthesis and simultaneous *in-situ* hot pressing process has a number of advantages over the previous one⁸ utilizing Ti, Al_4C_3 and graphite as initial powders. To understand the process well, it is important to study the reaction path for the formation of Ti_3AlC_2 from elemental powders of Ti, Al and graphite. As described above, Ti_3AlC_2 was formed in the pressureless sintering procedure, which provides an opportunity for investigating the reaction path from the starting elemental powders by DTA because pressure was unnecessary when the DTA experiments were conducted.

Fig. 4 shows a typical DTA curve for a pellet of the mixed elemental powders of Ti, Al and graphite with the Ti : Al : C molar ratio of 3 : 1.1 : 1.8 at a heating rate of $10^\circ C \text{ min}^{-1}$ under Ar atmosphere. It can be seen from Fig. 4 that there are several endothermic and exothermic peaks during the heating process. These peaks include a major endothermic peak at $660^\circ C$ and a minor one at around $1350^\circ C$, respectively; and major exothermic peaks at around $740^\circ C$, $895^\circ C$ and $1420^\circ C$, respectively. The major endothermic peak at $660^\circ C$ corresponds to the melting of aluminium, which created a warm liquid environment for the reactions that will be ignited at higher temperature. To understand the phase evolution during the heating process, parallel runs were carried out in the temperature range $800\text{--}1400^\circ C$, *i.e.* compacts of the mixed elemental powders were heated from ambient temperature to the requisite temperature and held at that temperature for 5 minutes without the application of pressure and then cooled rapidly down to room temperature. The samples after parallel runs were examined by XRD, SEM and EDS for phase identification, microstructure observation and qualitative elemental analysis, respectively. The powder XRD patterns of the samples heated in the temperature range $800\text{--}1400^\circ C$ are plotted in Fig. 5(a)–(d) and the corresponding results of phase analyses are summarized in Table 3. The corresponding back-scattered electron micrographs of the samples heated at various temperatures are presented in Fig. 6(a)–(d) to show the microstructure evolution of the samples with temperature. For the sample heated at $800^\circ C$, the newly formed phases, Ti–Al intermetallics of TiAl and Ti_3Al in crystalline form, are identified *via* XRD. The microstructure of the sample shows that gray island-like particles are separated by a black substrate (see Fig. 6(a)). Carefully performed SEM-EDS studies revealed

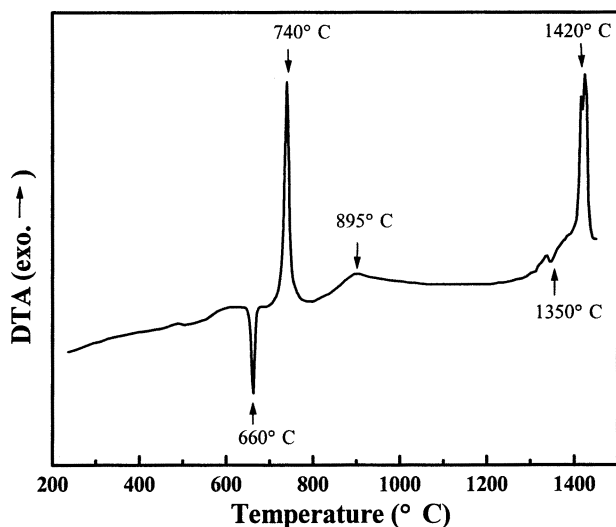


Fig. 4 Typical DTA curve at a heating rate of $10^\circ C \text{ min}^{-1}$ for a pellet of the starting materials indicating the endothermic peaks at $660^\circ C$ and $1350^\circ C$; and the exothermic peaks at $740^\circ C$, $895^\circ C$ and $1420^\circ C$, respectively.

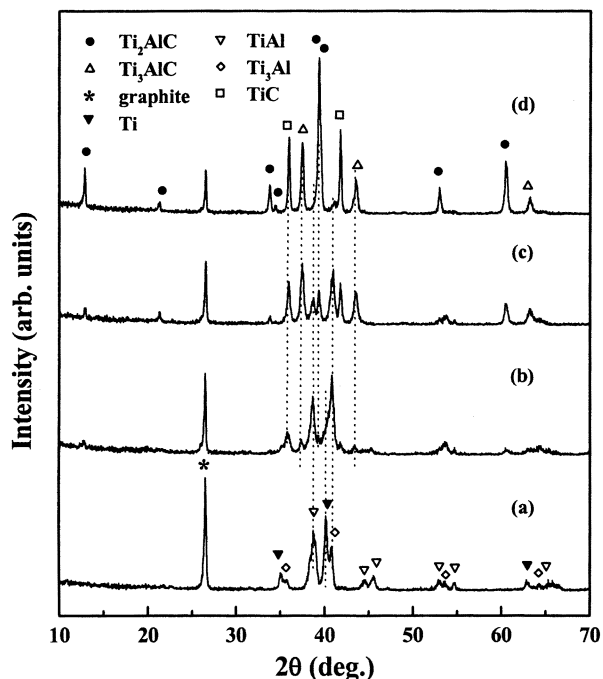


Fig. 5 Powder XRD patterns of the compacted mixtures of starting elemental materials heated at (a) $800^\circ C$, (b) $1000^\circ C$, (c) $1200^\circ C$ and (d) $1400^\circ C$ for 5 minutes.

Table 3 Summary of phase analysis of the samples heated in the temperature range of $800^\circ C\text{--}1400^\circ C$ for 5 minutes

Temperature	Phases present in the samples
$800^\circ C$	Graphite, Ti, TiAl, Ti_3Al
$1000^\circ C$	Graphite, Ti_3Al , TiAl, Ti_3AlC , Ti, Ti_2AlC , TiC
$1200^\circ C$	Graphite, Ti_3AlC , Ti_3Al , TiC, Ti_2AlC , TiAl
$1400^\circ C$	Ti_2AlC , TiC, Ti_3AlC , graphite, Ti_3Al

that the black substrate was graphite and the gray regions contained both elements of Ti and Al, while the inner parts of the gray regions were free of Al and were identified as pure Ti. In combination with the results of DTA, XRD and EDS analyses, it seemed that Al particles melted at $660^\circ C$ and subsequently wrapped around the Ti particles, and led to the formation of Ti–Al intermetallics at $740^\circ C$ (Fig. 4). As the temperature increased to $1000^\circ C$, the diffraction peaks associated with carbides of Ti_3AlC , Ti_2AlC and TiC are detected, which means that carbides began to form as the result of the diffusion of carbon in the Ti–Al intermetallics between $800^\circ C$ and $1000^\circ C$. The broad exothermic peak at around $895^\circ C$ in the DTA curve (Fig. 4) indicates a warm reaction takes place in the temperature range of $800^\circ C$ to $1000^\circ C$. It is seen from Fig. 6(b) that the significant change in the microstructure of the sample heated at $1000^\circ C$ is the growing of gray regions and the shrinkage of black ones. The gray regions seem to have a close connection with each other. As the temperature was further increased to $1200^\circ C$, the intensities of diffraction peaks from Ti_3AlC , Ti_2AlC and TiC became stronger (Fig. 5(c)), when compared to those in the sample heated at $1000^\circ C$ (Fig. 5(b)); traces of Ti_3AlC_2 were not yet detected. Further shrinkage of the black regions and increase of the gray ones are observed in the back-scattered electron micrograph of the sample treated at $1200^\circ C$ (see Fig. 6(c)). Therefore, we suppose that in the temperature range $1000\text{--}1200^\circ C$, warm diffusion reactions dominated because no new phases formed at $1200^\circ C$, which is in good agreement with the DTA curve (Fig. 4). Heating the elemental powders at $1400^\circ C$ for 5 minutes resulted in the increase of the intensities of

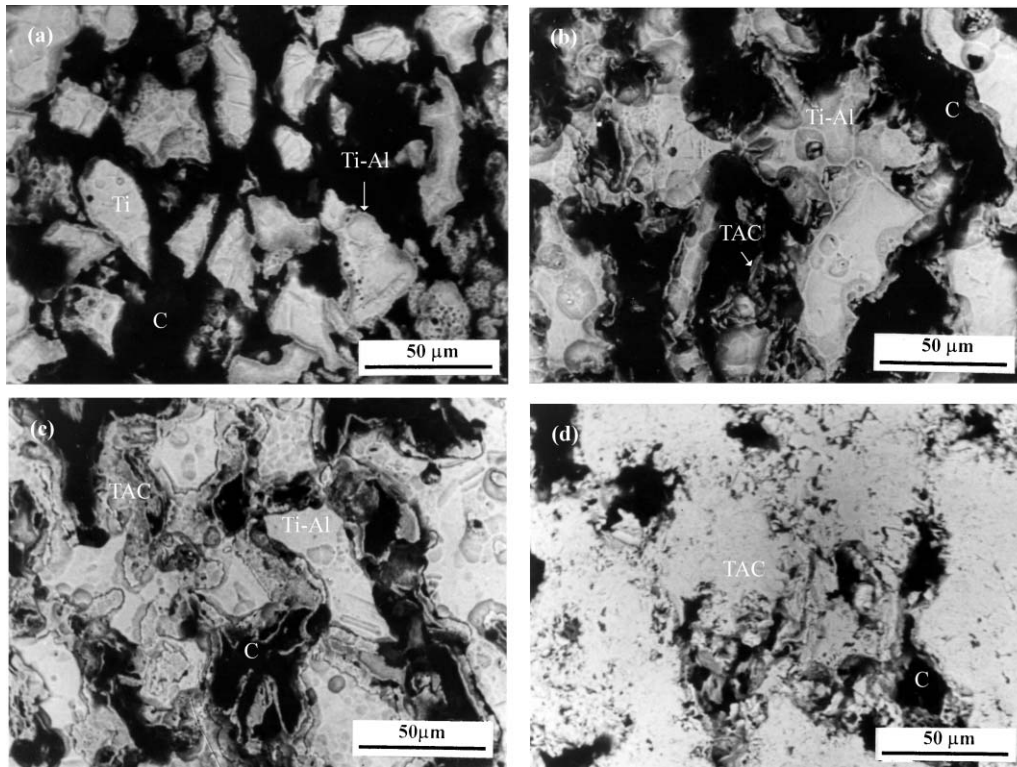


Fig. 6 Corresponding back-scattered electron micrographs of the samples heated at (a) 800 °C, (b) 1000 °C, (c) 1200 °C and (d) 1400 °C for 5 minutes. C = graphite; Ti–Al = Ti₃Al, TiAl; TAC = Ti₂AlC, Ti₃AlC, TiC.

diffraction peaks from carbides like Ti₂AlC, Ti₃AlC and TiC (see Fig. 5(d)). From the back-scattered electron micrograph presented in Fig. 6(d), it is found that black regions containing mostly unreacted graphite shrank further, and were isolated by gray connected regions that consisted of Ti₂AlC, Ti₃AlC and TiC. However, as the temperature was further raised to 1500 °C, no other phase but Ti₃AlC₂ is present as shown in the powder XRD pattern (Fig. 2(c)). The SEM micrograph of the etched sample heated at 1500 °C is shown in Fig. 7. In this regard, it is reasonable to conclude that the formation of Ti₃AlC₂ was the result of reactions between Ti₂AlC, TiC, Ti₃AlC and graphite in the temperature range 1400–1500 °C. This conclusion was confirmed by the sharp exothermic peak at 1420 °C in the typical DTA curve (Fig. 4). It is also interesting to note from Fig. 4 that there is a minor endothermic peak around 1350 °C in the DTA curve followed by a sharp exothermic peak that accounts for the formation of Ti₃AlC₂. So it is plausible to regard this minor peak as the melting of

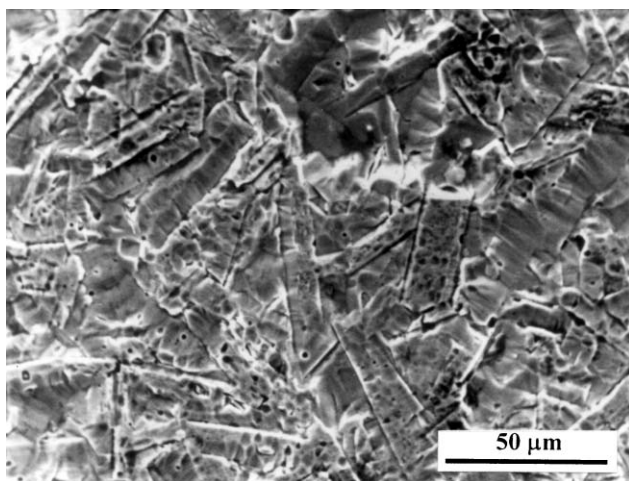
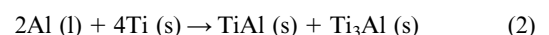


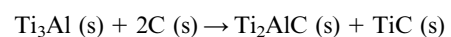
Fig. 7 SEM micrograph of the etched sample heated at 1500 °C for 5 minutes.

some intermediate phase. The intermediate phase is most likely the non-stoichiometric Ti–Al intermetallics. The melting of some intermediate phase gave a liquid environment that was favorable for the reactions at higher temperature (1420 °C) to form Ti₃AlC₂ as well as its densification. The term solid–liquid reaction used in this work just comes from the endothermic reactions (660 °C for the melting of Al, 1350 °C for the melting of some intermediate phase) that gave a liquid environment and favored the exothermic reactions at higher temperatures (740 °C for the formations of Ti–Al intermetallics, 1420 °C for the formation of Ti₃AlC₂). In general, it is reasonable to attribute the advantages of fabricating fully dense Ti₃AlC₂ in the present work to the solid–liquid reactions.

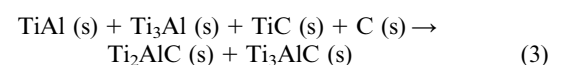
Based on the above results, we propose the reaction path of Ti₃AlC₂ from the elemental powders of Ti, Al and graphite. Firstly, Al melted at 660 °C and coated Ti particles to form Ti–Al intermetallics like Ti₃Al and TiAl at some 740 °C as described in eqn. (1) and (2).



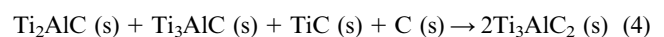
Secondly, at elevated temperature, the diffusion of carbon in Ti–Al intermetallics resulted in the formation of carbides like Ti₂AlC, Ti₃AlC and TiC as follows.



and



Finally, Ti₃AlC₂ formed as the result of the reactions between Ti₂AlC, Ti₃AlC, TiC and unreacted graphite at about 1420 °C.



The reaction path obtained in the present work suggests that

the synthesis of Ti_3AlC_2 can also be realized using the initial materials, such as Ti_2AlC and TiC , Ti_3AlC and graphite, Ti_3Al and graphite.

4 Conclusion

Fully dense polycrystalline Ti_3AlC_2 was fabricated by a solid-liquid reaction synthesis and simultaneous *in-situ* hot pressing process using Ti, Al and graphite as starting materials. This process demonstrates the advantages of short synthesis time, simultaneous synthesis and densification, and high purity. The solid-liquid reactions during the synthesis process are the major contribution to the rapid formation of Ti_3AlC_2 as well as its densification. The present fabrication route provides an easy approach to prepare bulk Ti_3AlC_2 on a large scale as well as to understand and use this technologically important material. The reaction path for the formation of Ti_3AlC_2 from Ti, Al and graphite is proposed as follows: Al powders melted at some $660^\circ C$ and Al melt coated Ti particles to form Ti-Al intermetallics like $TiAl$ and Ti_3Al at about $740^\circ C$; the diffusion of carbon in the Ti-Al intermetallics at elevated temperature led to the formation of carbides Ti_2AlC , Ti_3AlC and TiC ; at $1420^\circ C$ the reactions between these formed carbides and unreacted graphite yielded Ti_3AlC_2 .

Acknowledgements

This work was financially supported by the National Outstanding Young Scientist Foundation for Y. C. Zhou under Grant No. 59925208, the National Science Foundation of China (NSFC) under Grant No. 50072034, '863' program and the IMR Innovative Research Foundation.

References

- 1 M. A. Pietzka and J. C. Schuster, *J. Phase Equilib.*, 1994, **15**, 392.
- 2 W. Jeitschko and H. Novotny, *Monatsh. Chem.*, 1967, **98**, 329.
- 3 M. W. Barsoum and T. El-Raghy, *J. Am. Ceram. Soc.*, 1996, **79**, 1953.
- 4 Y. C. Zhou, Z. M. Sun, J. H. Sun, Y. Zhang and J. Zhou, *Z. Metallkd.*, 2000, **91**, 329.
- 5 H.-I. Yoo, M. W. Barsoum and T. El-Raghy, *Nature*, 2000, **407**, 581.
- 6 M. W. Barsoum, T. El-Raghy and L. U. J. T. Ogbuji, *J. Electrochem. Soc.*, 1997, **144**, 2508.
- 7 Z. M. Sun, Y. C. Zhou and M. S. Li, *Corros. Sci.*, 2001, **43**, 1095.
- 8 N. V. Tzenov and M. W. Barsoum, *J. Am. Ceram. Soc.*, 2000, **83**, 825.
- 9 M. W. Barsoum and T. El-Raghy, *J. Appl. Phys.*, 2000, **87**, 1701.
- 10 Y. C. Zhou, Z. M. Sun, S. Q. Chen and Y. Zhang, *Mater. Res. Innovat.*, 1998, **2**, 142.
- 11 X. H. Wang and Y. C. Zhou, *Z. Metallkd.*, 2002, **93**, 66.
- 12 H. Y. Dong, C. K. Yan, S. Q. Chen and Y. C. Zhou, *J. Mater. Chem.*, 2001, **11**, 1402.