

Combustion synthesis of ternary carbide Ti_3AlC_2 in Ti–Al–C system

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Abstract

In the present work, a method for fabrication of Ti_3AlC_2 by combustion synthesis was developed. Low cost titanium, aluminum and carbon powders were used as raw materials. The effects of the initial ratio among the above-mentioned materials on the combustion behavior and phase formations in the final products were investigated. The experimental results showed that the combustion reaction usually preferred to form a mixture of titanium carbide and aluminum. However, the desired product of Ti_3AlC_2 can be obtained through adjusting the initial ratio of the elemental powders or adding TiC as additives. The formation mechanism of ternary phases, Ti_3AlC_2 and Ti_2AlC , is that the previously formed crystallites of TiC dissolve into the melting Ti–Al composition, and then, ternary phases precipitate from liquid phase and grow into layered morphology. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Titanium aluminium carbide (Ti_3AlC_2), a member of the ternary carbides, was first synthesized by Pietzka and Schuster.^{1,2} Ti_3AlC_2 was recently found to possess unusual properties combining the merits of both metals and ceramics. Like metals it is thermally and electrically conductive, easy to be machined with conventional tools and resistant to thermal shock; like ceramics it presents a high strength, high melting point and thermal stability.³ In contrast to the normal brittle ceramics, Ti_3AlC_2 exhibits some abnormal room-temperature compressive plasticity.³

Ti_3AlC_2 was found to be isostructure with Ti_3SiC_2 .^{4–6} It belongs to a hexagonal crystalline system with lattice parameters of $a = 0.30753$ nm and $c = 1.8578$ nm.^{1,2} The theoretical density of Ti_3AlC_2 is equal to 4.25 g/cm³. Recent high-resolution transmission electron microscopy images have shown that Ti_3AlC_2 exhibits a layered structure, where three almost-close-packed layers of Ti atoms are separated by a layer of Al atoms.⁷

Pietzka and Schuster^{1,2} synthesized Ti_3AlC_2 by sintering cold-compacted powder mixtures of Ti, TiAl, Al_4C_3 , and C under an argon gas atmosphere.

Tzenov and Barsoum³ also synthesized Ti_3AlC_2 through a hot isostatic pressure (HIP) sintering process by using Ti, Al_4C_3 , and C as raw materials.

However, all above mentioned methods for the synthesis of Ti_3AlC_2 need very rigorous conditions, such as high pressure and long sintering time. Moreover, all these methods used Al_4C_3 as the aluminium source for the purpose of avoiding Al lost during the synthesizing process because of the low melting point and high evaporation pressure.

It was reported that Ti_2AlC phase was found in the final product by igniting the mixture of Ti, Al and graphite powders, which the process was designated as combustion synthesis (CS).⁸ Furthermore, many researchers have done some works on combustion synthesis of the Ti–Al–C system composition with aluminium, titanium and carbon as raw materials.^{9–11} However, no ternary carbide was found in their products.

The effort of the present work was focused on the fabrication of Ti_3AlC_2 through the combustion synthesis process by using aluminium, titanium and carbon black as raw materials, of which the main characteristic is the low processing cost.

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2. Experimental procedure

Titanium (99% pure, –300 mesh, GRINM, Beijing, PR China), aluminium (99% pure, –400 mesh, GRINM, Beijing, PR China) and carbon black (Beijing chemical Co., PR China) were used as raw materials. The compositions of the samples were selected from the Ti–Al–C ternary phase diagram,² which are shown in Fig. 1. The specimens obtained after the combustion were designated according to the atomic ratio of Ti, Al, and C. For example, TAC211 means that the atomic ratio of Ti, Al, and C was 2:1:1 in the raw powder mixtures. Typically, the powder mixtures were ball-milled in a plenary rotator at 125 rpm for 8 h, and then cold-pressed into cylindrical bars with dimensions of 50 mm

in length and 25 mm in diameter. The bars were put into a CS reactor, which has been already illustrated in a previous paper.¹² The combustion reaction was ignited by passing an electric current (30 A) through a w-shaped tungsten filament as the reactor was evacuated to a vacuum of 2.33 Pa.

For comparing the differences between the specimen obtained by CS and the specimen obtained by hot pressing (HP), sample HP312 was cold pressed into a pie with the dimension of 10 mm in diameter and 5 mm in height, and the obtained pie was wrapped in graphite sheets and placed in a graphite die, followed by hot pressing at 1400 °C for 4 h under an argon atmosphere.

The phases formed were identified by XRD (Cu target, K_{α} , Rigaku D/max-RB, Japan), and microstructures of the products were analysed by SEM (JSM-6, Japan) with associated facilities for energy dispersive spectroscopy (EDS).

The starting compositions, reaction process and final crystalline phases in different samples are all listed in Table 1.

3. Results and discussion

3.1. Certification about the formation of the Ti_3AlC_2 phase in the combustion product

The XRD result of TAC211 are shown in Fig. 2. The peaks of Ti_2AlC and TiC could be identified. However, there were some peaks that could not be designated from the PDF cards. But these unknown peaks fitted very well with the peaks of Ti_3AlC_2 , which was a new phase reported in recent literature.³ Ti_3AlC_2 phase formation was further confirmed by the appearance of the peak located in $2\theta=9.5^\circ$, which particularly belongs to Ti_3AlC_2 . A typical SEM micrograph of the TAC211 is shown in Fig. 3(a). It could be seen that a layered microstructure had been formed, which corresponded to the structural characteristics of Ti_3AlC_2 and Ti_2AlC .

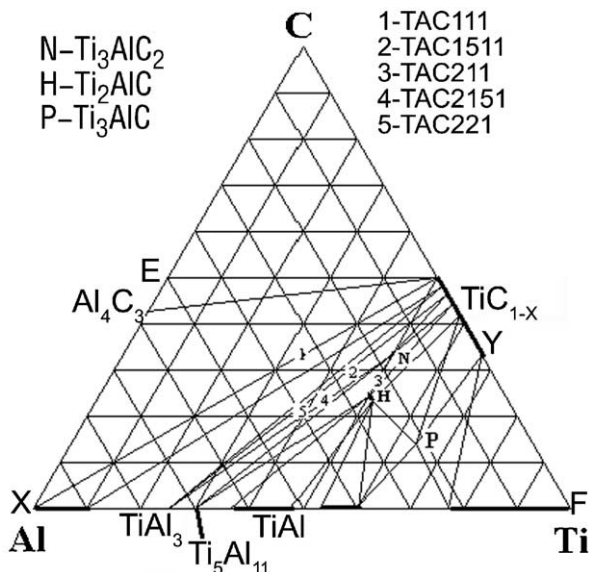


Fig. 1. Isothermal section at 1300 °C of the Ti–Al–C phase diagram.

Table 1
Starting compositions, reaction process and final crystalline phases in different samples

Sample name	Stoichiometry (molar ratio) Ti:Al:C	TiC/wt.%	Location in the phase diagram	Experimental phases of the samples	F value*
TAC111	1:01:01	0	TiC _{1-x} –Al binary line	TiC, Al	0
TAC15 1 1	1.5:1:1	0	TiAl ₃ –TiC _{1-x} –N	TiC, Al, Ti ₃ AlC ₂	0
TAC211	2:01:01	0	H–N binary line	Ti ₃ AlC ₂ , TiC, Ti ₂ AlC	1.005
TAC2 15 1	2:1.5:01	0	TiAl ₃ –N–Ti ₅ Al ₁₁	Ti ₃ AlC ₂ , TiC, Al ₃ Ti	1.308
TAC221	2:02:01	0	TiAl ₃ –N binary line	Ti ₃ AlC ₂ , TiC, Al ₃ Ti	3.249
TAC312	3:01:02	0	N point	TiC, Al, Ti ₃ AlC ₂	0.14
TAC312-20	3:01:02	20	N point	Ti ₃ AlC ₂ , TiC	1.99
TAC312-30	3:01:02	30	N point	Ti ₃ AlC ₂ , TiC	2.96
HP312	3:01:02	0	N point	TiC	0

* $F = I_{Ti_3AlC_2(002)} / I_{TiC(111)}$.

Fig. 3(b) shows the EDS results of the layered crystal, which is marked with a symbol + in Fig. 3(a). The quantitative atomic ratio of Ti and Al was 75.06:24.94, which was quite consistent with the predicted one of 3:1.

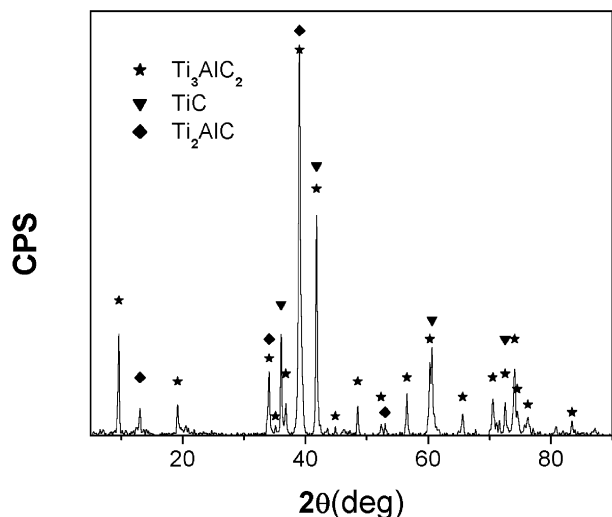


Fig. 2. Phase formation in the products from sample TAC211.

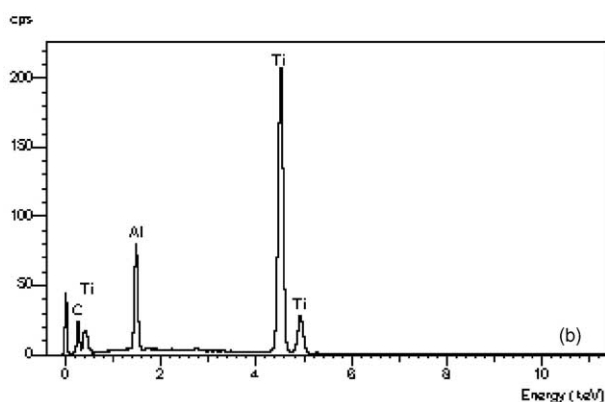
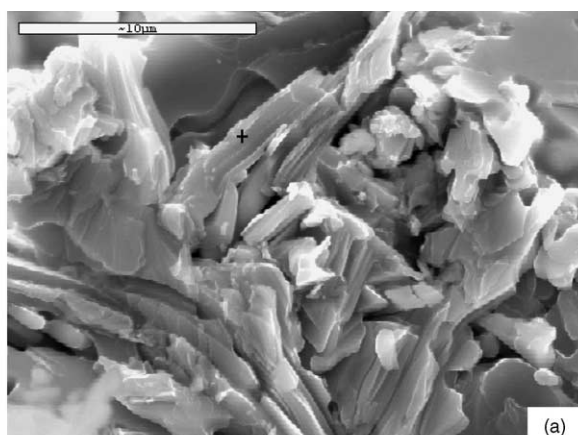


Fig. 3. Morphology of the reaction products obtained from sample TAC211 (a) representative layered areas of TAC211 (b) EDS results of the layered structure marked in (a) with the sign '+'.

The above analysis confirmed that ternary carbides, especially Ti_3AlC_2 could be formed in the CS products by igniting the powder mixture of titanium, aluminium, and carbon black.

3.2. Effect of composition on the phase formations

3.2.1. Effect of the initial ratio of the elemental powders on the phase formations

Fig. 4 shows the XRD patterns of the samples TAC111, TAC1511, TAC211, TAC2151 and TAC221. The peak of Ti_3AlC_2 at $2\theta=9.5^\circ(002)$ and the peak of TiC at $36.1^\circ(111)$ were chosen to represent the relative concentration of these two phases because other phases' peaks do not overlap these two peaks. F was defined as the ratio of $I_{Ti_3AlC_2(002)}/I_{TiC(111)}$, which $I_{Ti_3AlC_2(002)}$ and $I_{TiC(111)}$ represent the intensity of the XRD peaks (002) and (111) of the phases Ti_3AlC_2 and TiC , respectively. The F value was also listed in Table 1.

Considering samples TAC111, TAC1511 and TAC211 in which the atomic proportion of Al and C remained equal to 1, while the Ti content increased from 1 in the sample TAC111 to 2 in the sample TAC211, it was found that Al disappeared and the ternary phases appeared with the increase of Ti, as shown in Fig. 4. The three ratios were on the line EF as shown in Fig. 1. With the increase of Ti, the ratio point moved from the $Ti_{1-x}Al$ binary line to ternary phases locations. This indicated that the surplus of Ti was beneficial to the formation of ternary phases at the atomic ratio Al:C = 1.

Considering TAC211, TAC2151 and TAC221 in which the atomic proportion of Al:C changed from 1:1 in the sample TAC211 to 1.5:1 in the sample TAC2151 and to 2:1 in the sample TAC221, it was found that Ti_2AlC disappeared, while Al_3Ti emerged as Fig. 4

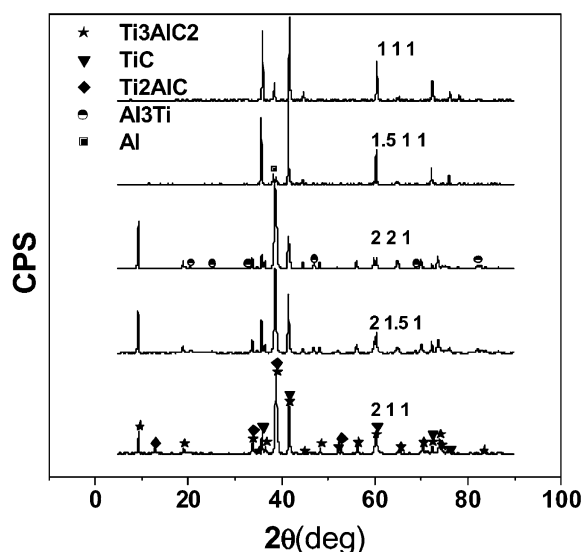


Fig. 4. Phase formations of the reaction products from samples: TAC211, TAC2151, TAC221, TAC1511 and TAC111.

shows. These three ratios were on the line XY as shown in Fig. 1. With the increase of Al, the ratio point moved from the H–N binary line to the $\text{TiAl}_3\text{–N–Ti}_5\text{Al}_{11}$ ternary phases locations, then to the $\text{TiAl}_3\text{–N}$ binary line. This suggested that the surplus of Al was beneficial to the formation of Al_3Ti and, at the same time, for increasing the value of F as the atomic ratio of $\text{Ti:C} = 2$.

The final products of the samples did not completely confirm to the phase diagram because of the Al lose during the combustion synthesis. Table 1 shows the deviation of composition points to the products phase location. It could be found that the amount of Al element in the ultimate products was reduced a little compared with the primitive compositions. This reduction derived from the evaporation of Al from the samples during the combustion reaction due to the low melting point of aluminium and its high vapour-pressure.⁹

This reduction was further confirmed by the product of sample HP312, in which only TiC was found in the final product, while all the aluminium disappeared because the processing time by HP was long enough for evaporating Al completely.

3.2.2. Effect of TiC additive on the phase formations

Fig. 5 shows the XRD patterns of the products of the sample TAC312, sample TAC312–20 and sample TAC312–30 in which 20 or 30 wt% of TiC was separately added as the additive. When the atomic proportion of Ti, Al and C remained equal to 3:1:2 and no TiC was added, as referred to TAC312, the phases of the product were TiC with a little amount of Ti_3AlC_2 phase. However, if the same amount of TiC was added in the sample TAC312 as referred to TAC312–20 and TAC312–30, the ternary phase Ti_3AlC_2 became the dominant phase, in the meanwhile the remaining TiC decreased greatly. This was very interesting since the added TiC decreased the amount of the remaining TiC.

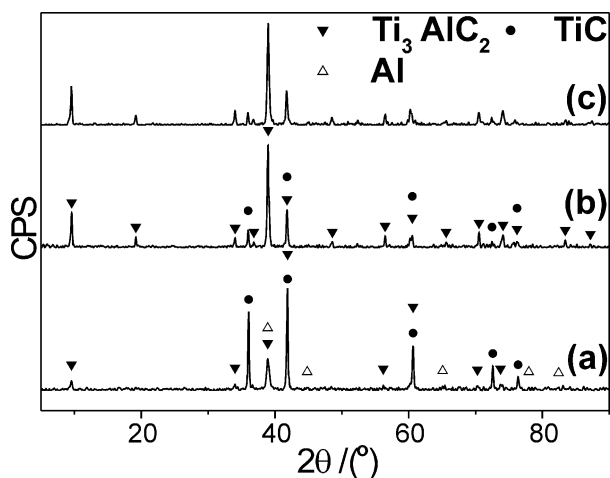


Fig. 5. X-ray diffraction patterns of combustion products in the Ti–Al–C system: (a) TAC312, without TiC addition; (b) TAC312–20, with 20 wt.% TiC; (c) TAC312–30, with 30 wt.% TiC.

3.3. Effects of different elemental ratios on the product morphology

Fig. 6(a) shows the morphology of TAC1511. Combining XRD results in Fig. 4 and the EDS results in Fig. 6(e), it could be observed that the TiC particles were coated with Al. Similar results were also found by Yoon Choi.⁹

Fig. 6(b)–(d) shows the morphology of TAC211, TAC2151 and TAC221, respectively. All the products exhibited similar layered structures characteristic of the Ti–Al–C ternary phases. Moreover, a small amount of equiaxed particles could be found in some areas of the products, which is the representative morphology of TiC.

3.4. Reaction mechanism in Ti–Al–C system

In the present work, Ti–Al–C ternary phases (especially Ti_3AlC_2) were formed for some Ti:Al:C ratios in the starting compositions. Based on previous and the present experimental results, a mechanism of the formation of ternary phases in the Ti–Al–C system was proposed as follows.

When the mixtures of Ti, Al and C powders were ignited at the top of the sample, the combustion wave quickly propagated down through the sample. Firstly, Al would melt and spread into the pores of the sample due to its low melting point. As the combustion temperature increased, a reaction at the interface between Ti and carbon particles started to occur forming a thin layer of TiC_{1-x} and releasing some heat. Then, the formed thin layer of TiC_{1-x} would dissolve into the Ti–Al melt. When the Ti–Al melt became sufficiently supersaturated in carbon, the nucleation of TiC would occur, as reported in previous literature.^{10,13} Under some suitable conditions, for instance when the atomic ratio $\text{Ti:C} = 1$, the carbon supply was sufficient and the Gibbs energy for the formation of TiC is low as shown in Fig. 7.¹⁴ The formed TiC nuclei began to grow. This formation mechanism of TiC has been observed and experimentally certified by many researchers.^{10,13} The reason that no ternary carbide was formed in the previous work^{9–11} was that all the composition points they used were in the TiC–Al binary line which gave TiC and Al as the ultimate products, as shown in Fig. 1.

In our experiments, ternary carbide Ti_3AlC_2 was formed in some certain ratios. Then how did the ternary carbide Ti_3AlC_2 form and grow? Was the ternary carbide Ti_3AlC_2 formed by one step or by some intermediate steps?

Because Ti_3AlC_2 was stable at temperatures of 1100 and 1300 °C but decomposed above 1450 °C,^{2,4} in the temperature rising period, as shown in Fig. 8, the time was too short to form Ti_3AlC_2 or a small amount of Ti_3AlC_2 formed then decomposed due to the high com-

bustion temperatures. While in the cooling period, it had enough time and suitable temperatures for Ti_3AlC_2 to occur and grow. In other words, nucleation and growth of the ternary carbide Ti_3AlC_2 should take place during the cooling period, which can not occur before the formation of TiC.

This deduction was further confirmed by the experimental results of sample TAC312-20 and TAC312-30 with some amount of TiC as diluent in the raw powder

mixtures, in which the ternary phase Ti_3AlC_2 became the dominant phase and the remained TiC in the final product decreased greatly, as shown in Fig. 5. The effect of TiC on the formation process of Ti_3AlC_2 could be explained from a kinetic process and thermodynamic process. In sample TAC312, without TiC addition, TiC was formed from Ti and C through the dissolving and precipitating mechanism. The newly formed TiC could not meet with the demand of TiC to synthesize ternary

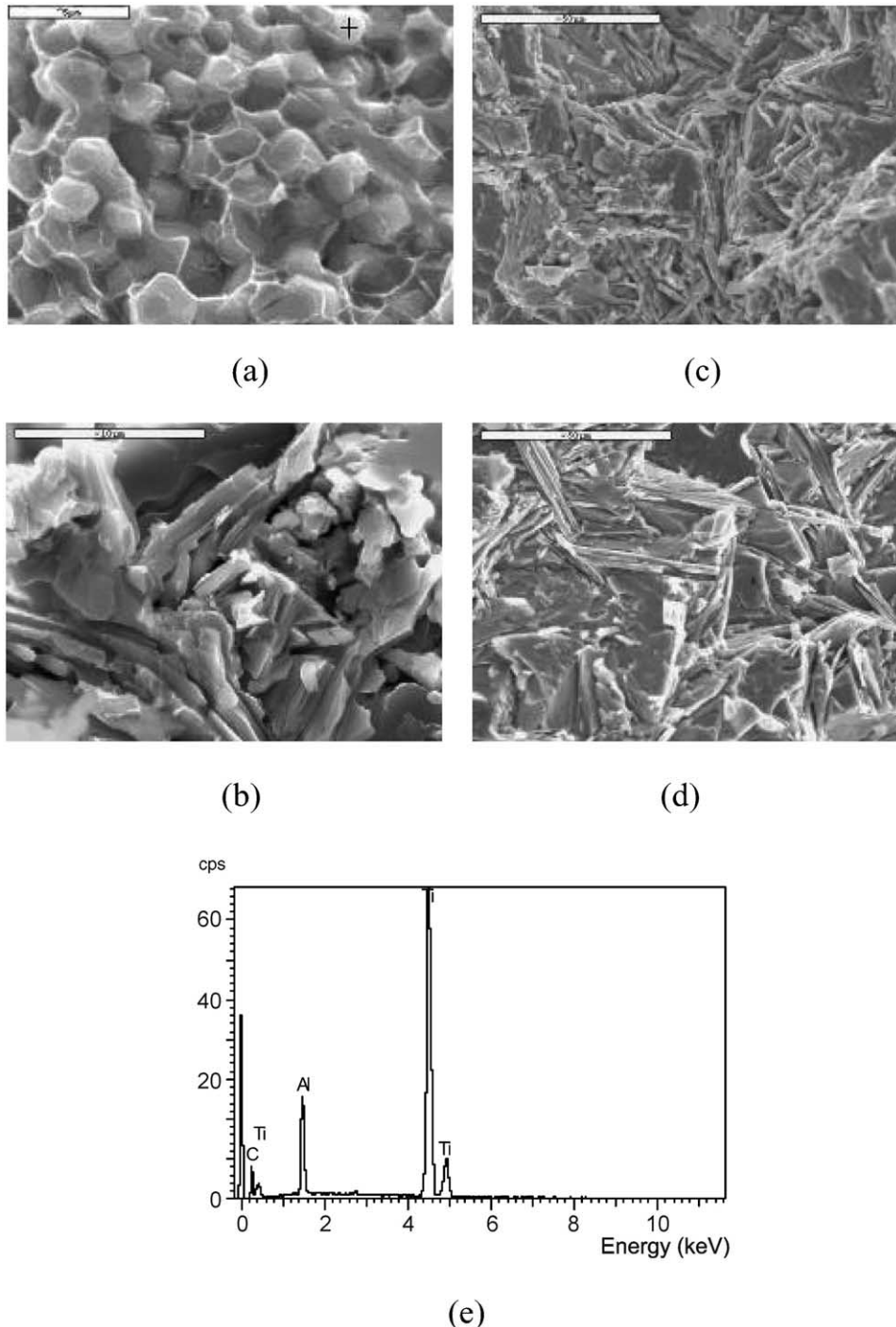


Fig. 6. Morphology and EDS results of samples: (a) TAC1511; (b) TAC211; (c) TAC2151; (d) TAC221; (e) EDS results of (a) '++'.

carbide Ti_3AlC_2 . When the reaction temperature cooled down, ternary carbide Ti_3AlC_2 couldn't be formed under the temperatures and then the main phase was TiC other than ternary carbide Ti_3AlC_2 . As to sample TAC312-30 in which 30 wt.% of TiC was added as additive, the delayed supply of TiC could be overcome and ternary carbide Ti_3AlC_2 could directly form from TiC. Then the velocity of forming ternary carbide Ti_3AlC_2 was increased with the high concentration of TiC. Thus the main phase of sample TAC312-30 was ternary carbide Ti_3AlC_2 other than TiC. From the point of thermodynamic process, TiC additive could also lower the reaction temperature thus reducing the decomposition of ternary carbide Ti_3AlC_2 .

Meanwhile, as the Al increase, the viscosity of the Ti–Al melt decreases making more and more TiC particles dissolve into the melt and transform into the ternary phase Ti_3AlC_2 , which was confirmed by samples TAC211, TAC2151 and TAC221.

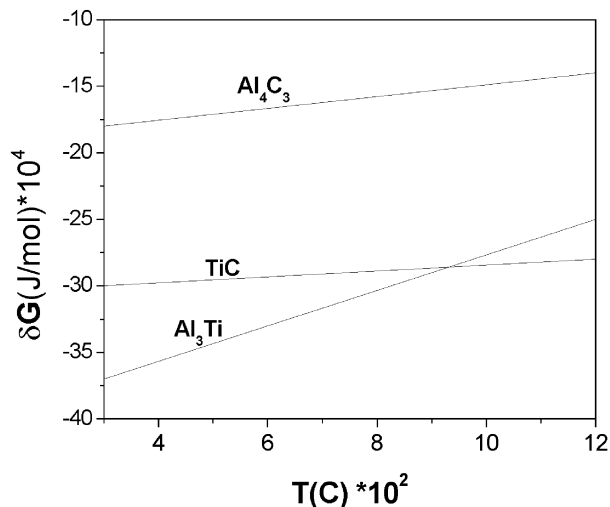


Fig. 7. Gibbs energy for the formation of TiC, Al_3Ti and Al_4C_3 under different temperatures (Ti:Al:C = 1:2:1, molar ratio).

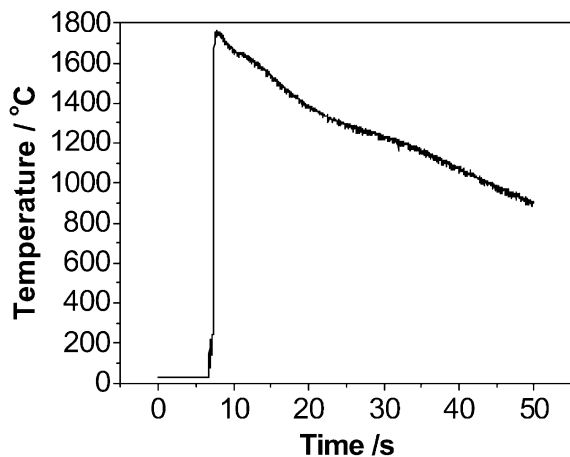


Fig. 8. Temperature–time history of the Ti–Al–C system during the combustion reaction.

The above experimental results suggested that the formation mechanism of ternary phases, Ti_3AlC_2 and Ti_2AlC should go as follows. In the temperature rising period and temperatures above 1450 °C period, Ti–Al melt and TiC crystallites were firstly formed releasing a lot of heat. Then previously formed TiC crystallites began to dissolve into the Ti–Al melt, followed by the precipitation of ternary phases that grow into a layered morphology when the temperature lowered than 1450 °C.

The reaction path should go as follows:



The whole process of synthesizing Ti_3AlC_2 in combustion synthesis could be divided into three stages: preheating stage, initial reacting stage, dissolution and precipitation reacting stage, as was schematically shown in Fig. 9.

3.4.1. Preheating stage

When the combustion wave propagated down, Al would firstly melt and spread and formed Ti–Al melt began to cover the surface of the carbon black.

3.4.2. Initial reacting stage

A reaction at the interface between Ti and carbon particles started to occur forming a thin layer of TiC_{1-X} and releasing some heat. Then, the formed thin layer of TiC_{1-X} would dissolve into the Ti–Al melt. When the Ti–Al melt became sufficiently supersaturated in carbon, the nucleation of TiC would occur.

3.4.3. Dissolution and precipitation reacting stage

Previously formed TiC crystallites dissolved into the Ti–Al melt, and ternary phases began to precipitate from the melt growing into a layered morphology.

Furthermore, rapid temperature rising velocity and very short reaction time, which are the main characteristics of combustion synthesis, revealed to be very important for preventing the excessive losses of Al due to its low melting point and its high vapour-pressure. This can reasonably explain why the layered ternary phases, Ti_3AlC_2 and Ti_2AlC , could be formed by combustion synthesis, while they could not be obtained by HP when starting from the same batch compositions.

4. Conclusions

- (1) The rapid temperature rising velocity and very short reaction time of the combustion synthesis

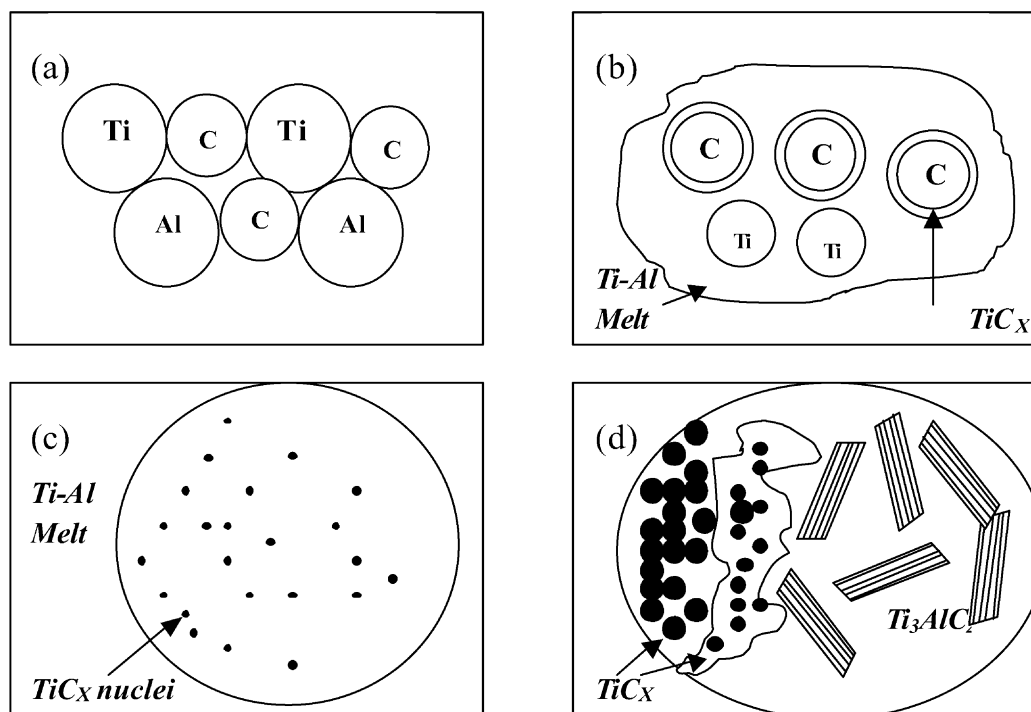


Fig. 9. Proposed reaction mechanisms showing the formation sequence of Ti_3AlC_2 from the elemental powders in CS: (a) Starting powders, (b) appearance of the Ti–Al melt and TiC_x layer, (c) formation of TiC_x nuclei in the Ti–Al melt, (d) some TiC_x nuclei dissolve into the Ti–Al melt and precipitate from the melt forming layered Ti_3AlC_2 and some grow into round TiC crystal wrapped in the melt.

enabled the formation of ternary phase Ti_3AlC_2 by using Ti, Al and C powders as raw materials.

- (2) Adding TiC additive were beneficial for the formation of the ternary phase Ti_3AlC_2 , which could be explained from kinetic process and thermodynamic process.
- (3) The formation mechanism of Ti_3AlC_2 by combustion synthesis is a solution-precipitation mechanism, in which carbon powders in the sample are surrounded by a Ti–Al melt layer and react with titanium in the layer to synthesize TiC particles, and then TiC dissolves into the Ti–Al melt, followed by the precipitation of ternary phase Ti_3AlC_2 which grows into a layered morphology. The model of combustion synthesis of Ti_3AlC_2 can be divided into three stages: pre-heating stage, initial reacting stage, dissolution and precipitation stage.

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