

Fabrication and Properties of Nano-TiC_x/Cu-Cr-Zr Alloy Composites

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Abstract. Nano-sized TiC_x/Cu master alloy was prepared by the in situ method of combustion synthesis and hot press consolidation in Cu-Ti-Cr-Zr system. The nano-TiC_x/Cu-Cr-Zr alloy composites were fabricated by dispersing the nano-sized TiC_x/Cu master alloy into molten Cu-Cr-Zr alloy via stir casting. It was revealed that the average grain size of TiC_x/Cu-Cr-Zr alloy composites was significantly refined from 90 μm to 20 μm, the Brinell Hardness of nano-TiC_x/Cu-Cr-Zr alloy composites increased from 75.1 HB to 86.8 HB, and the wear resistance increased by 12.6%, compared with the Cu-Cr-Zr alloy. The electric conductivity slightly decreased from 64.71% IACS to 52.93% IACS. The improvements of hardness and wear resistance result from nano-TiC_x and grain refinement strengthening.

Keywords: nano-TiC_x; Cu-Cr-Zr alloy; stir casting; wear resistance; combustion synthesis

1 Introduction

Good electrical, thermal conductivity, corrosion resistant and welding performance, in addition to mechanical properties make Cu-Cr-Zr alloy an attractive material for a wide range of applications such as electricity, electronics, machinery, metallurgy and other industrial fields [1-4]. However, the hardness and wear resistance is a permanent problem for copper based materials.

In order to improve the hardness and wear resistance of Cu-Cr-Zr alloy, several reinforcement methods are put forward. One is alloying, appropriate elements are introduced to form a solution; Heat treatment is also used to achieve high strength and high conductivity copper alloy [5, 6]. Machining deformation is also an effective method to strengthen Cu-Cr-Zr alloy. Another approach to enhance the hardness and wear resistance

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of Cu without such detriment to the conductivity is to introduce a hard second phase into the copper to form the production of a copper matrix composite^[7].

Introducing a second phase into the metal, the advantages of both metal and the second phase are preserved^[8-12]. According to the theory of conduction, the second phase in metal has weaker influence in scattering of electron compared with the atomic solution^[8]. Therefore, the second phase is the best method in strengthening Cu-Cr-Zr alloy. In situ method include the following advantages compared with ex situ, clean interface, good wettability and high strength combination, besides, the particle is round in shape and uniform in distribution^[10, 13-15]. Experiments show that the finer of the particles resulting in more number and smaller particle spacing, the better the material performance improvement of a certain volume fraction^[16, 17]. However, there is hardly any report about in situ ceramic particles, especially in situ nano-sized TiC_x enhancing Cu matrix composites^[18, 19].

Therefore, in this study, combustion synthesis (CS) and hot press (HP) are combined to fabricate the nano-sized TiC_x -Cu master alloy. Stirring casting is chosen as a main method to disperse the nano-sized TiC_x /Cu master alloy in the Cu-Cr-Zr alloy. The hardness, wear resistance and conductivity of as-cast Cu-Cr-Zr alloy and nano- TiC_x /Cu-Cr-Zr alloy composites were investigated in detail.

2 Materials and Experimental Procedures

The master alloy was fabricated by combustion synthesis of power mixture in Cu-Ti-CNTs system. The starting materials were made of commercial powders of Cu (99.7% purity, $\sim 45\mu m$), Ti (99.5% purity, $\sim 25\mu m$) and CNTs (95% purity, 20-30nm in diameter and $30\mu m$ in length), which was used to synthetic the master alloy. The reactant powders were mixed in a stainless steel container for 24h to ensure homogeneity, and then pressed into cylindrical compacts (about 28 mm in diameter and 30 ± 5 mm in length) using a stainless steel die to obtain densities of $65\pm 2\%$ theoretical density.

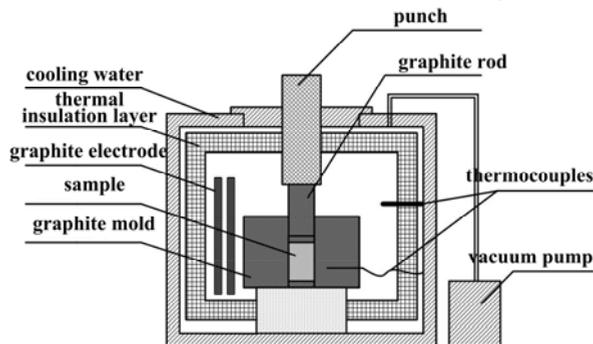


Fig.1 Schematic of the equipment for the combustion synthesis and hot press consolidation experiment.

The combustion synthesis (CS) experiments were conducted in a self-made vacuum thermal explosion furnace as illustrated in Fig.1. The compact was placed in a graphite mould and heated at the heating rate of $30^\circ C/min$ under a protective atmosphere of argon to prevent titanium or carbon loss through oxidation. When the temperature which was measured by Ni-Cr/Ni-Si thermocouples suddenly rose rapidly, indicating that the formation reaction of the ceramics was ignited, the sample was quickly pressed with the

uniaxially pressure of 42 MPa just when it was still hot and soft, and the master alloy is ready when it was cooled down to the ambient temperature.

TABLE 1 THE CHEMICAL COMPOSITION OF CU-CR-ZR ALLOY

Element	Cu	Cr	Zr	Si	Fe	Mg	Al
wt.%	Bal.	0.65	0.60	0.05	0.05	0.15	0.18

The composite was fabricated by dispersing the nano-sized TiC_x/Cu master alloy into the Cu-Cr-Zr alloy. The chemical composition of Cu-Cr-Zr alloy is shown in table 1. Cu-Cr-Zr alloy was placed in a graphite crucible and heated in an induction furnace, and then the nano-sized TiC_x/Cu master alloy was added into the molten Cu-Cr-Zr alloy which would be protected by carbon powder. Once the nano-sized TiC_x/Cu master alloy was molten, poured the melt into the prepared mold.

The phases present of the nano-sized TiC_x/Cu master alloy and nano- TiC_x/Cu -Cr-Zr alloy composites materials were characterized using X-ray diffraction (XRD, Rigaku D/Max 2500PC, Japan). The bulk samples were then dissolved in a $FeCl_3$ -HCl distilled water solution to remove the Cu coating on the surfaces of the TiC_x grains. The morphologies of the extracted TiC_x grains were then observed using a field emission scanning electron microscope (FESEM, JSM 6700F, Japan). The microstructure of as-cast Cu-Cr-Zr alloy and nano- TiC_x/Cu -Cr-Zr alloy composites are observed by Olympus optical microscope (XJZ-6, Japan).

3 Results and Discussion

3.1 Master Alloy.

Fig.2 (a) shows the XRD patterns for the master alloy. It can be seen that all the products consist of Cu and TiC_x phases, without any intermediate phases, it indicates that the pure composites could be successfully fabricated by the method of combustion synthesis and hot press consolidation. The master alloy is identified as TiC_x/Cu master alloy. Fig.2 (b) shows the FESEM images of the extracted TiC_x grains in master alloy. As indicated, most of the TiC_x grains are typical spherical with sizes about 50nm, and the rests are near spherical.

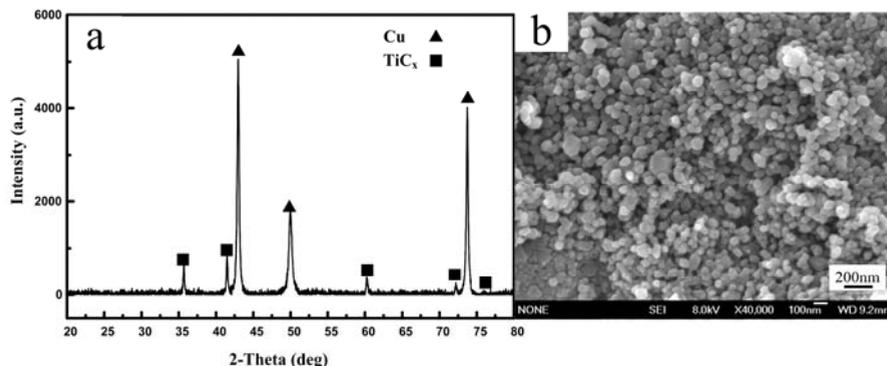


Fig.2 a) XRD patterns and b) FESEM images of the TiC_x grains for the master alloy

According to previous studies, the size of in situ TiC_x in particles enhanced Cu matrix composites is almost micron size which is mainly because of the carbon source. However,

CNTs is used as carbon source to increase the reactivity in the research, TiC_x fabricated by CS is easy to react, and adiabatic temperature is reduced. The main mechanism of thermal explosion in Cu-Ti-CNTs system is dissolution-precipitation [15]. With the increase of temperature, the Ti_xCu_y compounds are firstly formed due to the solid diffusion between Ti and Cu, once the temperatures reached to the molten point of the Ti_xCu_y compounds, the melting of Ti_xCu_y compounds occurs, and the Cu-Ti liquid forms and spreads over the CNTs particles. The formation of the Cu-Ti liquid promotes further diffusion of C atoms away from the bulk CNTs particles, as well as the formation of the Cu-Ti-C liquid. As more and more C atoms diffused into the liquids, some TiC_x can be formed at the interface between the liquid CNTs particles. With the increase of temperature, the C atoms in the CNTs particle become activated and continuously diffuse into the liquids. CNTs particles become smaller and are gradually consumed, as a result, TiC_x particulates are gradually precipitated out from the liquid, finally, the CNTs particles are consumed completely. CNTs are smaller in a single volume and more in number when the total volume is defined. CNTs is propitious to transmit when it is chosen as the carbon source, which is more conducive to react, consequently, the adiabatic temperature is reduced contributing to refine TiC_x grains.

3.2 Nano- TiC_x /Cu-Cr-Zr Alloy Composites.

Fig.3 shows the XRD patterns for the as-cast Cu-Cr-Zr alloy and 4wt.% nano- TiC_x /Cu-Cr-Zr alloy composites. It can be seen that the nano- TiC_x /Cu-Cr-Zr alloy composites of Cu and TiC_x phases, without any intermediate phases, it indicates that the nano- TiC_x /Cu-Cr-Zr alloy composites could be successfully fabricated by dispersing nano-sized TiC_x /Cu master alloy into Cu-Cr-Zr alloy.

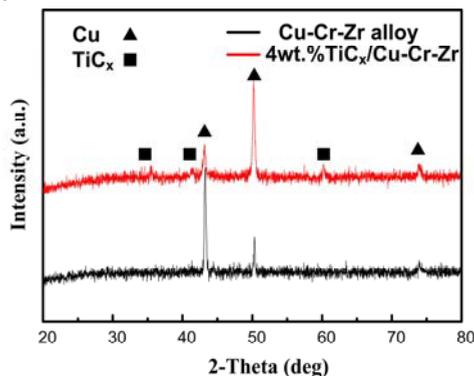


Fig.3 XRD patterns for the as-cast Cu-Cr-Zr alloy and 4wt.% nano- TiC_x /Cu-Cr-Zr alloy composites

Microstructure of the as-cast Cu-Cr-Zr alloy and 4wt.% nano- TiC_x /Cu-Cr-Zr alloy composites are presented in Fig.4(a,b), respectively. The micrographs show the microstructure of as-cast Cu-Cr-Zr alloy and nano- TiC_x /Cu-Cr-Zr alloy composites. Fig.4 (a) shows the grains of as-cast Cu-Cr-Zr alloy is coarse dendrite with the size mainly about in 90 μ m. However, the grains of the 4wt.% TiC_x /Cu-Cr-Zr alloy composites is equiaxed-crystal with the size about in 20 μ m, furthermore, the size is relatively uniform and the grain boundary is more obvious, as shown in fig.4(b). The different morphology of the grains indicated that the incorporation of nano- TiC_x refined the grain of Cu-Cr-Zr alloy successfully.

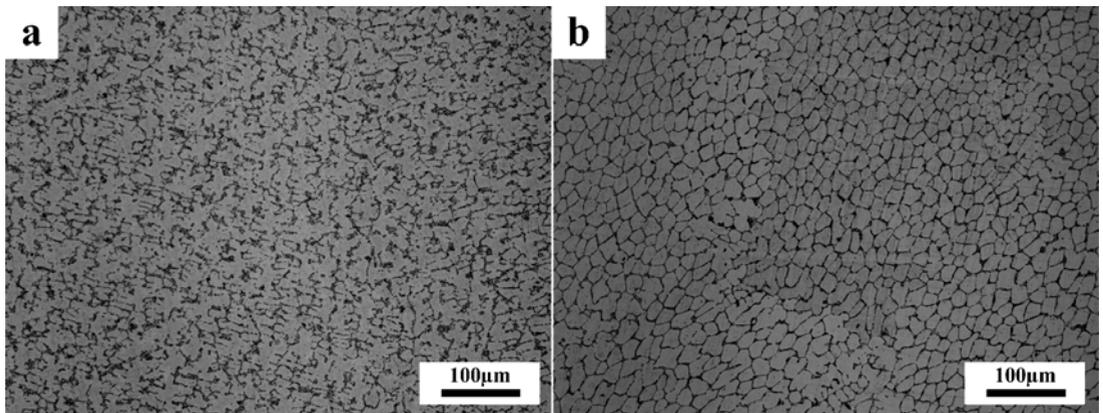


Fig.4 The microstructures of (a) as-cast Cu-Cr-Zr alloy and (b) 4wt.% nano-Ti_x/Cu-Cr-Zr alloy composites

As known, the morphology change of the dendrites could be an important factor for improving the wear resistance properties. Report has revealed about the nano-sized Ti_x refined the α -Al dendrites as heterogeneous nucleation sites [20]. Here we also suggest that the nano-sized Ti_x particles acted as heterogeneous nucleation sites of the Cu crystal during solidification, resulting in a more refined microstructure. More boundaries are formed because of the refined dendrites in the nano-Ti_x/Cu-Cr-Zr alloy composites. The high boundary concentration and the ceramic particles play an important role as barriers to the enablement the deformation, which is helpful to improve the hardness and wear resistant.

3.3 Hardness and Wear Resistance.

Hardness and wear resistance are the main existing problems of Cu-Cr-Zr alloy so far. The hardness, wear resistance and conductivity experimental results are shown below.

TABLE 2 THE BRINELL HARDNESS AND CONDUCTIVITY OF AS-CAST CU-CR-ZR ALLOY, NANO-TiC_x/CU-CR-ZR ALLOY COMPOSITES AND NANO-SIZED TiC_x/CU MASTER ALLOY

	as-cast Cu-Cr-Zr alloy	nano-TiC _x /Cu-Cr-Zr alloy composites	nano-sized TiC _x /Cu master alloy
Hardness (HB)	75.1±1.0	86.8±1.0	107.2±1.0
Conductivity (%)	64.71	52.93	43.59

Table 2 shows the Brinell Hardness and the conductivity of as-cast Cu-Cr-Zr alloy,

nano-TiC_x/Cu-Cr-Zr alloy composites and nano-sized TiC_x/Cu master alloy. The Brinell Hardness of nano-TiC_x/Cu-Cr-Zr alloy composites increased from 75.1HB to 86.8HB compared with as-cast Cu-Cr-Zr alloy, the conductivity are 64.71%IACS, 52.93%IACS and 43.6%IACS respectively for as-cast Cu-Cr-Zr alloy, nano-TiC_x/Cu-Cr-Zr alloy composites and nano-sized TiC_x/Cu master alloy.

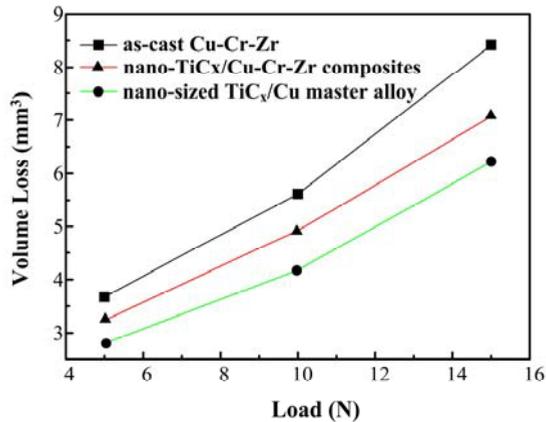


Fig.5 The wear volume applied different loads (5N, 10N, 15N) under the counterface of 2.0 μ m Al₂O₃ particles for the as-cast Cu-Cr-Zr alloy, Nano-TiC_x/Cu-Cr-Zr alloy composites and nano-sized TiC_x-Cu master alloy

The volume wear loss of Nano-TiC_x/Cu-Cr-Zr alloy composites reduced from 3.674 mm³ (5N), 5.618 mm³ (10N) and 8.416 mm³ (15N) to 3.243 mm³ (5N), 4.9225 mm³ (10N) and 7.065 mm³ (15N) respectively compared with as-cast Cu-Cr-Zr alloy, as shown in Fig.5.

On the whole, the dispersion of nano-sized TiC_x/Cu master alloy into the Cu-Cr-Zr alloy refined the grains. Under the condition of the pin-on-disc sliding wear, wear resistance is only determined by the hardness. Nano-TiC_x plays the role as second hard particles, which improved the hardness. As a result, the wear resistance is improved to a large extent. However, both the grain refinement resulted in the increase of grain boundary and nano-TiC_x increase the scattering of free electron movement, interface resistance increased, the conductivity of 4wt.% nano-TiC_x/Cu-Cr-Zr alloy composites is reduced to a certain extent.

4 Conclusions

In summary, nano-sized TiC_x-Cu master alloy was fabricated by CS+HP. Nano-TiC_x/Cu-Cr-Zr alloy composites were fabricated by dispersing the nano-sized TiC_x/Cu master alloy into molten Cu-Cr-Zr alloy via stir casting successfully. With the addition of TiC_x, the grain size of the nano-TiC_x/Cu-Cr-Zr alloy composites decreased from 90 μ m to 20 μ m. It is beneficial to improve the mechanical property of Cu-Cr-Zr alloy, which Brinell Hardness increased from 75.1 HB to 86.8 HB. Compare with the Cu-Cr-Zr alloy, wear resistance of the nano-TiC_x/Cu-Cr-Zr alloy composites increased by 12.6% and the electric conductivity slightly decreased from 64.71% IACS to 52.93% IACS. The improvements of hardness and wear resistance result from nano-TiC_x and grain refinement strengthening.

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