Microstructural evolution and competitive reaction behavior of Ti-B₄C system under solid-state sintering

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Abstract: By using experimental investigations and theoretical calculations, microstructural evolution and competitive reaction behavior of Ti-B₄C system under solid-state sintering is confirmed. Firstly, B₄C decomposes into B and C atoms followed by diffusing into Ti side immediately, and TiB whiskers form in Ti matrix. Then, Ti atoms diffuse into B₄C via vacancies left by the diffused B and C atoms, leading TiB₂ and carbon substance to form in B₄C side. Subsequently, reaction product carbon diffuses into Ti side and concentration of C in Ti side increases accordingly, resulting in the formation of TiC particles in Ti matrix. With further processing of reaction, both amount and size of products increases gradually. When TiB₂ phases grow into a monolithic layer, diffusion behavior between Ti and B₄C is inhabited, carbon presents to be a loose layer between un-reacted B₄C and TiB₂, and the in situ reaction also stops finally.

Keywords: Metal-matrix composites; Powder metallurgy; Diffusion; Microstructure; Surface and interface

1. Introduction

Because of high elastic modulus and hardness, good biocompatibility and wear

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resistance, similar density and thermal expansion coefficients with titanium matrix, TiC, TiB and TiB₂ ceramics are considered as the best reinforcements for titanium matrix composites (TMCs)[1-3]. Especially, these ceramic phases can be introduced into Ti matrix by in-situ reactions from Ti-B₄C system, which makes matrix-reinforcements interface clean[4]. Hence, intensive attentions have been drawn to Ti-B₄C systems with a wide range of B₄C contents, resulting in (TiC+TiB)/Ti or (TiC+TiB₂)/Ti composites for structural applications as well as TiC-TiB₂ ceramic composites for wear-resistance parts liking forming dies and cutting tools[5-8].

It is well recognized that, there are two potential reaction paths between Ti and B₄C, resulting in the formation of (TiC+TiB) and (TiC+TiB₂), respectively[9,10]. TiB phase always presents to be whisker-like shape and hence leads to greater improvements in stiffness, strength and creep resistance than the particle-like TiB₂ phase, while TiB₂ have much higher modulus and hardness than TiB [11]. To obtain the best performance, TMCs for structural materials always favor (TiC+TiB), but that for wear-resistance parts favor (TiC+TiB₂). Hence, reaction path of Ti-B₄C system should be chosen exactly according to the specific application conditions. Up to now, the reaction path is always predicted by Gibbs free energy change (ΔG), which suggests that reaction products of Ti-B₄C system should be (TiC+TiB) at temperatures higher than 900°C [12]. However, experimental results do not always agree with this conclusion [13-15]. It can be therefore considered that, ΔG criterion is not sufficient to predict reaction path of Ti-B₄C system.

On the other hand, the properties of composites depend not only on the type

but also on size, morphologies and amount of reinforcements. To adjust the later factors, formation mechanism of products should be firstly clarified. Tjong and Ma pointed out in a review paper that [12], the products of Ti-B₄C system under different preparation conditions yield different mechanisms. For example, in the case of combustion assisted casting (CAC) or self-propagation high temperature synthesis (SHS), the formation of products obeys nucleation and growth mechanism. While in the case of traditional casting, the reaction is processed by solid-liquid interface diffusion followed by precipitation. But in the case of solid diffusion reaction such as mechanical alloying (MA) process, the reaction mechanism can be attributed to gradual diffusion of contact powders or SHS reaction ignited by high ball milling energy. However, it is regretful that, there is limited report about microstructural evolution and reaction mechanism of Ti-B₄C system under solid-state sintering, although it is one of the most popular methods to prepare TMCs.

In this paper, to clarify the in-situ reaction behavior of Ti-B₄C system under solid-state, including reaction path and formation process of products, a series of static and in-situ experiments were carried out to investigate microstructural evolution, phase transformation and diffusion behavior during the reaction process between Ti and B₄C. Then, theoretical calculations were performed to study the competitive relationships of potential chemical reactions. Based on the results of experimental research and theoretical analysis, a schematic diagram about the microstructural evolution and reaction behavior of Ti-B₄C system under solid-state was proposed.

2. Experimental details

2.1 DTA analysis

Pure Ti powder (TC-450, $\sim 20\mu\text{m}$) was firstly mixed with 10wt% fine B_4C powder ($\sim 0.5\mu\text{m}$) by rocking milling machine (RM-05, Seiwa Giken) at 60Hz for 2hrs with a ball to powder ratio of 1:5. Then, the powder mixture was cold-pressed into a thin foil by stainless module. DTA was performed under the protection of Ar gas on a thermal analysis system (DTG-60/60H, Shimadzu). The heating rate was $10^\circ\text{C}/\text{min}$ and the highest temperature was 1000°C .

2.2 Preparation and characterizations of reaction couple

Ti- B_4C reaction couple was prepared by the method of spark plasma sintering (SPS). Firstly, B_4C plate with a dimension of $\Phi 10 \times 5\text{mm}$ was prepared from fine B_4C powder ($0.5\mu\text{m}$) by SPS at 1800°C for 20min, and then grinded by diamond paper and polished by 25nm Al_2O_3 suspension. After being cleaned by ultrasonic cleaner with alcohol, the plate was placed onto the inferior punch of SPS mouldle, and then filled with pure Ti powder (TC-450, $20\mu\text{m}$). Subsequently, the upper punch was put into the module, and sintered at 1000°C for 60min. The pressure of SPS was 30MPa and the heating rate was $2^\circ\text{C}/\text{min}$.

The reaction couple was cut axially, and then grinded and polished on the cutting surface. Then, the reaction layer between Ti and B_4C plate was obtained. Electron probe micro analyzer (EPMA) attached to field-emission scanning electronic microscopy (JXA-8530F, JEOL) was employed to investigate the distribution of elements. Field-emission scanning electronic microscopy (JEOL-6010) and

transmission electronic microscopy (TEM-2010, JEOL) were used to study microstructure and phase structure of reaction products, where TEM samples were prepared by Focus Ion Beam machine (FIB-2000A, Hitachi).

2.3 Static and in situ studying on microstructural evolution

In order to slow down the reaction rate for better observing microstructural evolution process, coarse B₄C powder (~100μm) was used. Pure Ti powder (TC-450, ~20μm) was firstly mixed with 10wt% coarse B₄C powder, and then cold-compacted into small cylinders (Φ10×5mm) with a pressure as high as 600MPa.

The static study was carried out by heating the cold compacts at 700, 800 and 900°C for 5min as well as 1000°C for 5, 20, 40, and 60min, respectively, and immediately followed by water quenching. Microstructure and phase composition of water quenched samples were investigated by field-emission scanning electronic microscopy and X-ray diffraction (XRD-6100, Shimadzu), respectively. In situ study was carried out on a high temperature observation system with the aid of laser scanning confocal microscopy (LSCM) [16] under the protection of Ar gas. The green compact was heated to 1100°C with a rate of 7°C/s, and then held for about 10min followed by cooling down. Microstructural evolution during the whole heating process was recorded continuously and saved as a video file.

3. Results

3.1 DTA curve

Fig.1 shows the DTA curve of Ti-B₄C powder compact during heating process. It can be found that, there is a turning point when the temperature is about 920°C.

After this point, the DTA curve turns to raise tardily, which means there is an exothermic reaction started at about 920°C. Such a result agrees approximately with that observed by Ref.[17,18], suggesting that in-situ reaction between Ti and B₄C maybe start at about 920°C.

Figure1

3.2 Phase compositions and distribution of products

In order to clarify the phase composition as well as their distribution of reaction products, a series of characterizing methods were applied on Ti-B₄C reaction couple, and the results are shown in Fig.2. From SEM morphologies and EPMA mapping results, the reaction zone ranged from B₄C side to Ti side can be divided into four layers, viz., a loose layer (~1μm) almost fully consisted of C element, a monolithic layer (~2-4μm) mainly consisted of Ti and B, Ti matrix (5~8μm) dispersed with a large amount of whisker-like and particle-like phases, as well as Ti matrix (~30μm) dispersed with a small amount of whisker-like and particle-like phases, respectively. The whisker-like phase mainly consists of Ti and B elements, while the particle-like phase mainly consists of Ti and C elements.

Figure 2

Because the reaction couple was prepared by sintering at high temperature (1000 °C) for a relative long time (60min), Ti-B-C equilibrium ternary phase diagram[19] is reasonable to be used for evaluating the reaction behavior between Ti and B₄C. It can be deduced from the ternary phase diagram that, there should be four phase regions between Ti and B₄C, viz. B₄C+C+TiB₂, TiB₂+TiC+C, TiB₂+TiB+TiC and

TiB+TiC+ α -Ti, respectively. Correspondingly, the reaction layer ranged from B₄C side to Ti side can also be divided into four regions that agreeing well with Ti-B-C ternary phase, as shown in the SEM image of Fig.2. Therefore, it can be confirmed that, the loose layer is C substance, monolithic layer is TiB₂, whisker-like phase is TiB and particle-like phase is TiC. Such a result can be further confirmed by the TEM results, and also agrees well with other previous works [10, 20, 21]. However, although the phase composition of products as well as their locational relationships with reactants Ti and B₄C can be confirmed by characterizing the reaction couple, detailed microstructural evolution still remain unknown. Therefore, static and in-situ investigations are applied subsequently.

3.3 Static microstructural evolution

Fig.3 shows XRD patterns of water-quenched Ti-B₄C compacts. It can be found that, when the heating temperature is lower than 900°C, the compacts only consist of α -Ti and B₄C. By heating at 900°C for 5min, a weak peak corresponding to TiB₂ appears. Further heating to 1000°C, some peaks corresponding to TiC and TiB phase appear, and their intensities increase with the prolongation of holding time. It hence seems to be that, TiB₂ forms firstly, and then TiC and TiB form subsequently with the process of Ti-B₄C in-situ reaction. However, due to the relatively low resolving ability, such a conclusion obtained from XRD analysis may be not accurate enough, and even some incompatible results appear. For example, when the heating temperature is lower than 900°C, the intensity of peaks corresponding to reactant B₄C decreases obviously but no product forms. Therefore, it is necessary to investigate more

detailed phase evolution information by microstructure observation with SEM.

Figure 3

Fig.4 shows microstructures of the water-quenched samples studied by XRD analysis before. By heating at 700°C for 5min, there are some gaps between B₄C and Ti particles as well as different Ti particles, indicating that the sample is not well compacted and no reaction between Ti and B₄C occurs inside it (Fig.4a). After heating at 800°C for 5min, there are a large amount of fine needle-like phases in the Ti side around the interface, meaning the reaction between Ti and B₄C has started (Fig.4b). By heating at 900°C for 5min, a grey layer appears between Ti and B₄C particle, and some need-like phases are attached to this layer towards the Ti side (Fig.4c). Further increase heating temperature to 1000°C for 10min, this grey layer becomes denser, and the need-like phases also become coarser and longer (Fig.4d). Microstructures of the compact after heating at 1000°C for 30 and 60min are similar to that heated for 10min, except that the grey layer becomes thicker and some particles with a size of about 4μm appear in the Ti side (Fig.4e and f). It can be confirmed that, according to the morphologies and phase structure characterizing by TEM and XRD, TiB whisker, TiB₂ intermetallic layer and TiC particle forms in turn as products with the processing of in-situ reaction.

Figure 4

3.4 Dynamic microstructural evolution

Fig.5 shows the in-situ observation results of Ti-B₄C powder compact during heating process. Although the magnification of LSCM is limited, the positional

relationships between the products and reactants can be clearly seen, and the decomposition of B_4C as well as the diffusion behavior of Ti, B and C atoms can also be clarified. It is clear that, with the prolongation of holding time, a large amount of fine black phases appear, and their location trends to be far away from B_4C particles gradually. On the other hand, the sharp corner of B_4C particle turns to be smooth, and the edge of B_4C particle trends to move inward. Combining with microstructural evolution results obtained by static water quenching, it can be confirmed that, B and C atoms diffuse from B_4C particle into Ti matrix to form TiB and TiC, while Ti atoms diffuse into B_4C particle to form TiB_2 intermetallic layer.

Figure 5

4. Discussion

From the above mentioned, it is clear that, the reaction behavior between Ti- B_4C can be described as the inter-diffusion between Ti and B_4C , as well as competitive reactions in both Ti-rich and B_4C -rich zone. A schematic diagram for microstructural evolution around Ti- B_4C interface is shown in Fig.6. It is common that, the diffusion of atoms in solid solutions is always easier than that in compounds [22]. Hence, the inter-diffusion between Ti and B_4C should firstly start with the decomposition of B_4C and diffusion of decomposed products B and C atoms into Ti matrix (Fig.6b₁). After the diffusion of B and C atoms, some vacancies generate in B_4C side, and then Ti atoms diffuse from Ti matrix into B_4C side by vacancy diffusion (Fig.6c₁). Subsequently, some potential reactions would complete with each other in both Ti-rich and B_4C side, resulting in the formation and growth of different reaction

products.

Figure 6

4.1 Reaction behavior in Ti matrix

Firstly, with the diffusion of B and C into Ti matrix, the zone of the interface near to Ti side mainly composed of Ti and a small amount of B and C atoms, as shown in Fig.6b₁. Then, the following potential chemical reactions maybe occur in this area according to binary phase diagram of Ti-B and Ti-C systems [23, 24], since no ternary phase is found in Ti-B-C ternary system.

In order to evaluate the competitive relationships of different reaction systems, we introduce threshold activity of reactant $\alpha_R^{\min}$, i.e. the minimal concentration for ensuring the proceeding of reaction, and the detailed calculation process is given in Appendix A. Because the above reactions occurred in Ti-rich zone, it can be confirmed that reactions (1)-(3) depend on B or C rather than Ti. Therefore, we can use the threshold activity of B or C to evaluate competitive relationships of reactions (1)-(3), and the corresponding results are summarized in Table1. It is easy to see that, threshold activity of B for reaction (2) is lower than that for reaction (1), but higher than that of C for reaction (3), which means TiC will form as primary product and then TiB rather than TiB₂ forms in Ti matrix. However, such a result from theoretical analysis seems to be conflicted with experimental results, where TiB phases firstly

form during in-situ reaction process. Hence, it is necessary to investigate the concentrations of B and C in the Ti matrix near to Ti-B₄C interface.

Based on Fick's second law, the concentration of B and C atoms in Ti matrix away from Ti-B₄C interface can be calculated accordingly in Appendix B, and a schematic result is shown in Fig.7. It can be found that, the diffusion distance of C is much longer than that of B at the same diffusion time, agreeing well with previous report which pointed out that the diffusion velocity of C in Ti is much higher than that of B[25]. Since both B and C atoms are the decomposition products of B₄C, the amount of B atoms should be higher than that of C. If we use the area of concentration curves and coordinate axis to represent the total amount of diffused B and C atoms, it can be confirmed that the concentration of B at Ti-B₄C interface is much higher than that of C, viz, $c_{0,B} \gg c_{0,C}$, because of its shorter diffusion distance. Hence, although the threshold activity of B for reaction (2) is a little higher than that of C for reaction (3), TiB still forms prior to TiC. Due to the special crystal structure and growth dynamics[26], TiB phase finally presents as whisker-like shape, as shown in Fig.6b₂.

Figure 7

4.2 Reaction behavior in B₄C side

When Ti atoms diffuse into B₄C side via vacancies left by the diffused B and C atoms, the B₄C side near to Ti-B₄C interface can be considered to consist mainly of B₄C and a small amount of Ti atoms, as shown in Fig.6c₁. Then, the following chemical reactions would happen in this area.

Since this area was rich in B_4C but poor in Ti atoms, the above reactions should depend on Ti rather than B_4C . The threshold activities of Ti for each reaction are also summarized in Table 1. It can be found that, the threshold activity of Ti for reaction (5) is the lowest, suggesting that reaction (5) will win from the competitions.

In the initial stage of in-situ reaction, the amount of Ti atoms in B_4C side is limited, leading to the formation of a small amount of dispersed TiB_2 phase and C substance, as shown in Fig.6c₂. C substance diffuses into Ti side and leads to the increase of C content inside it. As a result, TiC phase forms in the Ti side close to Ti- B_4C interface, as shown in Fig.6b₃. With the further processing of in-situ reaction, TiB_2 phase grows into a monolithic layer, and the diffusion of C will be inhabited, resulting in a C substance layer between un-reacted B_4C and TiB_2 intermetallic layer, as shown in Fig.6c₃. At the same time, the in-situ reaction between Ti and B_4C would also stop because Ti, B and C atoms can hardly diffuse across such a compact TiB_2 intermetallic layer. This phenomenon also could be used to explain why the in-situ reaction did not process fully in our previous work where big B_4C particles were applied in Ti- B_4C powder system [27].

Of course, it is necessary to pointed out that, the above discussion on

microstructural evolution and competitive reaction behavior is an overall tendency, there are several details are not considered carefully. For example, we point out that decomposition of B_4C and diffusion of the decomposed products B and C atoms, is the prerequisite of the diffusion of Ti into B_4C since Ti diffuses via vacancies inside B_4C . However, B_4C is not free of defects since the beginning of reaction. On the other hand, we treat the diffusion of atoms is in only one direction, for example, from Ti to B_4C or from B_4C to Ti, but atoms will diffuse back at the same time. Although the discussion section is not perfect, it is still reasonable, since the un-considered factors are equivocal and can be ignored compared with the diffusion behavior pointed out in this paper.

5. Conclusions

Based on the results of experimental investigations and theoretical calculations, in situ reaction behavior of Ti- B_4C system under solid-state has been clarified in this paper, which can be described as the following stages:

1. B_4C decomposes in to B and C atoms, and then diffuses into Ti side immediately, resulting in a zone consisted of $Ti+[B]+[C]$ in the Ti side near to Ti- B_4C interface. Then, TiB whisker forms by winning from the competition with TiB_2 due to its lower threshold activity for B elements and the competition with TiC due to the higher concentration of B than C in Ti matrix.

2. Ti atoms diffuses into B_4C side via vacancies left by the diffused B and C atoms, resulting in a zone consisted of $B_4C+[Ti]$. Then, TiB_2 and C form as the products of reaction between Ti and B_4C , since the lowest threshold activity for Ti elements. C

diffuses into the Ti side quickly, and then the concentration of C inside it increases accordingly, leading to the formation of TiC particles in the Ti side.

3. With further processing of in-situ reaction, the size and amount of all the products increases. When TiB₂ particles in the B₄C side grow into a density layer, the product C cannot further diffuse into the Ti side, and then aggregates into a loose C substance layer between un-reacted B₄C and TiB₂ intermetallic layer. On the other hand, B and C atoms come from the decomposition of B₄C as well as Ti atoms in the matrix also could not diffuse cross such a density intermetallic layer, leading to the end of in situ reaction between Ti and B₄C.

Appendix A: Calculation on threshold activity

For a binary reaction system depended on reactant X, α_X^{min} can be calculated by Eq.(A1)[28]:

$$\alpha_X^{min} = \left[\frac{1}{\alpha_Y^S} \left(\frac{\Delta G_T^0}{RT} \right) \right]^{\frac{1}{n_X}} \quad (A.1)$$

where, α_X^{min} is the threshold activity of reactant X, α_Y^S is the activity of reactant Y, T is reaction temperature, ΔG_T^0 is the change in standard Gibbs free energy at temperature T, R is gas constant, n_X is stoichiometric coefficient of reactant X.

The change in standard Gibbs free energy at temperature T is given as follows[29]:

$$\Delta G_T^0 = \Delta H_T^0 - T \times \Delta S_T^0 \quad (A.2)$$

where, ΔH_T^0 and ΔS_T^0 are the changes in standard enthalpy and entropy at temperature T, and can be calculated by Eq.(A.3-A.6).

$$\Delta H_T^0 = \sum n_i (H_T^0)_i \quad (A.3)$$

$$\Delta S_T^0 = \sum n_i (S_T^0)_i \quad (\text{A.4})$$

$$(H_T^0)_i = (\Delta_f H_{298}^0)_i + \int_{298}^T C_{p,i} dT + \Delta H_i \quad (\text{A.5})$$

$$(S_T^0)_i = (S_{298}^0)_i + \int_{298}^T C_{p,i} dT + \frac{\Delta H_i}{T_s} \quad (\text{A.6})$$

where, $(H_T^0)_i$ and $(S_T^0)_i$ are standard enthalpy and entropy at temperature T , respectively; n_i are stoichiometric coefficients; $(\Delta_f H_{298}^0)_i$ and $(S_{298}^0)_i$ are standard molar formation enthalpy and entropy at 298K, respectively; ΔH_i is latent heat of phase change at temperature T_s .

It should be mentioned that, the activity of un-depended reactant α_Y^S cannot be obtained from current references, so we assume $\alpha_Y^S=1$ since the concentration of reactant B is almost 100at% in all the reaction system and the value of α_Y^S is not very important for the comparison of α_X^{min} . Other thermodynamic data for the above calculations comes from Ref.[29].

Appendix B: Calculation on concentration field of diffusion atoms

After the diffusion of decomposed products B and C atoms into Ti matrix, concentration of B or C in Ti side near to Ti-B₄C interface can be expressed by Fick's second law[30].

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (\text{B.1})$$

where, c is concentration of solution atoms B or C; t is diffusion time; x is perpendicular distance in the Ti matrix away from Ti-B₄C interface; D is diffusion coefficient of B or C in Ti matrix, and can be calculated by Eq.(B.2).

$$D = A \cdot \exp\left(-\frac{Q}{RT}\right) \quad (\text{B.2})$$

where, A is frequency factor, Q is activation energy of diffusion.

The initial and boundary conditions for Eq.(B.1) are given as follows:

Initial condition (t=0):

$$c = 0 \text{ at } x \geq 0, \quad (\text{B.3})$$

Boundary conditions (t>0):

$$c = c_0 \text{ at } x = 0 \quad (\text{B.4})$$

$$c = 0 \text{ at } x = \infty \quad (\text{B.5})$$

Where, C_0 is concentration of B or C at the Ti-B₄C interface. Then the solution for Eq.(B1) can be expressed by Eq.(B6).

$$c(x, t) = \frac{c_0}{2} \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad (\text{B.6})$$

In this paper, the reaction temperature is T=1273K, and holding time is t=3600s, and the frequency factor and activation energy data can be found in Ref.[11] and [30]. Then the concentration of B and C in Ti matrix can be established.

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Table1 Threshold activities of depended reactant for potential chemical reactions at 1273K

S.N.	Chemical equations	Depended reactant	Threshold activity
(1)	$Ti+2B=TiB_2$	B	5.96×10^{-7}
(2)	$Ti+B=TiB$	B	3.97×10^{-7}
(3)	$Ti+C=TiC$	C	1.05×10^{-7}
(4)	$Ti+B_4C=TiC+4B$	Ti	6.54×10^{-5}
(5)	$2Ti+B_4C=TiB_2+C$	Ti	5.89×10^{-12}
(6)	$3Ti+B_4C=TiB_2+TiC$	Ti	2.02×10^{-10}
(7)	$4Ti+B_4C=4TiB+C$	Ti	1.98×10^{-6}
(8)	$5Ti+B_4C=4TiB+TiC$	Ti	1.10×10^{-6}

Figure captions:

Fig.1 DTA curve of Ti-B₄C powder compact during heating process.

Fig.2 Characterizing results on the reaction layer of Ti-B₄C reaction couple by SEM, EPMA and TEM, respectively. Where a schematic Ti-B-C diagram [19] was introduced to analyze the distribution of reaction products, and the TEM samples were cut from the areas marked in the SEM image by FIB correspondingly.

Fig.3 XRD patterns of water-quenched compacts after heating by different crafts, where “700-5” means heating at 700°C for 5mins.

Fig.4 Microstructure of Ti-B₄C green compact after heating at (a) 700, (b) 800 and (c) 900°C for 5min as well as 1000°C for (d) 10, (e) 30 and (f) 60min, respectively. Where the eyeshot is focused on the interface between Ti and B₄C particle, and the up dark area is B₄C.

Fig.5 Microstructure of Ti-B₄C green compact by holding at 1100°C for (a) 5s, (b) 40s, (c) 330s and (d) 540s, respectively. Where, the images are captured from a continuous video that recorded the whole heating process of Ti-B₄C green compact.

Fig.6 Schematic microstructural evolution around the Ti-B₄C interface in the case of solid-state sintering. (a) initial state where no reaction occurs, (b₁-b₃) formation and growth of whisker-like TiB and particle-like TiC phases in the Ti side, (c₁-c₃) formation and growth of TiB₂ and C phase as well as the diffusion and pileup of C substance in the B₄C side, (d) final structure around the Ti-B₄C interface, where the zones marked by “I~IV” correspond to that shown in the ternary phase diagrams of Ti-B-C phase and experimental results shown in Fig.2.

Fig.7 Concentrations of boron and carbon in the front of Ti-B₄C interface.

Fig.1

Figure2

Fig.2

Fig.3

Fig.4

Fig.5

Figure6

Fig.6

Fig.7