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Effect of La addition on the particle characteristics, mechanical and electrical properties of in situ Cu-TiB_2 composites

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ABSTRACT

In situ Cu-TiB_2 composites can be synthesized via metallurgical process by mixing Cu-B and Cu-Ti master alloys before casting. In this paper, La, as a rare earth element was added to the composites to improve the comprehensive properties and the effects of its addition on the microstructures, mechanical and electrical characteristics of Cu-TiB_2 composites were investigated. Results show that addition of La significantly diminishes the average size and facilitates a homogeneous distribution of TiB_2 particles in the copper matrix. As a result, an improvement in mechanical properties was achieved. In particular, a remarkable change in the conductivity of the composites appears with the variation of La content. The mechanisms of particle refinement and improvements in properties by La alloying were analyzed.

1. Introduction

High strength and high conductivity copper alloys have many industrial applications, such as rail transit contact wires, integrated circuit lead frames, the electrodes of resistance welding and so on [1–4]. Owing to desired combination of mechanical properties, electrical conductivity and thermal conductivity, copper matrix composites (CMCs) has attracted so much attention in recent years. Many routes, such as powder metallurgy, mechanical alloying, internal oxidation, self-propagating high-temperature synthesis (SHS), etc. have been developed to fabricate CMCs [5–11]. Compared to the conventional ex situ methods, in situ reaction synthesis produces superior wetting interface between particle and matrix, and the CMCs thus prepared exhibit preferable integrated performances (i.e. tensile strength and electrical conductivity). Therefore, in situ reaction synthesis, as a promising route to fabricate high quality CCMs, has been extensively investigated in the past fifteen years [12–15]. Among various in situ routes, the casting process is of particular interest owing to its lower cost and potential for mass production.

Compared to the unreinforced copper, the improved properties of the CMCs mainly originate from the second-phase particles, such as carbides (TiC, SiC), borides (TiB_2, ZrB_2) and oxides (Al_2O_3) [10,16–21]. Among these particles, TiB_2 is deemed to be a good candidate to reinforce CMCs because of its high hardness value (HV: 34 GPa), high elastic modulus (574 GPa), good electrical conductivity (14.4 μΩ cm) and good thermodynamic stability [22]. Moreover, TiB_2 particles are thermodynamically stable and can easily form through in situ reactions between titanium and boron elements in copper melt [23,24]. In this process, in order to maximize the reinforcing efficiency of TiB_2, it is desirable to have the tiny in situ TiB_2 particles as much as possible homogeneously distributed throughout the copper matrix according to the Orowan strengthening mechanism. This goal, however, is generally hard to meet since the high surface energy of TiB_2 particles will lead to severe agglomeration of TiB_2 particles after solidification. It has been reported in the literature that rare earth elements are widely used in various processes to improve the microstructures and mechanical properties of copper and CMCs [25–29]. These beneficial effects were attributed to the special physical and chemical characteristics of rare earth elements. For example, La could effectively refine the microstructures in the as-cast Cu-Zr composites, resulting in the improvement of the hardness and conductivity simultaneously [30]. Therefore, the rare earth elements seem to be good candidates

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to modify the properties of copper and CMCs for its less cost.

In this study, La, chosen as a representative of the rare earth elements, was added to prepare in situ TiB_2 particulate reinforced CMCs. The effects of La on the particle size and distribution of TiB_2, mechanical properties and conductivity of Cu-TiB_2 composites were examined.

2. Experimental procedure

Pure Cu (99.97% purity, weight percentage, all in the same unit unless otherwise specified) was used as the matrix. Cu-5B and Cu-10Ti master alloys were used as the reactive agents. Pure La (99.99% purity) was added into the composites. The composites were prepared in a vacuum medium frequency induction melting furnace. When the temperature of Cu melt reached 1300 °C, La, Cu-B and Cu-Ti master alloys were incorporated into the melt sequentially. After holding for 5 min, TiB_2 particles were formed via chemical reactions between Ti and B. Subsequently, the melt was poured into a cylindrical graphite mould (45 mm in diameter and 220 mm in height) which was preheated to 300 °C. After homogeneous annealing at 960 °C for 3 h, the as-cast billets were rolled at 850 °C with a 17% reduction (from 30 mm to 25 mm) and then further rolled to 1.5 mm with a total of 94% reduction at room temperature. A series of Cu-1 wt% TiB_2 composites with 0.02, 0.04, 0.06 and 0.08 wt% La were produced. For comparison, a reference sample without La addition was also prepared.

The samples were mechanically ground, polished and etched with a corrosive agent (3 g $FeCl_3$, 2 mL HCl and 95 mL C_2H_5OH) for metallographic examination. The microstructure and TiB_2 distribution in the copper matrix were observed under a scanning electron microscopy (SEM, Zeiss supra 55) operated at secondary electron mode with an accelerating voltage of 15 kV complemented by energy-dispersive spectroscopy (EDS). Phases in the in situ Cu-1TiB_2 composites with and without La were identified using an X-ray diffractometer (XRD, EMPYREAN, Cu Kα radiation, scanning from 20° to 100° in 2θ at a scanning speed of 0.26738°/s). The morphology of TiB_2 particles, interface between TiB_2 and copper matrix and the dislocations and twin crystals in samples were investigated using Talos F200x field emission transmission electron microscopy at an accelerating voltage of 200 kV. The tensile specimens, with a dimension of 35 mm gauge length, 5 mm diameter, were machined from the samples according to the ASTME8 standard test methods for tension testing of metallic materials. Tensile tests with cross head speed of 2 mm min^{-1} were conducted at room temperature. Vickers hardness tests were performed under a load of 100 g for 10 s using a Vickers hardness tester (MH-6L). For each test, five measurements were performed at an interval of 1 mm and average experimental data were recorded. The electrical conductivities were measured by D60K eddy current conductivity meter. The samples size was bigger than 15 mm diameter and thicker than 2 mm. And five measurements were also performed for each test.

3. Results and discussions

3.1. Microstructures investigations

3.1.1. XRD analysis

The XRD patterns of Cu-1TiB_2% and Cu-1TiB_2-0.04La were shown in Fig. 1. The XRD spectrum clearly demonstrated that TiB_2 was successfully synthesized in the copper matrix via the casting process. But comparing the two spectra one may see that addition of La did not noticeably change the phase composition of the composite due to its trace amount of 0.04 wt%.

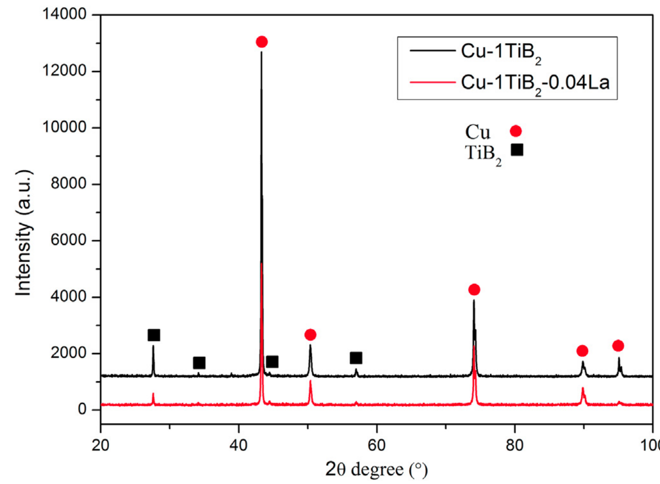

Fig. 1. XRD patterns of Cu-1 wt% TiB_2 and Cu-1 wt% TiB_2-0.04 wt% La composites.

3.1.2. SEM analysis

The microstructure of Cu-1TiB_2 with different mass faction of La are presented in Fig. 2. Fig. 2 (f) is the EDS analysis of the blocky particle in the Cu-TiB_2 sample with 0.04 La. From the SEM micrographs of the composites in Fig. 2a–c, a significant decreasing trend in particle size can be observed. The detailed size distribution of TiB_2 particles in the composites with different La content is plotted in Fig. 3. From the quantitative data, it is easy to see that the average particle size is refined from 1132 nm to 423 nm when the La addition is increased from none to 0.04 wt%, whilst an increasing trend followed once the La addition rate exceeded 0.04 wt%.

Besides, change in the morphology of the TiB_2 particles is also noticed in Fig. 2. An irregular angular shape was gradually smoothened and refined to round morphology, along with the decrease in particle size. The roundness has been defined to describe the morphology of particles. And it was calculated by the equation: Roundness $= 4\pi s/l^2$ [31], where l is the perimeter and s is the area of the particles in the SEM image which were measured by image-pro plus. According to the equation, the roundness of TiB_2 particles reduced from 1.41 for the reference sample, to 1.29 for the 0.04 wt% La composite, as shown in Fig. 4. Moreover, the roundness of the particle show an increase trend at La addition beyond 0.04 wt %.

Another interesting effect has caught attention is that the distribution of TiB_2 particles has also been improved, from a severe aggregation to relative dispersion via La addition (Fig. 2). But just like the size and roundness, the distribution of TiB_2 particles also deteriorates when extra La was added into the composite.

3.1.3. TEM analysis

From Fig. 5, acquiring from Cu-1TiB_2-0.08La, (a) presents the TEM observation of TiB_2 morphology. In Fig. 5 (b), it can be seen a lot of twins in the copper matrix, and the twins bend due to the prevention of particles in deformation. The interaction between TiB_2 particles and dislocations is also observed in the TEM image in Fig. 5 (b), it can be clearly seen that the dislocations pile up around TiB_2 particles after the deformation. Furthermore, the interface between copper and TiB_2 was perceptible from HRTEM images. The interface bonding state between copper and TiB_2 is shown in Fig. 5 (c) and (d), which indicates that in situ synthesized TiB_2/Cu composites own well interface and can result in a better mechanical properties.