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In-situ combustion synthesis of ultrafine TiB_2 particles reinforced Cu matrix composite

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Due to the lower strength of pure copper (Cu), ceramic particulate or whisker reinforced Cu matrix composites have attracted wide interest in recent years [1–3]. These materials exhibit a combination of excellent thermal and electrical conductivities, high strength retention at elevated temperatures, and high microstructural stability [3]. The potential applications include various electrodes, electrical switches, and X-ray tube components [4].

Titanium diboride (TiB_2) is well known for its high stiffness and hardness (only less than diamond). Also, in contrast to most ceramics, it is electrically and thermally conductive. Thus, the addition of TiB_2 to a metal matrix can greatly improve stiffness, hardness, and wear resistance without apparent loss of thermal expansion coefficient and electrical and thermal conductivities as compared to other ceramic reinforcements [5, 6]. Recently, TiB_2 reinforced metal matrix composites have been extensively investigated [3, 7, 8]. Lee *et al.* [9] indicated that the TiB_2–Cu composite exhibited much higher yield strength than pure copper.

Relatively, little work has been done on the combustion synthesis of copper-based composites [10, 11]. Combustion synthesis, also named self-propagating high temperature synthesis (SHS), is designed to use the extreme reaction heat generated during the formation of refractory substances for materials processing. The advantages of SHS technique include low energy requirement, relative simplicity of process and equipment, higher purity of the products, and low cost [12]. In this work, the preparation of the ultrafine TiB_2 particles reinforced Cu matrix composite by *in-situ* combustion synthesis was carried out, and its microstructure and properties are discussed.

The precursors used in this work were commercial grade titanium (40–70 μm), amorphous boron ($\approx$1 μm), and copper (70–100 μm) powders. The amount of Ti, B, and Cu powders added was estimated in term of the following re action:

$$\mathrm{Cu} + 30\mathrm{wt\%}\,(\mathrm{Ti} + 2\mathrm{B}) \rightarrow \mathrm{Cu} + 30\mathrm{wt\%}\,\mathrm{TiB_2} \quad (1)$$

The Ti, B, and Cu powders were dry-mixed in a stainless steel vial. Then the mixture was cold-pressed uniaxially into stainless steel dies under a pressure of 33 MPa to prepare cylindrical green compacts with a diameter of 55 mm. The compact was put into a specially designed SHS reactor with the details illustrated in our previous paper [13]. The synthesis of the Cu–TiB_2 composite was conducted through self-propagating exothermic reaction in conjunction with pseudo hot isostatic pressing.

The microstructure of the Cu–TiB_2 composite was characterized using scanning electron microscopy (SEM, JSM-5610LV). Hardness (HRA) was measured using a HRS150 machine with a diamond indenter under a load of 60 kgf. The tensile strength of the composite was measured using an Instron testing machine with a crosshead speed of 5 mm/min. Single-edge notched bend specimens (2 × 4 × 20 mm) with a notch of depth 2 mm and radius 0.2 mm were used to evaluate the fracture toughness at a crosshead speed of 0.05 mm/min.

The reaction formation enthalpy (ΔH) in reaction (1) was calculated using the thermodynamic data from Ref. [14]. The results are shown in Fig. 1. The reaction formation enthalpy ΔH is negative when the temperature is higher than 2176 K. This indicates that the reaction is exothermic above this temperature. Actually, 2176 K corresponds to the adiabatic temperature (T_{ad}) of the Cu–Ti–B ternary system. It is well known that T_{ad} is the maximum temperature to which the final products can be raised as a result of exothermic reaction without heat loss in a combustion process. T_{ad} is an important thermodynamic parameter for any combustion synthesis reactions, which can be used in a semi-quantitative way to estimate whether the synthesis of a given material system can be accomplished by a self-propagating process. Also, it is empirically suggested that combustion reactions cannot become self-sustaining unless $T_{ad} \geq 1800$ K [15]. For the Cu–Ti–B ternary system, the reaction can take place in a self-propagating mode as T_{ad} is higher than 1800 K.

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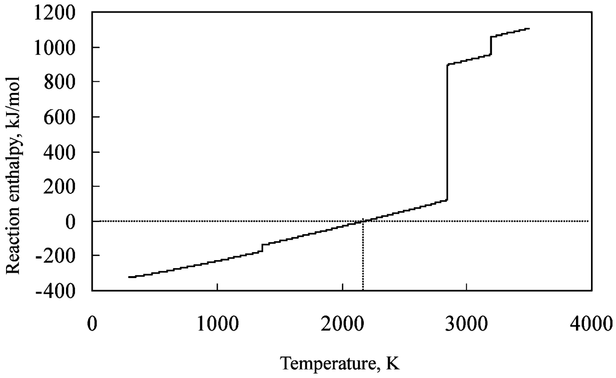

Figure 1 Reaction enthalpies of the Cu–30wt%TiB_2 composite.

During the combustion synthesis, Ti, B, and Cu may interact to form some possible products due to the existence of following chemical reactions:

$$Ti + B \rightarrow TiB \tag{2}$$

$$Ti + 2B \rightarrow TiB_2 \tag{3}$$

$$Ti + 4Cu \rightarrow TiCu_4 \tag{4}$$

$$Ti + Cu \rightarrow TiCu \tag{5}$$

$$2Ti + Cu \rightarrow Ti_2Cu \tag{6}$$

In order to determine the reaction directions and the synthesized products, the reaction free energy of Equations 2–6 was theoretically calculated according to the thermodynamics data [14] and the results are shown in Fig. 2. The calculated reaction free energy of TiB_2 is the lowest one among the five possible products. Therefore, TiB_2 is the most stable phase in the Ti–B–Cu system. The reaction free energy of $TiCu_x$ is negative so it is unlikely to form during the reaction.

Fig. 3 shows the X-ray diffraction patterns of the synthesized Cu–TiB_2 composite. It can be seen that copper and TiB_2 phases exist but no $TiCu_x$ intermetallic phase can be identified. With the propagation of combustion waves, the $TiCu_x$ interphase, which may form during the combustion, can react with boron to produce TiB_2 and copper. This is consistent with the thermodynamic calculations.

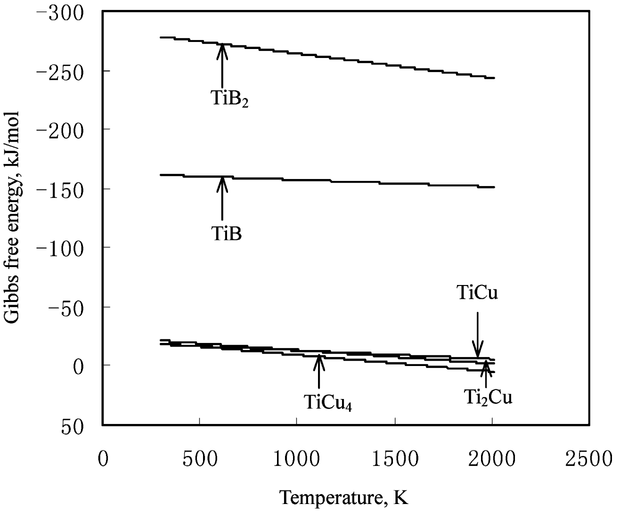

Figure 2 Variation of the Gibbs free energy as a function of temperature.

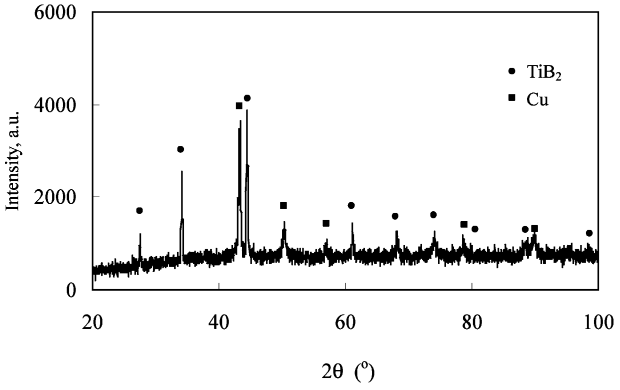

Figure 3 XRD pattern of the Cu–30wt%TiB_2 composite.

Fig. 4 shows the microstructure of the Cu–30wt%TiB_2 composite produced by combustion synthesis. It consists of spheroidal TiB_2 particles (dark phase) dispersed uniformly in the Cu matrix (white phase). It is noted that the size of the fine TiB_2 grains is about 70–300 nm. The microstructure of the Cu–60wt%TiB_2 composite produced under the same condition is shown in Fig. 5. It is clear that the size of TiB_2 particles in Cu–30wt%TiB_2 is much smaller than that in Cu–60wt%TiB_2. For the Cu–Ti–B ternary system, the combustion temperature is lowered due to the addition of Cu, which can lead to the grain refinement as the grain growth of TiB_2 is an exponential function of the combustion temperature. Also, the liquid metal surrounding TiB_2 particles can prevent the neighboring TiB_2 grains forming larger grains. These are also responsible for the microstructure evolution of the composites. Normally, TiB_2 has a C32 structure (hexagonal, $a = 3.033$ Å, $b = 3.06$ Å, and $c = 4.56$ Å), characterized by the alternate stacking of Ti planes and the graphite-like B network along the c-direction [16]. TiB_2 attempts to form a plate-like or fairly equiaxed morphology (Fig. 5) unless grain growth and agglomeration of TiB_2 particles are hindered, as happened to Cu–30wt%TiB_2 where spherical particles were obtained.

In Fig. 4, it is also seen that the interfacial bonding between TiB_2 particles and the copper matrix is very strong. However, in the Cu–60wt%TiB_2 with coarse ceramic particles, interfacial debonding or interface cracking was observed, as indicated by the arrows in Fig. 5. The wetting angle between TiB_2 and Cu is 142° in vacuum [17]. The wettability is so poor that a weak interfacial bonding in TiB_2–Cu is expected. On the other hand, the large mismatch of thermal expansion coefficient and elastic modulus between TiB_2 and Cu can create a large thermal stress in the interfaces during cooling, thereby inducing interface cracks. On the other hand, the strong interfacial bonding in the Cu–30wt%TiB_2 indicates that grain refinement can improve the wettability between the reinforcement and the matrix. Mechanical properties of the Cu–30wt%TiB_2 composite are shown in Table I. The introduction of ultrafine TiB_2 ceramic particles into the Cu matrix results in an apparent increase in hardness and tensile strength. Compared to pure copper, the increase in yield strength is about 116 MPa, which is attributed to the dispersion strengthening by the fine TiB_2 particles. As expected, fracture toughness (K_{IC}) of the composite

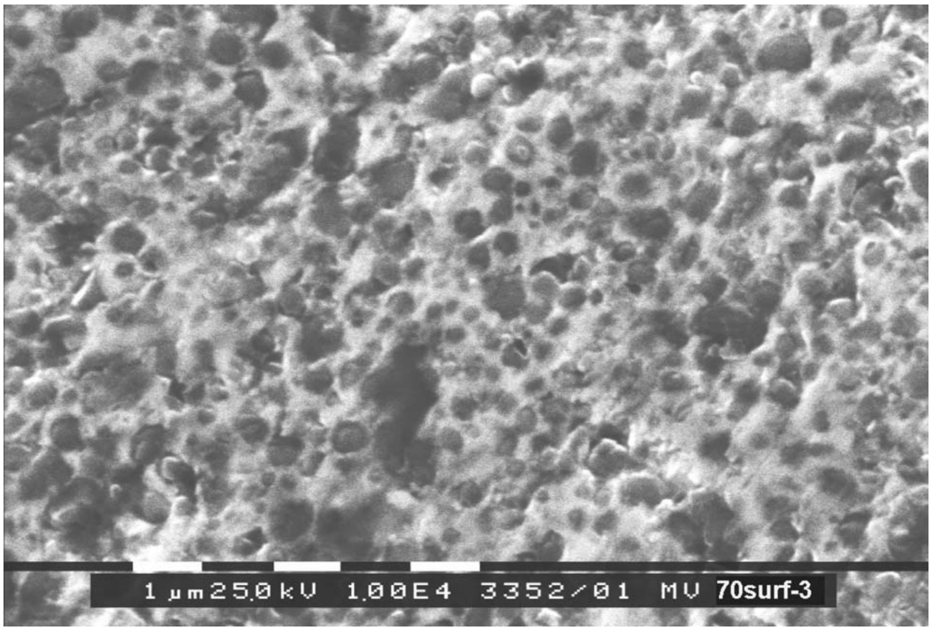

Figure 4 Microstructure of the Cu–30wt%TiB_2 composite.

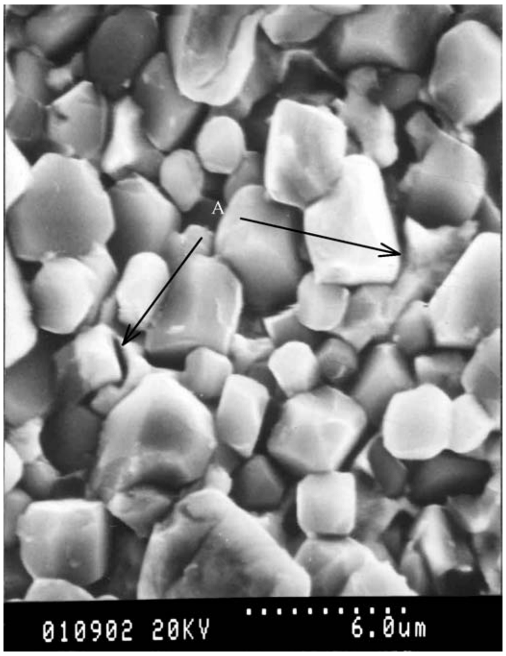

Figure 5 Microstructure of the Cu–60wt% TiB_2 composite.

TABLE I Mechanical properties of Cu–TiB_2 composite and pure copper

Materials	Hardness (HRC)	Yield strength (MPa)	K_{IC} (MPa m$^{1/2}$)
Pure Cu	37.3	195	>100
Cu–30wt% TiB_2 composite	48	311.56	10.44

is much lower than that of Cu but higher than TiB_2 [18].

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