

Reaction path of the synthesis of TiC–TiB₂ in Cu–Ti–B₄C system

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Abstract

The reaction path of TiC–TiB₂ formation in 20 wt.% Cu–Ti–B₄C powder mixtures was studied by using differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The Cu–Ti intermetallics (mainly Ti₂Cu and TiCu) were formed initially via solid-state diffusion reactions between Cu and Ti particles; and then the Cu–Ti liquids were formed from the eutectic reaction between Ti₂Cu and TiCu at about 965 °C and the melting of the Ti₂Cu. Cu–Ti liquid spread over the B₄C and Ti particles, subsequently carbon and boron atoms from the bulk B₄C continuously diffuse into the liquid phase to form liquid Cu–Ti–B–C. Finally, TiC and TiB₂ particulates precipitate out of the saturated liquid. The exothermic reaction was complete after the addition of Cu. The results showed that Cu not only participated in the reaction, but changed the reaction path between Ti and B₄C.

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1. Introduction

Titanium diboride (TiB₂) and titanium carbide (TiC) are important ceramic materials for high-temperature applications because of their high melting point, hardness, elastic modulus and electrical conductivity, and relatively low coefficient of thermal expansion [1,2]. Therefore, the composites that combine TiB₂ and TiC offer an attractive combination of excellent mechanical and electrical properties as well as corrosion resistance, particularly at relatively high-temperatures and/or in corrosive environments [1–4].

Traditional synthesis and fabrication methods including mechanical alloying [5], reactive hot pressing [4,6,7], transient plastic phase processing [8], self-propagating high-temperature synthesis (SHS) [9–11] and reactive sintering [12] have been developed to prepare TiC–TiB₂ composites using Ti–B₄C systems. Among these fabrication technologies, the SHS technology was attached to much attention, due to its low energy consumption, high time efficiency

and high product purity [13]. In general, ignition of the SHS reaction was controlled by the rate of surface reaction among the reactants, which, in turn, was determined by the contact surface area between them. Thus, the formation of liquid and its subsequent capillary spreading was essential to the ignition and the propagation of the combustion wave, because it substantially increased the contact surface area between reactants and provided an easier route for reactant mass transfer. The reactions in the Ti–B₄C system, however, are somewhat difficult to initiate due to high melting temperatures of the reactants and lack of a pre-activation reaction. A possible solution to these problems could be the incorporation of metals with a low-melting-point and/or reasonable reactivity with titanium for formation of low-melting intermetallics into the reactants. Thus, the thought occurred that a solid-solid reaction may be significantly affected by forming a liquid at a low-temperature by the adding of a low-melting-point metal to promote the formation of liquid and such increase the contact surface area between the reactants and provide an easier route for mass transfer. For instance, the addition of Ni to the Ti–B₄C system provides an easier route for reactant mass

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transfer and accelerates the occurrence of complete reaction [14], and a small addition of Al to the system was reported to significantly lower the reaction activation energy and dilute the exothermic extent [15,16].

In this study, an attempt has been made to evaluate the effect of Cu addition on the exothermic reaction in the Ti–B₄C system, and to determine the reaction path of the TiC–TiB₂ formation from Cu, Ti and B₄C powders. Differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM) has been for analysis. Although the information obtained from the DTA experiments is incomplete, it is valuable to help understanding the ignition behavior in the SHS reaction. It is expected that the preliminary results can be significant in promoting the understanding of the SHS process in the Cu–Ti–B₄C system.

2. Experimental

The starting materials were commercial powders of Cu (99.0%, ~3 μm), B₄C (99.5%, ~3.5 μm) and Ti (99.5%, ~45 μm), respectively. Ti and B₄C powders with a ratio corresponding to that of stoichiometric 2TiB₂–TiC were mixed with 20wt.% Cu. The reactant mixtures were studied by DTA (Model Rigaku–8150, Japan) using a heating rate of 30 °C/min in argon protective atmosphere. Because of the complexity of the reactions in the Cu–Ti–B₄C system, the DTA experiments were also performed on the mixtures of Cu–Ti, Cu–B₄C and Ti–B₄C powders, then followed by XRD analysis of the reaction products. The compositions of the investigated systems are shown in Table 1. The DTA temperature calibrations were made using copper standards heated at 30 °C/min in argon. All temperature data were shifted based on linear interpolation to literature values for the melting points of this standard (1083.4 °C). The samples retrieved from DTA were ground in an alumina mortar and analyzed using XRD (Model D/Max 2500PC Rigaku, Japan). Microstructures of the fracture surface of the DTA products were investigated by SEM (JSM6360–LV Japan) equipped with an energy-dispersive spectrometer (EDAX).

3. Results and discussion

3.1. Thermodynamics

The potential reactions that could take place in the Cu–Ti–B₄C system are given as follows:

Table 1
The material compositions of the Cu–Ti–B₄C, Cu–Ti, Cu–B₄C and Ti–B₄C systems

Sample	Material compositions (g)		
	Cu	Ti	B ₄ C
1	20	57.6	22.4
2	20	57.6	–
3	20	–	22.4
4	–	57.6	22.4



In order to determine the reaction directions and the synthesized products, the reaction change standard Gibbs free energies ΔG^0 of Eqs. (1)–(4) were theoretically calculated according to thermodynamics data [17,18], results are shown in Fig. 1. It can be observed that the ΔG^0 of all four reactions are negative, which indicates the above reactions are all favorable in the calculated temperature ranges. The TiC and TiB₂ phases possess higher thermodynamic stability than the TiCu, Ti₂Cu and TiB phases, implying that the latter, if formed, have a tendency to transform to the former at elevated temperatures. Therefore, TiB₂, TiC and Cu should be the stable phases in the products from Cu–Ti–B₄C systems.

3.2. Differential thermal analysis

Fig. 2a shows the DTA curves of the reactant mixtures from the Cu–Ti–B₄C, Cu–Ti, Ti–B₄C and Cu–B₄C systems, respectively, with a heating rate of 30 °C/min to a maximum temperature of 1200 °C in a flowing argon atmosphere. The phases in the reaction products were analyzed by XRD, results are presented in Fig. 2b. In the DTA curve for the Cu–B₄C system, there is only one endothermic peak with the minimum at 1097 °C, which corresponds to the melting of Cu. As indicated in Fig. 2b, the only Cu and B₄C phases are detected after heating the

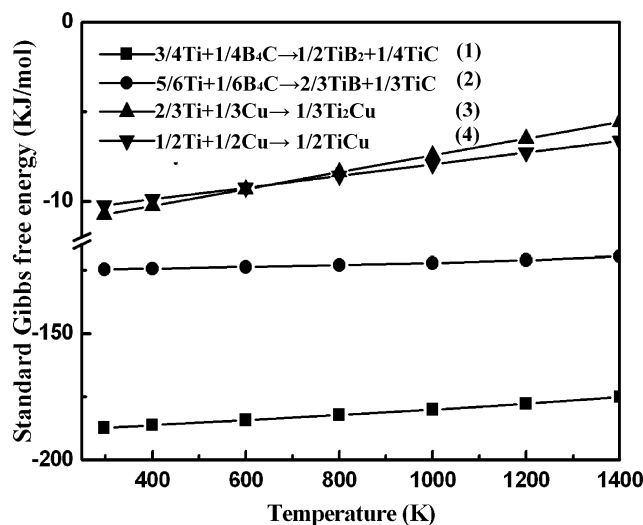


Fig. 1. Change of standard Gibbs free energy as the temperature for Eqs. (1)–(4).

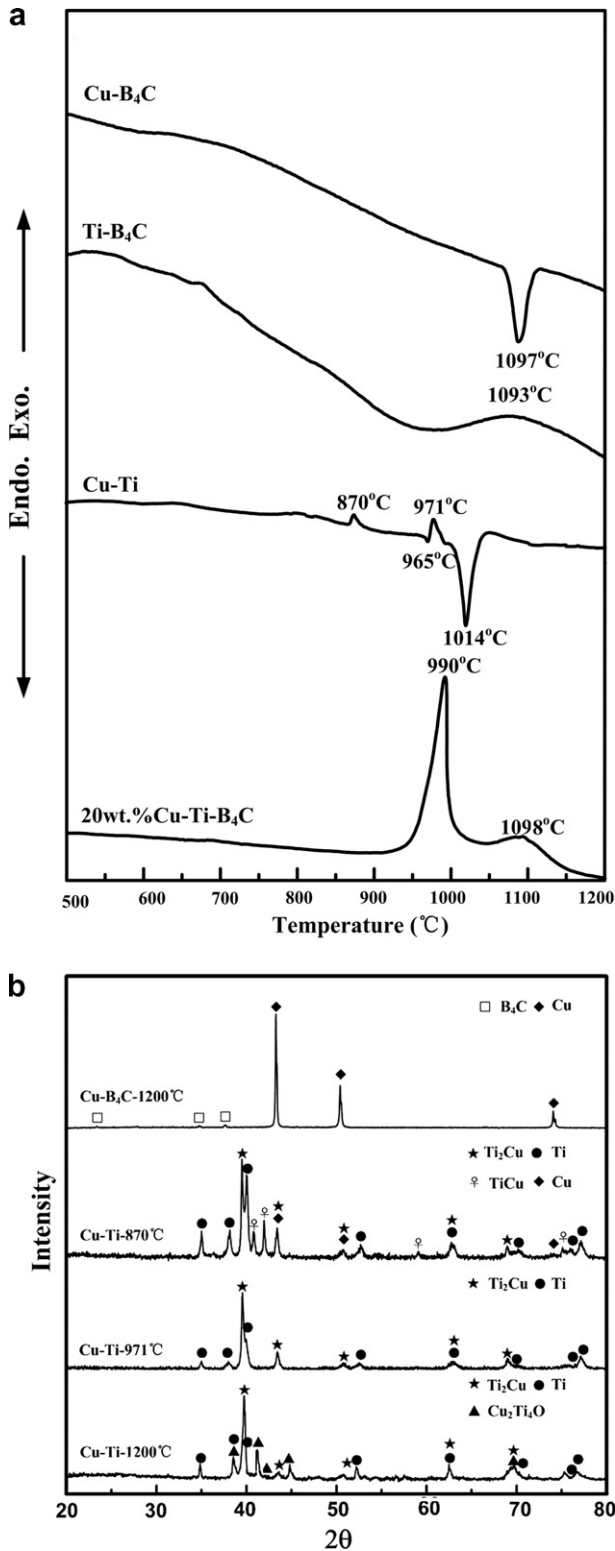


Fig. 2. (a) DTA curves for various composition reactants heated to 1200 °C at a heating rate of 30 °C/min in argon; (b) XRD patterns for the DTA products of Cu–B₄C, Ti–B₄C and Cu–Ti systems, quenched at different temperatures.

Cu–B₄C powder mixtures to 1200 °C. The results show that there is no obvious reaction between Cu and B₄C mixtures below 1200 °C.

From DTA curves of Cu–Ti system, it can be observed that two exothermic peaks with the maxima at 870 and 971 °C, and two endothermic peaks with the minima at 965 °C and 1014 °C appeared, respectively. According to [19], the complex reactions had occurred between Cu and Ti particles below 1200 °C. In order to make clear the reactions occurring during the heating process, interrupted experiments were conducted for Cu–Ti powder mixtures heated to 870 and 971 °C, respectively. The reaction products in the samples quenched from different temperatures were examined by XRD and the results are presented in Fig. 2b. Clearly, after heating the Cu–Ti powder mixtures to 870 °C, a large quantity of Ti₂Cu and TiCu were detected in unreacted starting powders. The results show that the solid-state diffusion reaction between Cu and Ti mixtures occurs at 870 °C. When increasing the temperature, one slightly endothermic peak with the minimum at 965 °C was observed in the DTA curves. According to the Cu–Ti phase diagram [20], Cu–Ti eutectic liquids can be formed at 960 °C (eutectic temperature) between TiCu and Ti₂Cu. Therefore, TiCu and Ti₂Cu may form Cu–Ti liquids corresponding to the endothermic peak with the minimum at 965 °C. With the increase of temperature to 971 °C, the identified phases in the products were Ti₂Cu and Ti. Cu–Ti liquid, which formed locally, spread over the unreacted titanium particles, leading to the formation of Ti₂Cu at the interface region between the Cu–Ti liquid and Ti particles. Thus, an exothermic peak with the maximum at 971 °C is observed because of the formation of Ti₂Cu at the interface region between the Cu–Ti liquid and the Ti particles. With a further increase of temperature, the heat released from exothermic reactions and continuous heating can lead to the melting of Ti₂Cu into Cu–Ti liquid, corresponding an endothermic peak at 1014 °C. After heating the mixtures to 1200 °C, large amounts of Ti₂Cu and Ti were identified during the subsequent solidification. Also, a small quantity of Cu₂Ti₄O was found, caused by the poor pressurization of the DTA apparatus.

In the DTA curve of the Ti–B₄C mixture heated to 1200 °C, only a very weak and wide exothermic hump with maximum at 1093 °C was observed, see Fig. 2a. The XRD analysis reveals the formation of TiC and considerable amounts of titanium borides such as TiB₂ and TiB in the final products in addition to the unreacted starting powders. This has been reported in another work of our group [14]. The weak exothermic effect can be attributed to the sluggish solid-state diffusion in the system. Moreover, according to [12], in their reactive sintering of Ti–B₄C compacts, the formation of TiC over TiB₂ was attributed to the diffusivity of carbon in titanium being significantly greater than that of boron. Thus, carbon readily combined with titanium to yield TiC. A concentration gradient of boron existed along the diffusion path between Ti and B₄C particles, resulting in the formation of TiB intermediate phase depending on the ratio of Ti:B.

After Cu was added to the Ti–B₄C mixtures, two intense exothermic peaks with maxima at 990 °C and 1098 °C

appeared, respectively, which was significantly different from the Ti–B₄C system. In order to make clear the reactions occurring during the heating process, interrupted experiments were conducted. Cu–Ti–B₄C powder mixtures were heated to 930, 990 and 1098 °C, respectively. The XRD results of the DTA products are presented in Fig. 3. After heating to 930 °C, Ti₂Cu and TiCu were detected in the unreacted starting powders, which is analogous to the Cu–Ti system. This indicates that a relatively slow solid-state diffusion reaction occurs between Cu and Ti particles, although the DTA curve show there is no strong exothermic peak. An insufficient or/and inhomogeneous contact may retard solid-state diffusion, and lead to an incomplete and slow reaction. In addition, the results suggest that a presence of B₄C may restrain the solid-state diffusion reaction at the interface between Cu and Ti particles.

After heating the mixtures to 990 °C, one strong endothermic peak was observed in the DTA curve of 20 wt.% Cu–Ti–B₄C. The corresponding XRD result shows that there are large quantities of TiC, TiB, TiB₂ and Ti₂Cu in the unreacted starting powders. The formation of these phases can be explained based on the Cu–Ti system. According to the DTA curve of Cu–Ti, TiCu together with Ti₂Cu can locally form Cu–Ti eutectic liquids at 965 °C, which then spreads over the B₄C and Ti particles. To develop a deeper understanding of the TiC and TiB₂ formation in 20 wt.% Cu–Ti–B₄C, typical back scatter images of the raw powders and products at various temperature of 965, 990 and 1200 °C respectively are shown in Figs. 4a–d. Microstructure observation was in agreement with the XRD results. Fig. 4a shows a back scatter image of the raw powders, where dark areas represent the starting B₄C particles, gray areas represent Ti particles, and bright areas represent Cu particles. Fig. 4b shows the typical micro-

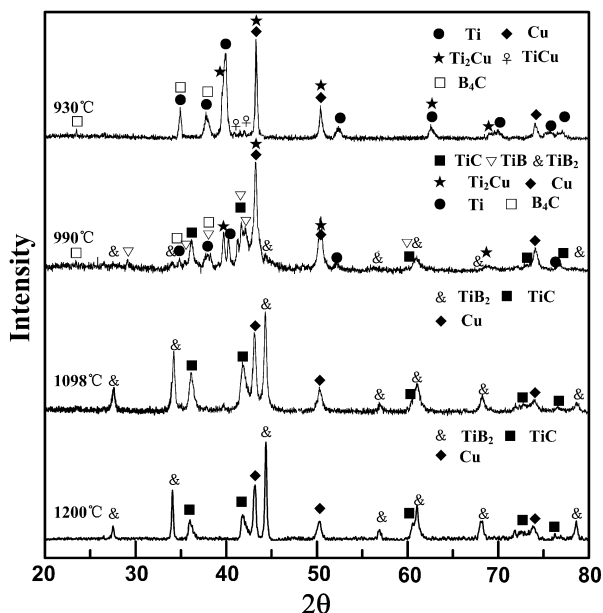


Fig. 3. XRD patterns of the DTA products synthesized in the 20 wt.% Cu–Ti–B₄C system quenched at 930, 990, 1098 and 1200 °C, respectively.

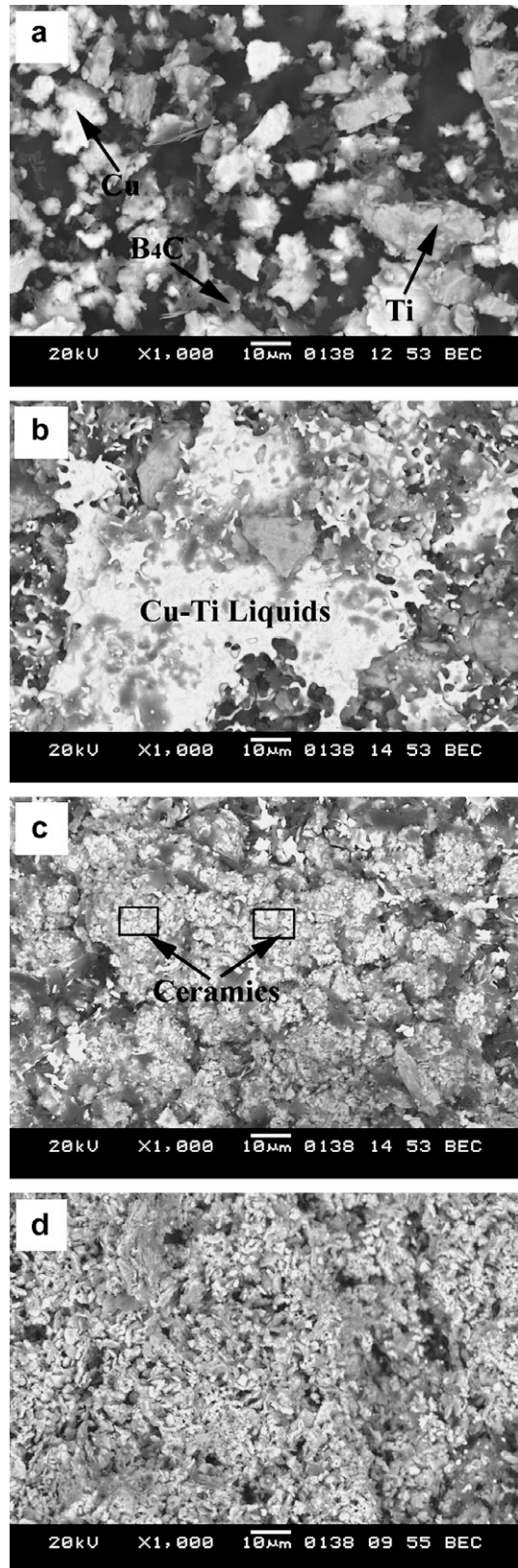
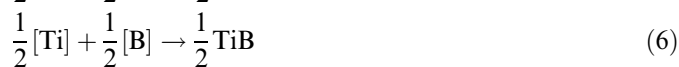


Fig. 4. Back scatter images of the DTA products synthesized in the 20 wt.% Cu–Ti–B₄C system at (a) room temperature, quenched at (b) 965 °C, (c) 990 °C and (d) 1200 °C, respectively.

structure of a product heated to at 965 °C; it can be observed that the Cu–Ti liquid formed and spread over

the unreacted Ti and B₄C particles. The formation of Cu–Ti–B–C liquid and continuous heating significantly promote further diffusion of carbon and boron away from the bulk B₄C [15]. Subsequently, TiC, TiB and TiB₂ particulates precipitate out of the saturated liquid. It can be deduced that Eqs. (5)–(7) were indicated as follows:



The transportation of Ti relies on diffusion and capillary-induced flow, which can greatly facilitate mass transfer and consequently promote the reaction. With further increase of temperature, the carbon and boron atoms in the B₄C crystals become activated and continuously diffuse into the liquids. At the same time, according to the DTA curve of Cu–Ti and corresponding XRD results (Figs. 2b and 3), formation of Ti₂Cu occurred at the interface region between the Cu–Ti liquid and unreacted Ti particles. Therefore, Ti₂Cu in the reaction products at 990 °C may have been formed both from diffusion reaction between reactants, as well as from Cu–Ti liquid during cooling. Moreover, the formation of the Cu–Ti liquid and its subsequent capillary-induced flow can increase the contact surface area between the unreacted Ti and B₄C particles, and such provide an easier route for mass transfer. This is of great importance since it significantly promotes the contact between B₄C and Ti particles, and reduces atomic diffusion distance. On the other hand, the heat generated by the reaction may further contribute to activating the subsequent reaction between Ti and B₄C particles. Therefore, the reaction also occurs directly between Ti and B₄C particles. A typical back scatter image of the product heated to 990 °C is shown in Fig. 4c. It can be seen that many small TiC, TiB and TiB₂ ceramic compounds precipitated out of the liquid regions.

After heating the mixtures to 1098 °C, Ti₂Cu disappeared and the thermodynamically stable phases (TiC, TiB₂ and Cu) were identified in the final products without any intermediate phase. When the mixtures were heated to 1200 °C, the composition of products did not change. According to the DTA curve of Cu–Ti, there is an endothermic peak at 1014 °C corresponding to the melting of Ti₂Cu. Thus, it is believed the second exothermic peak in Cu–Ti–B₄C mixtures was initiated by the melting of Ti₂Cu and the formation of large amounts of Cu–Ti liquid. After melting of Ti₂Cu, more Cu–Ti liquid formed and spread over the B₄C particles. Carbon and boron atoms continuously diffused into the Cu–Ti–B–C liquid, and then TiC and TiB₂ particulates were gradually precipitated out of the saturated liquid. With the consumption of Ti in the Cu–Ti liquid by the precipitation of TiC and TiB₂, free Cu is displaced. The reaction is terminated after Ti atoms

in the Cu–Ti liquids are depleted. A typical back scatter image of the product heated to 1200 °C is shown in Fig. 4d.

Compared with the DTA curve of the Ti–B₄C system, it can be seen that the reaction between Ti and B₄C is greatly facilitated by the formation of Cu–Ti liquid in the Cu–Ti–B₄C system. The results show that Cu not only participated in the reaction, but also changed the reaction path between Ti and B₄C. Due to the addition of Cu, the exothermic reaction was complete. The formation of the Cu–Ti liquids and their subsequent capillary spreading was essential for TiC–TiB₂ formation, because it substantially increased the contact surface area between reactants and provided an easier route for the reactant mass transfer.

4. Conclusions

Based on DTA and XRD analysis of Cu–Ti, Cu–B₄C, Ti–B₄C and 20 wt.% Cu–Ti–B₄C systems, the path of TiC–TiB₂ formation may be described as follows: intermetallic Cu–Ti (mainly Ti₂Cu and TiCu) formed initially via solid-state diffusion reactions between Cu and Ti particles; then Ti₂Cu and TiCu forms the Cu–Ti eutectic liquid at about 965 °C. The Cu–Ti liquid spreads over the B₄C and Ti particles. This formation of liquid and continuous heating significantly promote further diffusion of carbon and boron away from the bulk B₄C, as well as the formation of the Cu–Ti–B–C liquid. Finally, TiC and TiB₂ particulates precipitate out of the saturated liquid. When the temperature is increased further, the Ti₂Cu melts and more Cu–Ti liquid is formed and spread over the reactants, and then carbon and boron atoms continuously diffuse into the Cu–Ti–B–C liquid, and TiC and TiB₂ particulates gradually precipitate out of the saturated liquid.

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