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Effect of Cu content on the reaction behaviors of self-propagating high-temperature synthesis in Cu–Ti–B_4C system

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Abstract

The SHS reaction behaviors of the Cu–Ti–B_4C system with various Cu content were investigated. Theoretical calculation of the adiabatic temperatures reveals that the reaction in the Cu–Ti–B_4C system is self-sustainable for the presence of 0–72.22 wt.% Cu in the reactants without any preheat. With the increase of Cu content, the adiabatic temperatures, combustion temperatures and wave velocity decrease greatly, while the ignition time shows first a remarkable decrease and then an increase with the minimum value at 20 wt.% Cu. Moreover, with the increase of Cu content, the sizes of the TiC and TiB_2 grains decrease considerably.

Keywords: Self-propagating high-temperature synthesis (SHS); Ceramic; Cu; Reaction behavior

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1. Introduction

Self-propagating high-temperature synthesis (SHS) has received considerable attention in the last two decades as an alternative method for the synthesis of high-temperature materials [1–3]. The prominent advantages of this technique are its low cost and energy consumption, high time efficiency and purity of the reaction products. A wide variety of materials, such as borides [4], carbides [5], intermetallics [6,7], and ceramic–metal matrix composites [8–11] have been produced by this method.

Titanium carbide (TiC) and titanium diboride (TiB_2) ceramics possess desired properties such as low densities, high melting points, good thermal and chemical stability, high hardness and excellent wear resistance [12,13]. They are potential candidates for application in cutting tools, machine tool insert, new type of electrodes, high corrosion resistance coatings, wear-resistant parts and lighter armor materials. Moreover, they are also attractive for application in aircraft propulsion systems and space thermal protection systems. In the past years, reaction synthesis of the TiC–TiB_2 composites from Ti–B_4C reactants has been investigated by SHS technique [8,14,15].

The SHS reactions in Ti–B_4C system, however, are somewhat difficult to initiate due to high melting temperatures of the reactants and lack of a pre-activation reaction. The addition of metal with low melting point decreases the reaction temperature by forming a liquid at a low temperature and improves the surface reaction rate. The effects of the addition of metals such as Al and Ni to the Ti–B_4C mixtures on the SHS reaction behavior and mechanism have has been investigated by many researchers [16,17]. For instance, the addition of Al to the Ti–B_4C reactants facilitates the ignition occurrence, lowers the reaction exothermicity and modifies the resultant microstructure [16]. Due to its high electrical and thermal conductivities, Cu has been used in the power industry, electric industry and engineering industry. Ceramic particulate reinforced Cu matrix composites have attracted wide interest in recent years [18]. These materials exhibit a combination of the excellent thermal and electrical conductivities, high strength retention at elevated temperatures, and high microstructural stability [19].

Unfortunately, the research on the SHS reaction in the Cu–Ti–B_4C system is relatively rare. The principle objective of the present work is hence to investigate the reaction behaviors during the SHS of the Cu–Ti–B_4C system. This article provides

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a primary investigation on the feasibility of the SHS reaction in the Cu–Ti–B_4C system and the effects of the Cu content on the reaction behavior and the resultant products.

2. Experimental procedure

The raw materials used were commercial powders of Cu (99.0 wt.% purity, ∼3 μm), B_4C (99.5 wt.% purity, ∼3.5 μm) and Ti (99.5 wt.% purity, ∼38 μm), respectively. Ti and B_4C powders with a ratio corresponding to that of stoichiometric $2TiB_2$–TiC mixed with varying Cu contents were used for the powder blends. The reactant powders were mixed in a stainless-steel container for 8 h to ensure homogeneity, and then pressed into cylindrical preforms (about 22 mm in diameter and 12 ± 2 mm in length) using a stainless steel die to obtain densities of 65 ± 2% theoretical density.

More details about the experimental apparatus and procedure for the SHS reaction were given in a previous article [17]. It is worth noting that the current in the present experiment is selected as 90 A. The temperature in close vicinity to the center of the sample was measured by W/Re5–W/Re26 thermocouples and the signals were recorded and processed by a data acquisition system using an acquisition speed of 50 ms/point. The propagation velocity of the combustion waves was measured by recording the whole combustion event with a black-and-white CCD video camera (DALSA) at 995 frames per second. In addition, the ignition process for the reactions in the powder mixtures with various Cu contents were also studied by the differential thermal analysis (DTA, Rigaku-8150, Japan) experiments, which were conducted in a flowing argon gas (flowing rate: 60 ml/min) using a heating rate of 30 °C/min. The phase constituents of DTA products and the SHS products in the combustion chamber were identified by using X-ray diffraction (XRD) (Model D/Max 2500PC Rigaku, Japan). Morphology of the fracture surface was examined by using scanning electron microscopy (SEM) (Model JSM-5310, Japan) equipped with energy-dispersive spectrometer (EDS) (Model Link-ISIS, Britain).

3. Results and discussion

3.1. Theoretical calculation of the adiabatic temperature

The adiabatic temperature, T_{ad}, defined as the final theoretical temperature attained by a system undergoing an adiabatic condition, is an important parameter to evaluate whether the reaction can be self-sustaining or not. It has been empirically suggested that combustion reactions will not become self-sustaining unless $T_{ad} \geq 1800$ K [20]. The TiC and TiB_2 particulates could be synthesized by the following reaction:

$$x\mathrm{Cu} + 3\mathrm{Ti} + \mathrm{B_4C} = 2\mathrm{TiB_2} + \mathrm{TiC} + x\mathrm{Cu} \quad (1)$$

The enthalpies of the reactants and products are commonly given at 298 K, and the propagating mode is often initiated at room temperature without any pre-heat, the adiabatic temperature in this reaction system could be theoretically calculated using the thermodynamic data from Ref. [21] according to the following equation [22]:

$$\Delta H\,(298) + \int_{298}^{T_{ad}\,(298)} \sum n_j C_p(P_j)\,\mathrm{d}T + \sum_{298-T_{ad}\,(298)} n_j L(P_j) = 0 \quad (2)$$

where ΔH (298) is the reaction enthalpy at 298 K (761 kJ/mol [23]), n_j the stoichiometric constant, C_p and L are the heat capacity and latent heat, and P_j refers to the product, respectively. It is worth noting that we have to provide that no eutectic transformation occurs in the resultant TiC and TiB_2 phases during the calculation of T_{ad}. The calculated T_{ad} values as a function of the Cu content in the reactants are shown in Fig. 1. As indicated, T_{ad} decreases with the increase in the Cu content except for two plateaus in the range of 0–6.77 and 13.22–40.17 wt.% Cu, respectively, where T_{ad} stays at 3193 K (the melting point of TiB_2) and 2848 K (the boiling point of Cu), respectively. The appearance of two plateaus at 0–6.77 and 13.22–40.17 wt.% Cu are due to the absorption of heat caused by the melting of TiB_2 and the gasification of Cu, respectively. According to Merzhanov's empirical criterion [20], for the reaction to be self-sustaining in the absence of preheat, T_{ad} should not be less than 1800 K, corresponding to the maximum addition of 72.22 wt.% Cu in the reactants.

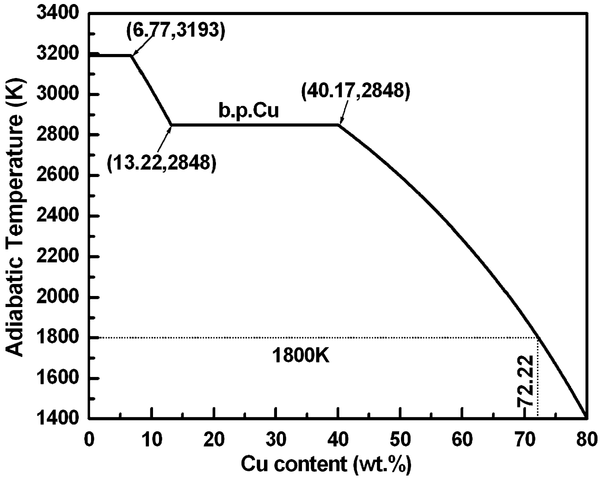

Fig. 1. Adiabatic temperature (T_{ad}) as a function of the Cu content.

3.2. Reaction behaviors

3.2.1. Temperature–time profile and combustion temperature

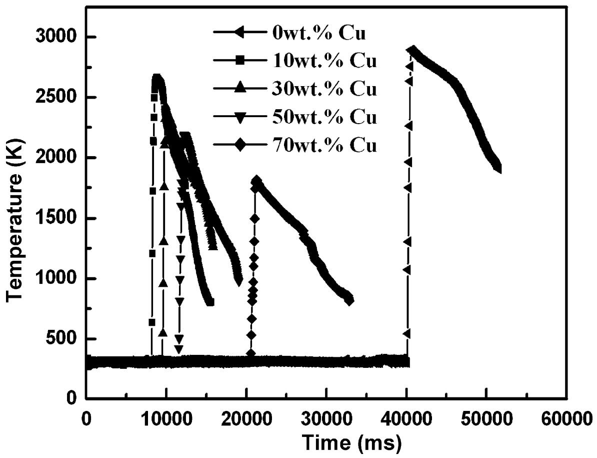

Fig. 2. Typical temperature–time profiles of the center of the samples with various Cu content.

Fig. 2 shows the typical temperature profiles for the Cu–Ti–B_4C preforms with various Cu contents during the SHS

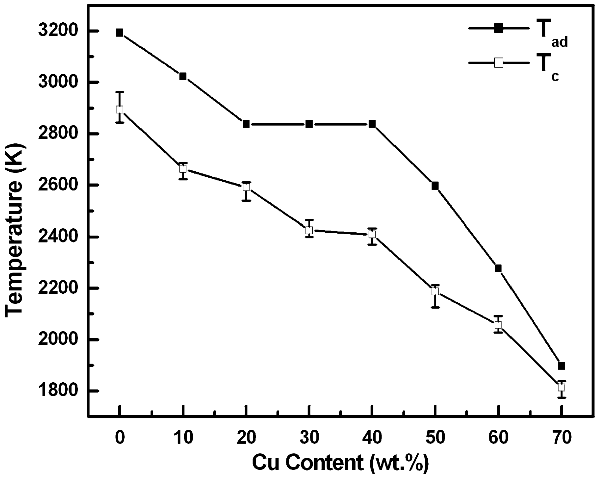

Fig. 3. The variation in the T_{ad} and T_c of the Cu–Ti–B_4C system with various Cu contents.

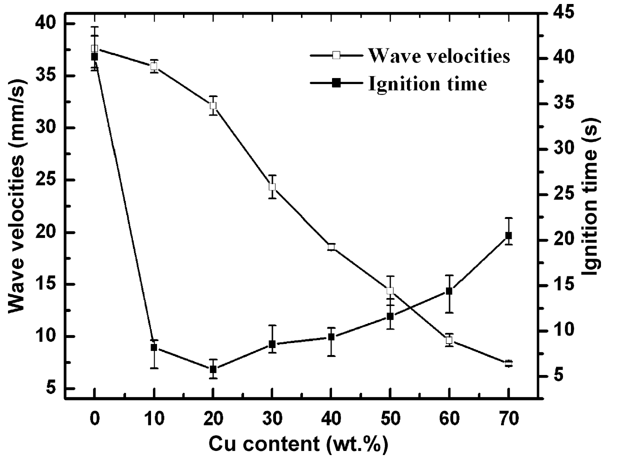

Fig. 4. The variation of the combustion wave velocities and ignition time with the Cu content in the reactants.

process. As can be seen, the temperature at the combustion front of the preforms within the range of the Cu content from 0 to 70 wt.% rises rapidly, without an appreciable preheating effect. Whereas, in the 80 wt.% Cu preform, the SHS reaction cannot occur in the actual experiment, so the temperature–time profile is not listed. This is in general accordance with the preceding T_{ad} calculation result, where the critical value of the Cu reactant is 72.22 wt.% for the reaction to be self-sustaining without preheat. Clearly, The self-propagating reaction in the Ti–B_4C preforms was difficult to initiate, yet it was easy in the Cu–Ti–B_4C samples with 10–70 wt.% Cu. Once initiated, however, the reaction in the Ti–B_4C compacts was more extensive than those in the Cu–Ti–B_4C preforms.

Fig. 3 shows the variation in the T_{ad} and maximum combustion temperature (T_c) of the Cu–Ti–B_4C system with various Cu content. The results indicate that the T_c decreases with the increase of Cu content. Moreover, it is worth noting that the experimentally determined T_c is generally lower than the theoretically calculated T_{ad} values because of heat loss during the reaction process. The decreasing T_c as a result of the Cu increase in the reactants also reduced the rate of heat loss in unit time. With the increase of Cu content, the heat from the reaction and the combustion temperature decrease. Then the temperature gradients become low, which result in the low rate of heat loss. As a consequence, the value of T_c and T_{ad} becomes closer.

3.2.2. *Wave velocity and ignition time*

Fig. 4 shows the variation of the combustion wave velocities and ignition time with the Cu content in the reactants. It is obvious that the combustion wave velocity decreases monotonically with the increase of the Cu content. Similar behavior was also reported by Shon et al. [24] in their study on the electrothermal combustion reaction in a Cu–Ti–C system. It is known that the combustion wave velocity depends largely on the combustion temperature and the thermal conductivity of the preforms. With the increase of Cu content in the reactants, the thermal conductivity of the preforms increases due to the high thermal conductivity of metal Cu, but the combustion temperature decreases significantly. Without the consideration of T_c, the wave velocity should increase. However, according to the present experimental results, the wave velocity decreases. The results indicate that the combustion temperature plays a more important role in the propagation velocity of the combustion wave than the thermal conductivity of the preforms.

The ignition delay time, which represents the time interval from the start of heating to the initiation of the self-propagating reaction, is called ignition time. The ignition time represents whether the reaction is easy to occur or not. It is obvious that the ignition time shows a first decrease and then a noticeable increase with the increase of Cu, implying that the SHS reaction proceeds more readily at a specified amount of the addition Cu. According to the present experimental results, the shortest ignition time is found at 20 wt.% Cu, as indicated in Fig. 4.

In order to understand the ignition behavior, DTA experiments were conducted. Actually, although the reaction in the DTA apparatus is different from the SHS reaction because of the disparity in the processing conditions, particularly for the heating rate and green density of the reactants, it is very similar to the ignition process and valuable to help understanding the ignition behavior in the SHS reaction. Fig. 5(a) and (b) shows the typical DTA curves and the XRD patterns of DTA products for the Cu–Ti–B_4C compacts with various Cu contents, respectively. It was observed during the experiments that two intense exothermic peaks with the maxima temperature at about 994 and 1094 °C appeared in the Cu–Ti–B_4C samples with 10 wt.% Cu content, respectively. For the 30 wt.% Cu sample, it can be observed that two intense exothermic peaks with the maxima temperature at about 989 and 1073 °C appeared, respectively. Besides the exothermic peak at about 985 °C, two exothermic peaks with the maxima at about 1068 and 1089 °C appeared in the 50 wt.% Cu–Ti–B_4C system, respectively. The temperatures of two exothermic peaks are very close, which may be caused by the continuous occurrence of several exothermic reactions. The DTA results in the present experiment are similar to those in the 20 wt.% Cu–Ti–B_4C system [24]. For the 20 wt.% Cu sample, two intense exothermic peaks with maxima temperature at 990 and 1098 °C appeared, respectively. According to [25],

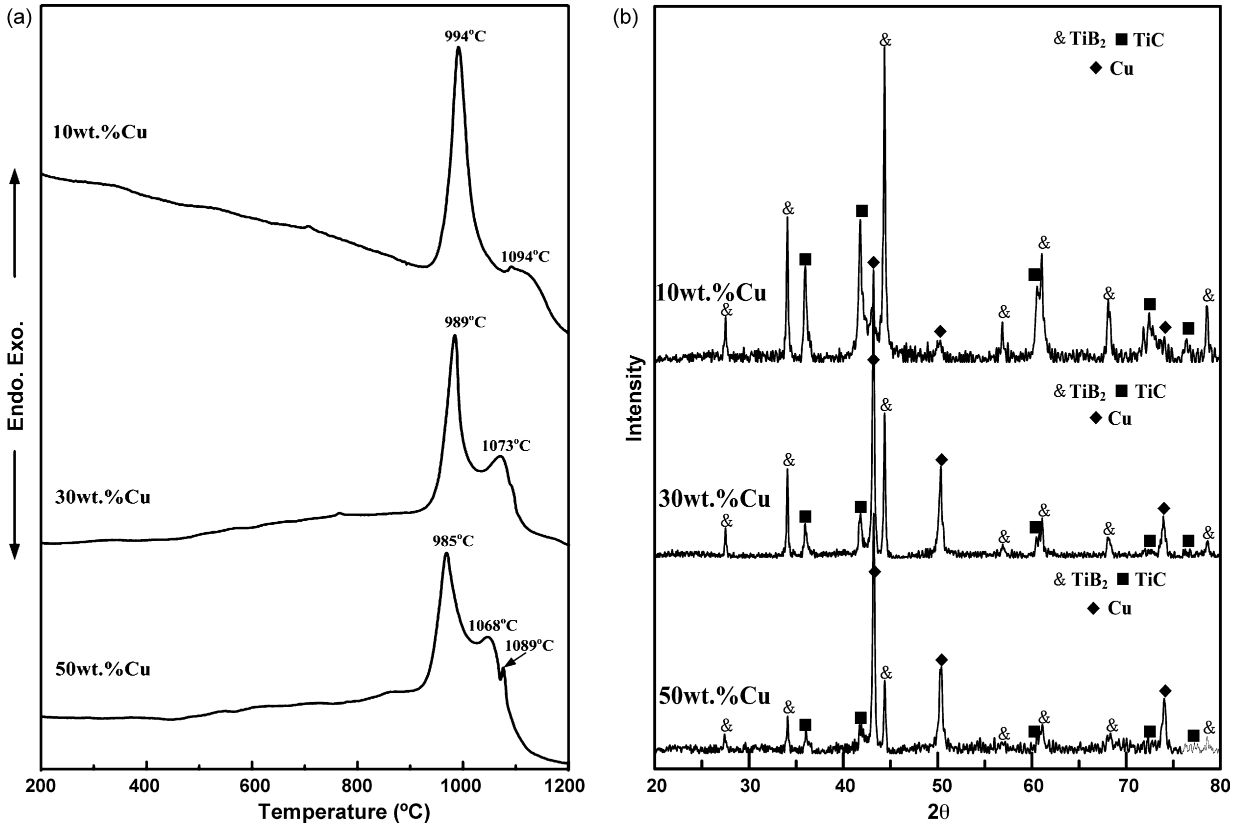

Fig. 5. (a) DTA curves of the Cu–Ti–B_4C compacts in the samples with various Cu contents and (b) XRD patterns of the DTA products.

the first exothermic peak mainly corresponded to the formation of a large numbers of the Ti_xCu_y intermetallics; and then the Ti_xCu_y intermetallics can form Cu–Ti liquid at about 960 °C. The formation of liquids and continuous heating significantly promote the further diffusion of carbon and boron away from the bulk B_4C and the formation of the Cu–Ti–B–C liquids, subsequently, TiC and TiB_2 particulates were precipitated out of the saturated liquids. The formation of the Cu–Ti liquids and its subsequent capillary-induced flow can increase the contact surface area between the reactants and provide an easier route for mass transfer. This is of great importance since it significantly promotes the contact of the reactants and reduces the atomic diffusion distance [16]. When the temperature increased further, more Cu–Ti liquids formed and spread over the reactants, and then the carbon and boron atoms continuously diffused into the Cu–Ti–B–C liquids and TiC and TiB_2 particulates were gradually precipitated out of the saturated liquids, which corresponded to the second exothermic peak with the maximum temperature at 1098 °C. According to the XRD patterns of the DTA products from the Cu–Ti–B_4C system with various Cu content quenched from 1200 °C, as shown in Fig. 5(b), it can be found that only TiC, TiB_2 and Cu are detected in the samples with 10, 30 and 50 wt.% Cu contents, without any intermediate phases, indicating that the reaction is complete. Therefore, it is reasonable to conclude that the reaction path in the investigated systems is similar to that in the 20 wt.% Cu–Ti–B_4C system.

Generally, the increase of metal content may change the reaction path and DTA curves; furthermore, the results in the present experiments indicate that the increase of Cu content can also affect the ignition process. According to the DTA results, the aforementioned ignition behavior can be well understood. The initiate of the SHS reaction in the Ti–B_4C compacts without Cu addition was difficult and the ignition time was much longer than those with Cu addition because the addition of Cu provides an easier route. In addition, with the addition of 10–70 wt.% Cu, the heat evolution from the formation of Ti_xCu_y intermetallics and the formation of subsequent Cu–Ti liquid exert a significant effect in the ignition of SHS. When a low content of Cu (10 wt.%) is added, the contact chances between Cu and Ti are small, in turn, the released heat from these reactions forming Ti_xCu_y intermetallics and the amount of Cu–Ti liquid are also low, which is unfavorable to promote the fast ignition of SHS. Oppositely, when a relatively high Cu content is added, the contact chances between Cu and Ti increase, the released heat from these reactions forming Ti_xCu_y intermetallics and the amount of Cu–Ti liquid also increase, but the thermal conductivity of the preforms increases substantially due to the high conductivity of excessive metal Cu. As a result, it is also difficult to ignite the SHS reaction. The combination of the heat evolution from the reactions and thermal conductivity of preforms makes the shortest ignition time appear in the 20 wt.% Cu–Ti–B_4C system.

3.3. Reaction products

Fig. 6 shows the XRD results of the SHS products from the 10, 30, 50 and 70 wt.% Cu–Ti–B_4C systems. As indicated, the prod-

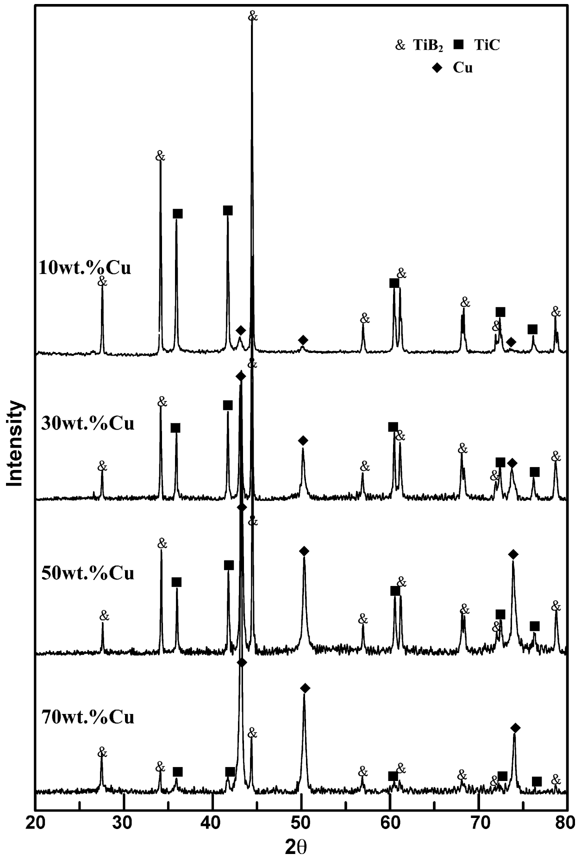

Fig. 6. XRD patterns of the SHS reaction products in the samples with various Cu contents.

ucts in the 10, 30, 50 and 70 wt.% Cu–Ti–B_4C system consist of TiC, TiB_2 and Cu, without any intermediate phases, indicating that the reaction is complete, which is similar to those in the DTA apparatus. Fig. 7 shows the typical microstructures at the fracture surfaces of the SHS products from the 10, 30 and 50 wt.% Cu–Ti–B_4C systems. The individual TiC and TiB_2 grains were developed. Clearly, the TiC particles display the typical spherical or round shape and TiB_2 particles appears hexagonal or rectangular. With the increase in the Cu reactant, the quantity of the TiC and TiB_2 grains reduces and their size decreases considerably. This is explained as follows. With the addition of Cu, the maximum combustion temperature is reduced and the TiC and TiB_2 sizes become smaller since the particle growth of TiC and TiB_2 is an exponential function of the combustion temperature. The particle growth of TiC and TiB_2, on the other hand, also depends on the dwell time at high temperatures. A higher combustion temperature and a longer dwell time obviously favor the crystal growth. Increasing the Cu content decreases the dwell time at high temperatures, and therefore the size of the particles turns to be smaller. Moreover, the increase of liquid metal surrounding ceramic particles gives rise to the increased diffusion path, reduces the driving force for ceramic particles growth, and prevents the sintering among ceramic particles to form larger particulates. These are also responsible for the microstructure evolution of the composites. Therefore, the sizes of the particulates turn to be smaller, with the increase of Cu content.

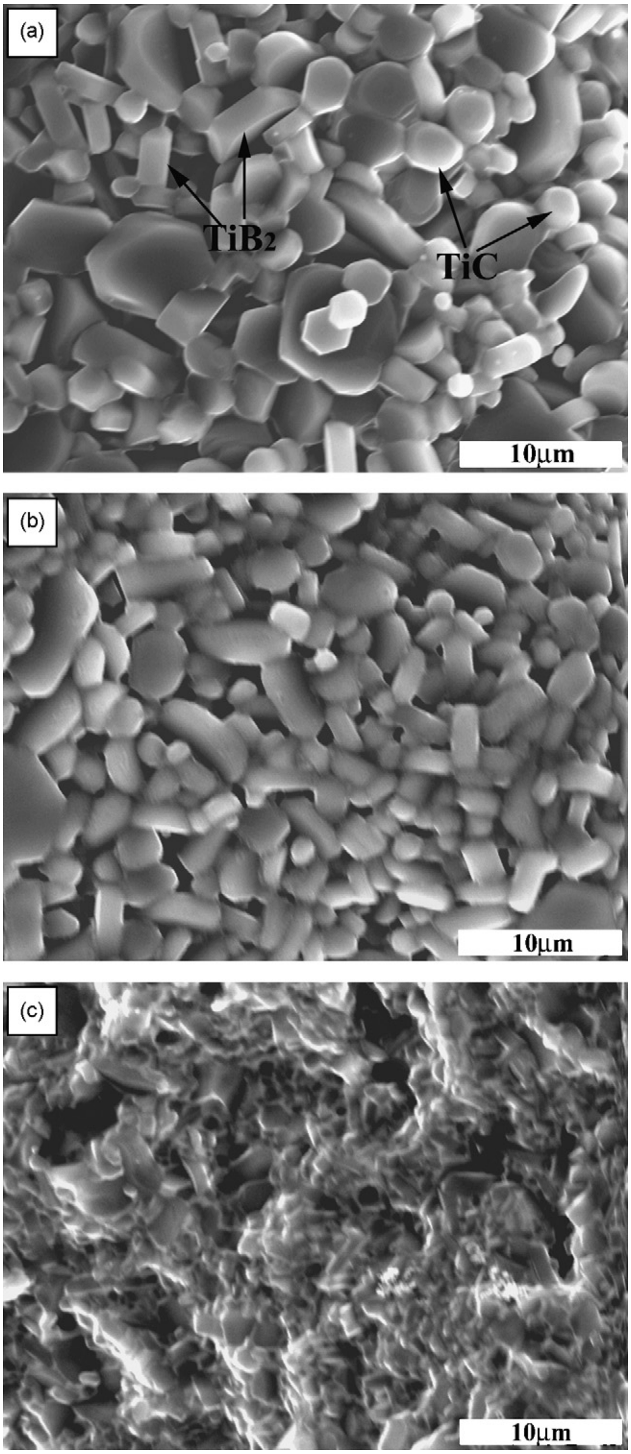

Fig. 7. The fracture surfaces of SHS products from Cu–Ti–B_4C systems with (a) 10 wt.% Cu, (b) 30 wt.% Cu and (c) 50 wt.% Cu.

4. Conclusions

In this work, the SHS reaction behaviors of the Cu–Ti–B_4C systems with various Cu contents were investigated. The following conclusions could be drawn:

(1) Theoretical calculation of the adiabatic temperatures reveals that the reaction in the Cu–Ti–B_4C system is self-sustainable

for the presence of 0–72.22 wt.% Cu in the reactants without any preheat, which is generally consistent with the experimental results. With the increase of Cu content, the adiabatic temperature decreases greatly.

(2) With the increase of Cu content, the combustion temperatures and wave velocity decreases greatly, while the ignition time shows first a remarkable decrease and then an increase with the minimum value at 20 wt.% Cu.

(3) The products in the 10–70 wt.% Cu–Ti–B_4C system consist of TiC, TiB_2 and Cu, without any intermediate phases. With the increase in the Cu reactant, the size of the TiC and TiB_2 grain decreases considerably.

Acknowledgements

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References

[1] S. Gennari, U.A. Tamburini, F. Maglia, G. Spinolo, A.Z. Munir, Acta Mater. 54 (2006) 2343–2351.
[2] W.C. Lee, S.L. Chung, J. Am. Ceram. Soc. 80 (1997) 53–61.
[3] G.Q. Xiao, Q.C. Fan, M.Z. Gua, Z.H. Jin, Mater. Sci. Eng. A 425 (2006) 318–325.
[4] D.A. Hoke, M.A. Meyers, J. Am. Ceram. Soc. 78 (1995) 275–284.
[5] A.H. Guerrero, Z. Huque, A.M. Kanury, Combust. Sci. Technol. 81 (1992) 115–128.
[6] K.A. Philpot, Z.A. Munir, J.B. Holt, J. Mater. Sci. 22 (1987) 159–169.
[7] B.K. Yen, T. Aizawa, J. Am. Ceram. Soc. 81 (1998) 1953–1956.
[8] X.H. Zhang, C.C. Zhu, W. Qu, X.D. He, V.L. Kvanin, Comp. Sci. Technol. 62 (2002) 2037–2041.
[9] J. Subrahmanyam, J. Mater. Res. 9 (1994) 2620–2626.
[10] Y. Taneoka, O. Odawara, J. Am. Ceram. Soc. 72 (1989) 1047–1049.
[11] X.H. Zhang, C. Yan, Z.Z. Yu, J. Mater. Sci. 39 (2004) 4683–4685.
[12] I. Gotman, N.A. Travitzky, E.Y. Gutmanas, Mater. Sci. Eng. A 244 (1998) 127–137.
[13] H. Zhao, Y.B. Cheng, Ceram. Int. 25 (1999) 353–358.
[14] I. Song, L. Wang, M. Wixom, L.T. Thompson, J. Mater. Sci. 35 (2000) 2611–2617.
[15] L. Klinger, I. Gotman, D. Horvitz, Mater. Sci. Eng. A 302 (2001) 92–99.
[16] P. Shen, B.L. Zou, C.B. Jin, Q.C. Jiang, Mater. Sci. Eng. A 454–457 (2007) 300–309.
[17] Y.F. Yang, H.Y. Wang, Y.H. Liang, R.Y. Zhao, Q.C. Jiang, Mater. Sci. Eng. 474 (2008) 355–362.
[18] X.H. Zhang, J.C. Han, X.D. He, J. Am. Ceram. Soc. 88 (2005) 89–94.
[19] P. Yin, D.D.L. Chung, J. Mater. Sci. 32 (1997) 1703–1709.
[20] Z.A. Munir, T.U. Anselmi, Mater. Sci. Rep. 3 (1989) 277–365.
[21] Y.J. Liang, Y.C. Che, Notebook of Thermodynamic Data of Inorganic, East-North University Press, Shen Yang, 1996.
[22] J.J. Moore, H.J. Feng, Prog. Mater. Sci. 39 (1995) 243–273.
[23] N. Kanetake, M. Kobashi, Scripta Mater. 54 (2006) 521–525.
[24] I.J. Shon, A.Z. Munir, J. Am. Ceram. Soc. 81 (1998) 3243–3248.
[25] Y.H. Liang, H.Y. Wang, Y.F. Yang, Y.L. Du, Q.C. Jiang, Int. J. Refract. Met. H, in press.