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The phase transformation and microstructure of TiAl/Ti_2AlC composites caused by hot pressing

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Abstract

Two series of raw materials were adopted to form TiAl/Ti_2AlC composites: Ti/Al/TiC and Ti/Al/C. Differential thermal analysis (DTA) of starting powers and X-ray diffraction (XRD) of samples sintered at different temperatures from 600 °C to 1300 °C by hot pressing were utilized to analyze the phase transformation and the mechanism of synthesis. Scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS) was utilized to investigate the morphology characteristics of the products. The experimental results showed that Ti reacted with Al to form TiAl intermetallics below 900 °C; and above 900 °C, TiAl reacted with TiC to produce dense TiAl/Ti_2AlC composites. The products sintered at 1200 °C had fine crystals and dense fibres, and the distribution of Ti_2AlC particles in TiAl matrix was homogeneous.

Keywords: A. Hot pressing; TiAl/Ti_2AlC composites; Phase transformation; Microstructure

1. Introduction

The intermetallic compound TiAl is a potential material for high temperature applications. However, its usage has been limited because of its poor fracture toughness at ambient temperature, insufficient strength at ambient and at elevated temperatures [1,2]. Layered ternary Ti_2AlC ceramic combines unusual properties of both metals and ceramics [3–5]. Therefore, the introduction of a small amount of Ti_2AlC particles into the TiAl matrix to form TiAl/Ti_2AlC composites may help to get the merits of both metals and ceramics.

In the beginning of 1990s, Mabuchi et al. and Ramaseshan et al. [6,7] fabricated TiAl/Ti_2AlC composites by Self-propagating High-temperature Synthesis (SHS) of Ti/Al/C powders mixtures. However, the synthetic products were of a loose form, existed a large number of holes. Recently, dense TiAl/Ti_2AlC composites could be synthesized by Spark Plasma Sintering (SPS) of Ti/Al/TiC powders mixtures [2,8]. In the present research, hot pressing method was used to produce dense TiAl/Ti_2AlC composites from Ti/Al/TiC and Ti/Al/C powders, and the phase transformation and the mechanism of synthesis were especially discussed.

2. Experimental procedures

It is known that TiAl intermetallics show their best mechanical properties with nonstoichiometric proportion of Ti–48 at.% Al [9,10]. So in our research, three series of raw materials were adopted: (a) the element Ti, Al with an atom ratio of $x(\text{Ti}):x(\text{Al}) = 52:48$ to investigate the reaction of the Ti–Al system, marked as A0; (b) Ti, Al and TiC powders with a mixture ratio of $x(\text{Ti}):x(\text{Al}) = 52:48$ and $\varphi(\text{TiC}) = 7\%$ (volume percent) to investigate the reaction of the Ti–Al–TiC system, marked as A7; (c) change the content of TiC in the mixture ratio of A7 into Ti and C, the element Ti, Al and active C powders with a mixture ratio of $x(\text{Ti}):x(\text{Al}):x(\text{C}) = 51.8:42.5:5.75$ to investigate the reaction of the Ti–Al–C system, and was compared with the Ti–Al–TiC system, marked as B7.

The starting materials used in this work were titanium carbide powders (8.4 μm, 99.2% purity), titanium powders (10.6 μm, 99.0% purity), aluminum powders (12.8 μm, 99.8% pure) and carbon black (13.2 μm, 99% pure). All these raw materials were from the Institute of Non-ferrous Metals, Beijing, China. Starting powder mixtures were ground for 24 h

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and then put in graphite dies with a diameter of 16 mm. The graphite dies were placed in a hot pressing furnace and heated at 5 °C/min to 300 °C and then heated at 60 °C/min to the final processing temperature of 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C and 1300 °C, respectively, hold for 2 h. During the whole process the powder mixture was pressed under a pressure of 30 MPa. Final samples were cooled slowly in the furnace. The chamber was filled with Ar atmosphere before and after sintering. The resultant samples were cylindrical with a thickness of 4–6 mm.

Differential thermal analysis (DTA, Model NETZSCH STA 449C Instruments) of starting powers and X-ray diffraction (XRD, D/max-RB) of samples sintered at different temperatures from 600 °C to 1300 °C by hot pressing were utilized to analyze the phase composition. Scanning electron microscopy (SEM, JSM-5610LV) coupled with the energy-dispersive spectroscopy (EDS, Model Phoenix) was employed to investigate the morphology characteristics of the products.

3. Results and discussion

3.1. Phase transformation of the Ti–Al–TiC system

3.1.1. DTA

Differential thermal analysis curves obtained from room temperature to 1200 °C are presented in Fig. 1. There are two curves in Fig. 1: one is the Ti–Al system, the other is the Ti–Al–TiC system. The features of both the curves are similar, which means the reaction procedure of this two systems are comparing. Below 700 °C, the features of two curves are almost entirely similar, with an endothermic peak at 660 °C, corresponding to the melting point of Al. At about 800 °C, two curves show obvious exothermic peaks, corresponding to the reaction of Ti–Al, and the reaction of element powder is more acute. At about 1000 °C, the curve of the Ti–Al–TiC system shows an exothermic peak, which means that a new matter was generated. It will be testified as Ti_2AlC in the following text.

3.1.2. XRD patterns

Figs. 2 and 3 show the X-ray diffraction patterns of A7 samples at different temperatures.

The X-ray diffraction patterns of samples in Fig. 2 were obtained below 900 °C. The peak value of TiC remains unconverted, so TiC did not participate in reaction. This result accords with DTA that the reaction occurred only between Ti and Al. When sintered at 600 °C, there were four phases: Ti, Al, TiC and $TiAl_3$, which indicated that solid state reaction occurred between Ti and Al and $TiAl_3$ was generated before the melting point of Al. When sintering temperature reached 700 °C, the diffraction peak of Al disappeared and that of $TiAl_3$ increased, so Al entirely reacted with Ti and generated intermetallics $TiAl_3$; but unreacted Ti still remained and the phases TiAl and Ti_3Al appeared synchronously. When sintering temperature reached 800 °C, the main phase was TiAl; the phase of $TiAl_3$ disappeared completely, the peak value of Ti_3Al increased and unreacted Ti still remained. When sintering temperature reached 900 °C, the diffraction peak of Ti almost vanished, which meant that Ti reacted completely; the main phases were TiAl and Ti_3Al and the peak value of TiAl increased.

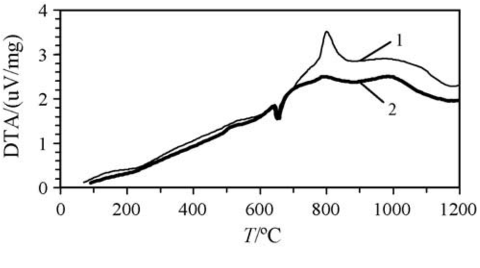

Fig. 1. DTA curves, composition of the curve 1 is $x(Ti):x(Al) = 52:48$, composition of the curve 2 is $x(Ti):x(Al) = 52:48$ and $\varphi(TiC) = 7\%$.

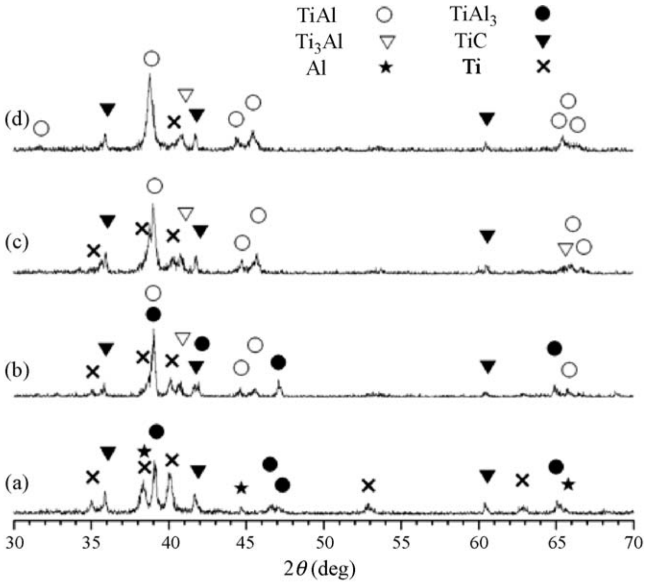

Fig. 2. A7 samples sintered at (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C.

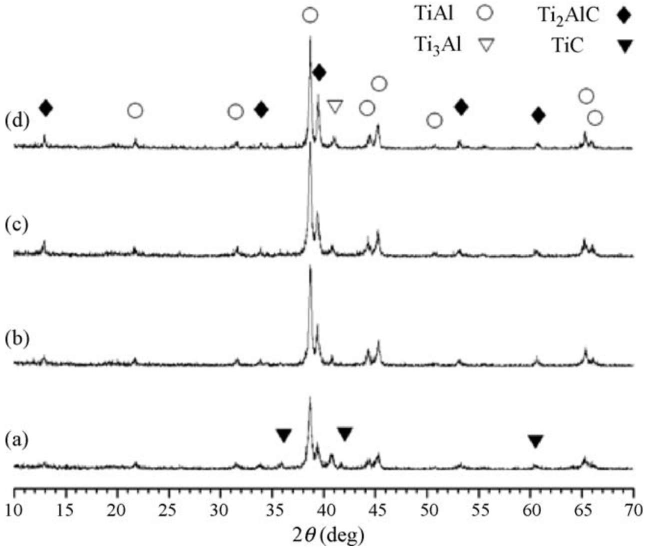

Fig. 3. A7 samples sintered at (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, and (d) 1300 °C.

Fig. 3 shows the X-ray diffraction patterns of samples obtained at 1000–1200 °C. When sintering temperature reached 1000 °C, it is evident that the TiC content reduced and the peak value of Ti_2AlC intensified gradually. It is considered that the reaction occurred: $TiAl + TiC \rightarrow Ti_2AlC$. At 1100 °C, the diffraction peak of TiC disappeared, which means that TiC completely participates in the reaction. At the same time, the diffraction peak of TiAl intensified gradually. The diffraction peak of TiAl showed intensively at 1200 °C, while dropped down at 1300 °C, so the crystal of TiAl developed gradually with the rising temperature and the best crystallinity of TiAl was at 1200 °C.

3.1.3. Mechanism of reaction

The reaction in the Ti–Al–TiC system could be divided into two stages: below 900 °C, Ti reacted with Al; above 900 °C, TiAl reacted with TiC.

$TiAl_3$ phase was detected in XRD patterns at 600 °C, which indicates that the powder particles of Ti and Al underwent a diffuse reaction below the melting point of Al. Above the melting point of Al, unreacted Al thawed, and liquid Al reacted with solid Ti to form $TiAl_3$ on the surface of Ti. Along with the reaction, the element of Al in $TiAl_3$ diffused into Ti, forming Ti_3Al and TiAl. At the anaphase of reaction, $TiAl_3$ worked out and TiAl increased gradually. The final products were coexistent Ti_3Al and TiAl. The reaction of element powder Ti and Al was controlled by diffusion, consisting in the generation of interphase $TiAl_3$.

When sintering temperature reached 900 °C, TiAl reacted with TiC to produce dense TiAl/Ti_2AlC composites. It is commonly considered that the reaction mechanism of this process is solution-precipitation [11]. That is, Ti reacted with Al and released abundant heat that caused the systematic temperature rise, and TiC dissolve into TiAl matrix; as the exothermic reaction finished, the systematic temperature dropped down and ternary phase Ti_2AlC precipitated. In the holding stage, ternary Ti_2AlC developed to a layered polycrystalline structure and composites pyknosis at the meanwhile.

3.2. Phase transformation of the Ti–Al–C system

3.2.1. XRD patterns

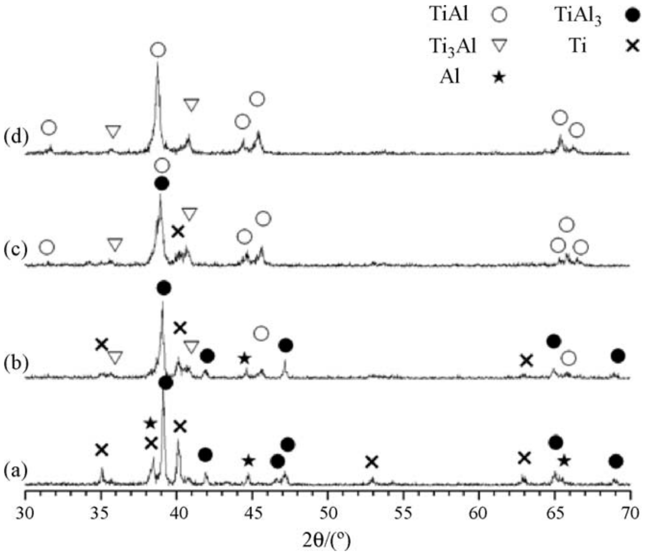

Fig. 4. B7 samples sintered at (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C.

Fig. 4 shows the X-ray diffraction patterns of B7 samples obtained below 900 °C. The reaction occurred between Ti and Al only. The reaction process of Ti and Al in the Ti–Al–C system was similar with that in the Ti–Al–TiC system; when sintered at 600 °C, there were three phases: Ti, Al and $TiAl_3$, which indicated that a solid state reaction occurred between Ti and Al and generated $TiAl_3$ below the melting point of Al. When sintering temperature reached 700 °C, the diffraction peak of Al disappeared and that of $TiAl_3$ increased, so Al entirely reacted with Ti, generating intermetallics $TiAl_3$; but unreacted Ti still remained and the phases TiAl and Ti_3Al appeared synchronously. When temperature reached 800 °C, the main phase was TiAl; the phase of $TiAl_3$ disappeared completely, the peak value of Ti_3Al increased and unreacted Ti still remained. When sintering temperature reached 900 °C, the diffraction peak of Ti almost vanished, so Ti reacted completely; the main phases were TiAl and Ti_3Al and the peak value of TiAl increased.

Fig. 5 is the X-ray diffraction patterns of B7 samples obtained at 1000–1200 °C. When sintering temperature reached 1000 °C and 1100 °C, the diffraction peak of TiC appeared and that of Ti disappeared, so C participated in the reaction: $Ti + C \rightarrow TiC$ at 1000 °C and 1100 °C. At the same time, the peak values of Ti_2AlC intensified gradually. It is considered that the following reaction occurred: $TiAl + TiC \rightarrow Ti_2AlC$. The diffraction peak of TiC disappeared at 1200 °C, which indicated that TiC completely participated in the reaction. At the same time, the diffraction peak of TiAl intensified gradually. The diffraction peak of TiAl showed

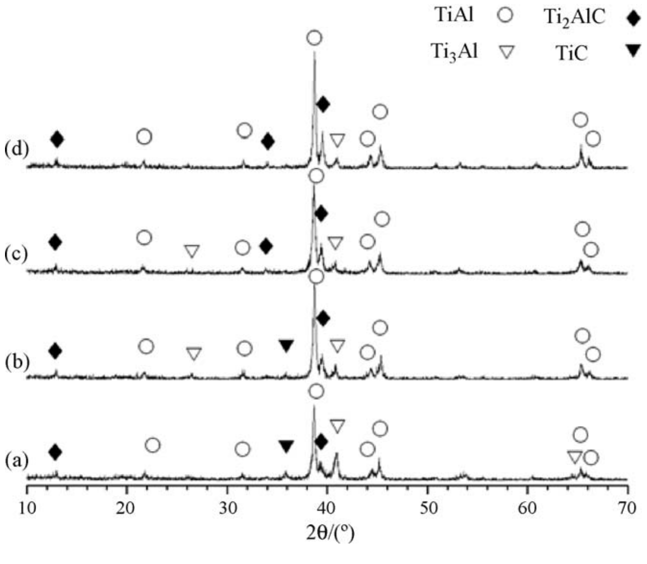

Fig. 5. B7 samples sintered at (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, and (d) 1300 °C.

sharpest at 1200 °C while dropped down at 1300 °C, which means that the crystal of TiAl developed gradually by the rising temperature and the best crystallinity of TiAl was at 1200 °C.

3.2.2. *Mechanism of thermodynamics*

The reaction procedure of the Ti–Al–C system could be divided into three stages. Below 900 °C, Ti reacted with Al to form TiAl intermetallics; above 900 °C, C reacted with remained Ti to form TiC triggered by the exothermal reaction of Ti and Al; TiAl reacted with TiC to produce dense TiAl/Ti_2AlC composites.

At the starting stage of the Ti–Al–C system, possible reactions should be as follows:

$$Ti + C \rightarrow TiC$$

$$3Al + Ti \rightarrow TiAl_3$$

$$4/3Al + C \rightarrow 1/3Al_4C_3$$

According to the solution thermodynamic argument [12], the free energies of $TiAl_3$, TiC and Al_4C_3 are:

$$\Delta G_{TiAl_3} = \Delta G^0_{TiAl_3} + RT\ln\lfloor \gamma_{Ti}\cdot X_{Ti} + (\gamma_{Al}\cdot X_{Al})^3\rfloor, \qquad \Delta G^0_{TiAl_3} = -52503 + 21.48T$$

$$\Delta G_{TiC} = \Delta G^0_{TiC} + RT\ln(\gamma_{Ti}\cdot X_{Ti} + \gamma_C\cdot X_C), \qquad \Delta G^0_{TiC} = -91951 + 34.38T$$

$$\Delta G_{Al_4C_3} = \Delta G^0_{Al_4C_3} + RT\ln[\gamma_C\cdot X_C + (\gamma_{Al}\cdot X_{Al})^{4/3}], \qquad \Delta G^0_{Al_4C_3} = -89611 + 32.84T$$

In the formulas above, ΔG_{TiAl_3}, ΔG_{TiC} and $\Delta G_{Al_4C_3}$ are the free energy of the formation of $TiAl_3$, TiC and Al_4C_3, respectively; $\Delta G^0_{TiAl_3}$, ΔG^0_{TiC} and $\Delta G^0_{Al_4C_3}$ the standard free energy of formation of $TiAl_3$, TiC and Al_4C_3, respectively; γ_{Ti}, γ_{Al} and γ_C the activity coefficient of Ti, Al and C; X_{Ti}, X_{Al} and X_C the molarity of Ti, Al and C, respectively.

By the formulas above, the free energy of the formation of $TiAl_3$, TiC and Al_4C_3 at different mixture ratios and temperatures can be calculated [13]. The results of the free energy of the formation changing with temperature are shown in Fig. 6, and the starting compositions were C/Ti = 1 and 50 at.% Al. In the whole temperature range: $\Delta G_{Al_4C_3} > \Delta G_{TiAl_3}$, $\Delta G_{Al_4C_3} > \Delta G_{TiC}$, which means that Al_4C_3 is an unstable phase in terms of thermodynamics. ΔG_{TiAl} and ΔG_{TiC} changing with temperature generate a crossing point T_{tr} (critical temperature). When $T < T_{tr}$, $\Delta G_{TiAl_3} < \Delta G_{TiC}$, $TiAl_3$ is more stable than TiC; and when $T > T_{tr}$, $\Delta G_{TiAl_3} > \Delta G_{TiC}$, TiC is more stable than $TiAl_3$.

Choi et al. [14] also verified via experiment that the reaction of Ti–Al occurred easily than that of Al–C. These experimental results are also in accord with the thermodynamic theory.

When the sintering temperature reached 1000 °C and 1100 °C, C began to participate in the reaction: $Ti + C \rightarrow TiC$.

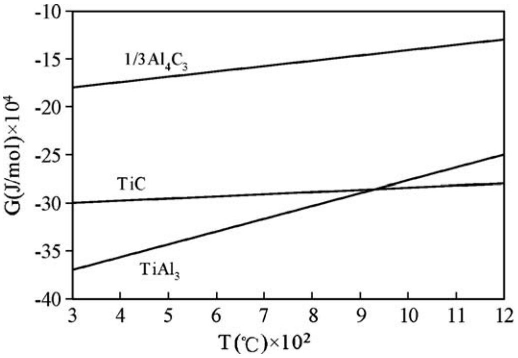

Fig. 6. Free energy of formation changed vs. temperature (C/Ti = 1, 50 at.% Al).

TiC. At the same time, the reaction occurred as follows:

$$TiAl + TiC \rightarrow Ti_2AlC$$

Sintered at 1200 °C, TiC reacted completely. TiC reacted with intermetallics TiAl to form Ti_2AlC.

It is commonly considered that the reaction mechanism of this process is solution-precipitation [7]. That is, Ti reacted with Al and release abundant heat which caused the systematic temperature rise and C react with unreacted Ti to form TiC; as the systematic temperature raised higher, TiC dissolved into TiAl matrix; as the exothermic reaction finished, the systematic temperature dropped down and ternary phase Ti_2AlC precipitated. In the holding stage, ternary Ti_2AlC developed to a layered polycrystalline structure and composites pyknosis at the meanwhile.

3.3. *Microstructure of A7 and B7 samples*

Shown in Fig. 7 are images of the A7 samples sintered at 1200 °C. Combined with EDS, SEM observations of the fracture surfaces shown in Fig. 7(a) displayed that TiAl phase was well-developed with a close and lamellated structure; TiAl particles had the sizes of 5 μm and 8–10 μm in thickness and elongated shape, respectively. Ti_2AlC particles had the sizes of 1 μm and 2 μm in thickness and elongated shape, respectively, with smooth border which is according with the character of solution-precipitation pattern. Fig. 7(b) shows a backscattered electron image of the polished surfaces. Two microzones with different contrast, gray and white, were selected and marked as c and d, corresponding with energy-dispersive spectra (EDS) shown in Fig. 7(c) and (d). The chemical analysis results are listed in Table 1. According to the atom ratio of Ti and Al, gray zones represent TiAl and white zones represent Ti_2AlC. The distribution of Ti_2AlC particles is homogeneous. In addition, Ti_2AlC are agglomerated particles, which needs to be studied in more detail.

Table 1
The atom ratio of A7 samples in the microzones.

	Ti (at.%)	Al (at.%)	*n*(Ti):*n*(Al) (at.%)
Zone c	49.16	50.84	0.97:1
Zone d	67.31	32.69	2.06:1

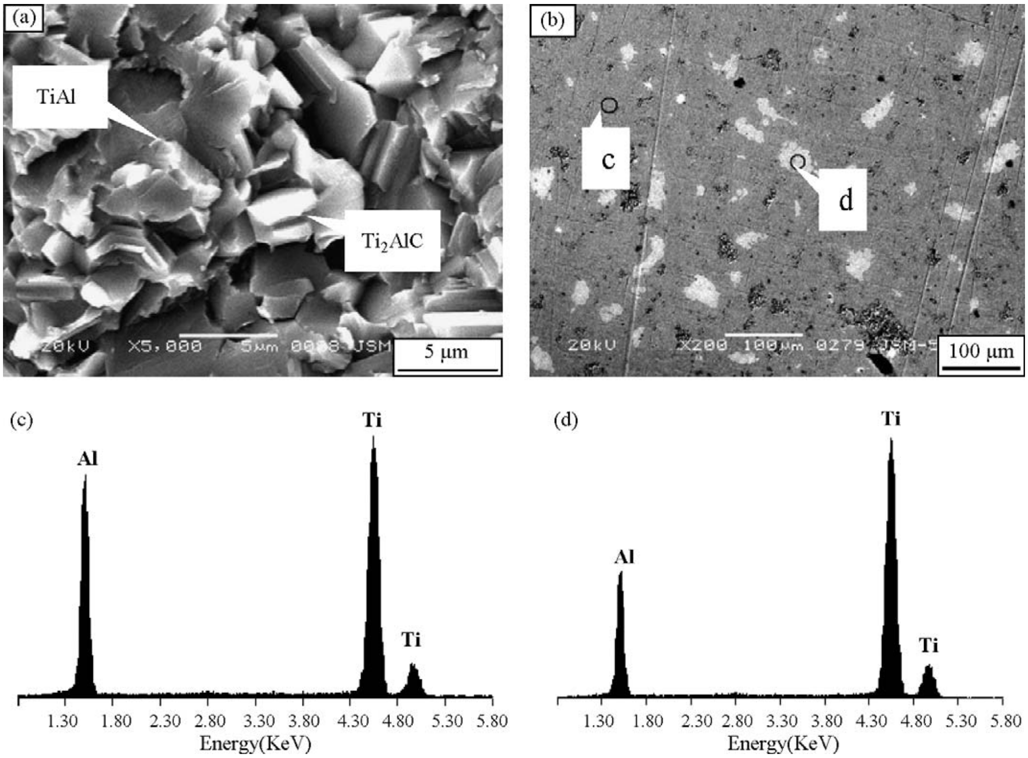

Fig. 7. Images of the A7 samples sintered at 1200 °C. (a) SEM image of the fracture surfaces, (b) backscattered electron image of the polished surfaces, (c) energy-dispersive spectra of zone c, and (d) energy-dispersive spectra of zone d.

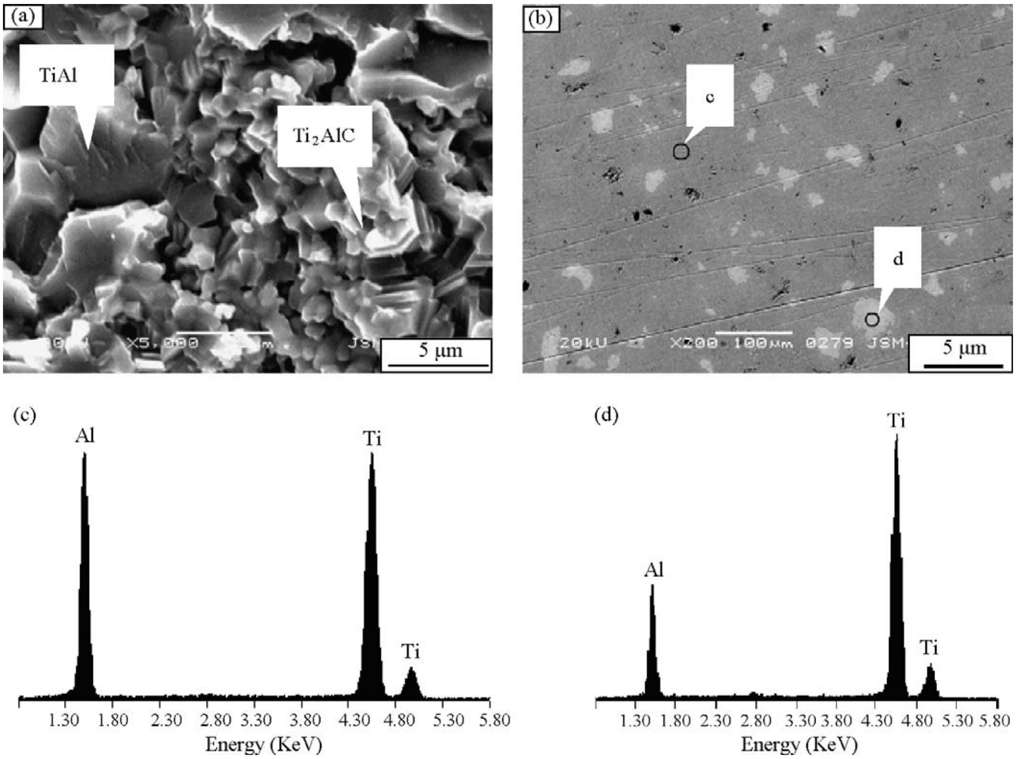

Fig. 8. Images of the B7 samples sintered at 1200 °C. (a) SEM image of the fracture surfaces, (b) backscattered electron image of the polished surfaces, (c) energy-dispersive spectra of zone c and (d) energy-dispersive spectra of zone d.

Table 2
The atom ratio of B7 samples in the microzones.

	Ti (at.%)	Al (at.%)	n(Ti):n(Al) (at.%)
Zone c	47.87	52.13	0.92:1
Zone d	68.36	31.64	2.16:1

Shown in Fig. 8 are images of the B7 samples sintered at 1200 °C. Combined with EDS, SEM observations of the fracture surfaces shown in Fig. 8(a) demonstrate that, TiAl phase was well-developed with a close and lamellated structure; TiAl particles had the sizes of 5 μm and 8–10 μm in thickness and elongated dimension, respectively. Ti_2AlC particles had the sizes of 1 μm and 2 μm in thickness and elongated dimension, respectively, with smooth border which accords with the character of solution-precipitation pattern. Fig. 8(b) shows a backscattered electron image of the polished surfaces. Two microzones with different contrast, gray and white, were selected and marked as c and d, corresponding to EDS shown in Fig. 8(c) and (d). The chemical analysis results as listed in Table 2 reveal that gray zones represent TiAl and white zones represent Ti_2AlC. The distribution of Ti_2AlC particles is homogeneous. Ti_2AlC are agglomerated particles.

4. Conclusions

(1) The reaction of the Ti–Al–TiC system could be divided into two stages. Below 900 °C, Ti reacted with Al to form TiAl intermetallics; above 900 °C, TiAl reacted with TiC to produce dense TiAl/Ti_2AlC composites.

(2) The reaction procedure of the Ti–Al–C system could be divided into three stages. Below 900 °C, Ti reacted with Al to form TiAl intermetallics; above 900 °C, C reacted with remained Ti to form TiC triggered by the exothermal reaction of Ti and Al; TiAl reacted with TiC to produce dense TiAl/Ti_2AlC composites.

(3) In the holding stage of the Ti–Al–TiC system and the Ti–Al–C system, ternary Ti_2AlC developed to layered polycrystals and composites pyknosis at the meanwhile. The mechanism of synthesis was investigated.

(4) The microstructures of the products sintered at 1200 °C were discussed by SEM coupled with EDS. The distribution of Ti_2AlC particles was homogeneous.

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