PREPARATION AND CHARACTERIZATION OF CU-5 %NI-XC (X = 2 %, 4 %, 6 %, 8 %) COMPOSITE MATERIALS

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Abstract. Cu-5%Ni-xC (x = 2%, 4%, 6%, 8% wt.) composite powders were prepared by mechanical alloying (MA). The effect of the C content and milling time on the microstructure and phase structure of the composite powders was studied. Then the composite powders were pressed into a tablet and Cu-Ni-C composite materials were obtained after the tablet was sintered at 800 °C. XRD analysis shows that only the Cu diffraction peak was observed after ball milling. The Cu diffraction peak gradually shifted to the low angle with the increase of the C content, which indicated that the Cu-Ni-C solid solution had been formed. As the C content increased (8%), a small amount of carbon was observed at the grain boundary and sub-grain boundary and separated out from the solid solution. As shown in the SEM images, when the C content is constant, the morphology of composite powders changes from larger flattened particles into smaller granular particles with the increase of milling time. Carbon particles are evenly dispersed in the composite powder. After cold welding and fracture reach dynamic balance in the milling process, the composite powders are agglomerated to form large particles at further ball milling. When the milling time is constant, the average particle size of the composite powder decreases with the increase of carbon. Then the change in particle size is significantly slowed down as the C content is more than 6%. The metallographic images of Cu-Ni-C composites have exhibited that the microstructure of the Cu-Ni-C composite materials becomes more uniform with the C content increase.

Keywords: mechanical alloying (MA); Cu-Ni-C composite materials; solid solution; the C content, microstructure.

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Problem statement. Because of the advantages of high conductivity, thermal conductivity, friction reduction, resistance to poor water quality and seawater corrosion, the Cu-Ni-C composites have attracted particular attention. It is a kind of material with great application prospects. It will play an important role in the field of automobile industry, household appliances, electronics and communications [1-8]. The Cu-Ni-C composite is used in electric contact materials and conductive wear-resistant materials, such as sliding conductive materials and brushes. The interface of composite material is combined with mechanical integration, and there is neither chemical reaction nor diffusion at the interface. For the powder metallurgical Cu-Ni-C composite material products, copper has a poor wettability of carbon, as well as the compression deformation of carbon. In addition, its interface can only be mechanically interlocked, and its binding strength is low. The reinforcement is easy to pull out, susceptible to stripping or shedding when it is subject to load [9–12]. Moreover, the difference between the two components of copper and carbon is very large, and it is difficult to mix them uniformly, which leads to subsequent sintering [13–15]. In this paper, the Cu-Ni-C powder materials were prepared by mechanical alloying (MA) [16, 17]. The phase structure and microstructure were studied. Furthermore, the Cu-Ni-C composites were prepared by atmosphere sintering, and the effect of the C content on microstructure and mechanical properties was discussed.

Basic material

1. Experimental data

1.1. Sample preparation

The Cu-Ni-C powder materials were synthesized by mechanical alloying using electrolytic copper powder (purity > 99.5 %, particle size of 300 mcm), graphite powder (purity > 99.0 %, particle size of 500 mcm), and nickel powder (purity > 99.5 %, particle size of 300 mcm) as starting materials. The copper-nickel-carbon powder mechanical alloy was made with the help of a planetary ball mill (QM-3PS2). The mixing ratio for Cu-5 % Ni-xC was x = 2 %, 4 %, 6 %, 8 % (wt.). The mass ratio of the grinding ball and the raw materials was 10:1. The filling coefficient was 1/3 and the speed of the ball mill was 450 r/min. A small amount of zinc stearate was added into the raw materials during the milling to prevent the powder from excessive adhesion to the ball mill wall and the grinding ball. The ball milling duration made up 10 h, 20 h, 30 h, 40 h and 50 h, respectively. In order to avoid oxidation and pollution of the powders, argon was used as a protective gas in the experiment. Then, the obtained Cu-Ni-C powders prepared by mechanical alloying were pressed into pellets (φ = 8 mm) using the axial compression method with the help of the hydraulic universal machine. The pressures are 10 kN, 20 kN, 30 kN, and 40 kN, respectively.

1.2. Sample testing

The morphology of the Cu-Ni-C composite powders was analyzed by the QUANTA-200 scanning electron microscope (SEM). The effect of the milling duration and the C content on the grain size and microstructure of composite powders was studied. The structure analysis of the powders was performed with an X-ray powder diffraction (ARL X'TRA) using Cu Kα radiation (λ = 1.5406 Å). The scanning speed was 0.04 o/s, and the scanning angle was 20º~100º. In addition, the HVS-1000 Digital Hardness Machine was used for hardness testing. The load was 100 g and the loading time was 15 s. The surface was polished before measurement. At least 5 different positions were measured at the surface of each sample and the average hardness values of the sample were calculated.

2. Results and Discussion

2.1. Microstructure of Cu-Ni-C

Fig. 1 shows the micromorphology of the Cu-5% Ni-6% C composite powders subject to ball milling over different time periods (10 – 50 h). It can be seen that flat composite powders are formed after the samples are ball-milled for 10 and 20 h (Fig. 1, *a – b*). The particle size of the composite powders decreases with the increase in the mechanical milling duration. Carbon particles are more evenly dispersed in the Cu-5% Ni-6% C composite powders. This indicates that the morphological characteristics of the raw materials are lost after copper, nickel and carbon powders are continually subject to cold welding and deformation. Then the composite particles with stratified structure and uneven grain size are formed. After ball milling for 20 h, the particle sizes of the Cu-5% Ni-6% C composite powders are about 2 – 3 μm. With the increasing ball milling time, the particle morphology and size of the composite powders clearly change. The composite powders become granular, and the particle sizes are distributed more uniformly (Fig. 1, *c – d*). The particle size of the composite powders after ball milling for 40 h are 1 – 2 μm. However, the particle size does not change significantly even though the balling duration increases (Fig. 1, *e*), which is caused by cold welding and fracture reaching a dynamic balance and the powder particle size being close to the limit value for the composite powders at ball milling for 40 h. Cold welding plays a major role, and the composite powders reunite to form large particles when the samples are ball-milled for 50 h. It can be seen that the particle size of the composite powders decreases first and then becomes steady with the increasing ball milling duration. Therefore, ball milling for 40 h was used in the subsequent period of the experiment to save costs.

Fig. 2 shows the SEM image of the Cu-5% Ni-xC (x = 2 %, 4 %, 6 % and 8 %) composite powders after ball milling for 40 h and the effect of the C content on the micromorphology. Because of the structure (FCC) of Cu, it is difficult to form powders with small particles. During ball milling of the composite powders, copper powders and nickel powders agglomerate (without graphite powder) into coarse particles [18 – 20]. It can be seen from Fig. 2 that the particle size and micromorphology of Cu-5% Ni-xC composite powder changes with the increasing of graphite content. The average particle size of the composite powders decreases with the increase of carbon content, which is due to the effect of the graphite self-lubrication on the re-welding of copper particles and nickel particles. When the C content is 2 – 6 %, the particle size of the composite powder refines significantly. When carbon content continues to increase (6 % to 8 %), the change of the particle size slows down. This indicates that the addition of carbon can effectively prevent the reunion and welding of Cu and Ni. The particle size of the composite powder cannot become too small when the C content is 2 %, even though the ball milling duration is long. The particle size decreased with the increase of the C content (2 %–6 %). When the C content is higher (8 %), the addition of C cannot make the composite powder more fine. The content of C has an optimal value (6 %), and the particle size of the composite powder is minimized.

Metallographic diagrams of the composite powder Cu-5% Ni-xC (x = 2 %, 4 %, 6 %, 8 %) pressed at 30 kN and sintered at 800 °C are shown in Fig. 3. It can be seen that the metallographic of the sintered samples is much evener and finer with the increase of the C content. The Cu-5% Ni-xC composite powder formed a fine structure in the process of ball milling. Cu and Ni cannot reunite due to the presence of C which prevents the migration of their particles. Therefore, the composite powder cannot grow up because of adding C, and the effect is more obvious with the increase of the C content. However, adding C affects the formation of sintering neck between copper and nickel particles and is unfavorable for the densification of the Cu-5% Ni-xC composite material. It can be seen from Fig. 3 that the porosity increases and density decreases with the increasing of the C content.

2.2. Phase analysis of Cu-Ni-C

Fig. 4 a shows the XRD patterns of the Cu-5% Ni-6% C composite powder after ball milling for different time periods. It can be seen that the diffraction peak of nickel and carbon disappeared after the sample ball milling for 10 h, and the pure Cu phase with face-centered cubic structure was formed. In addition, the analysis shows that nickel and carbon have been solid-dissolved in the copper solid solution. As the ball milling duration is extended, the Cu diffraction peak intensity decreases, and the diffraction peak is widened and moved to the lower degree. According to the Bragg equation $2d\sin\theta = n\lambda$, the diffraction peak moving to a low degree indicates the increase of the lattice. Therefore, the Cu-5% Ni-6% C solid solution has been formed. The Cu_2O diffraction peak spectral line appeared for the sample ball milling for 50 h, since the powder adsorbs oxygen during ball milling and the powder with small particle and large surface activity can easily be oxidized.

The XRD pattern of the composite powders Cu-5% Ni-xC (x = 2 %, 4 %, 6 %, 8 %) after milling for 40 h are shown in Fig. 4, *b*. It can be seen that the Ni and C diffraction peaks disappeared, and there is only the Cu diffraction peak. Copper diffraction peaks move to a low degree with the increase of the C content and there is no peak of nickel and carbon (x = 2 %, 4 %, 6 %). That indicates that the Cu-5% Ni-xC solid solutions are formed after ball milling for 40 h. However, there is a small peak in the sample of the Cu-5% Ni-8% C composite powder, which shows that a small amount of C does not ensure the solid solution. The formation of the supersaturated solid solution is due to the fact that the mixed powders are ground and rolled continuously by the milling ball during the milling process. That results in a high dislocation density in the microstructure for the composite powder. One of the reasons of the free surface, grain boundary and subgrain boundary increase is the composite powder grain refining. Thus, the short diffusion pathways are formed which are favorable for the diffusion of carbon.

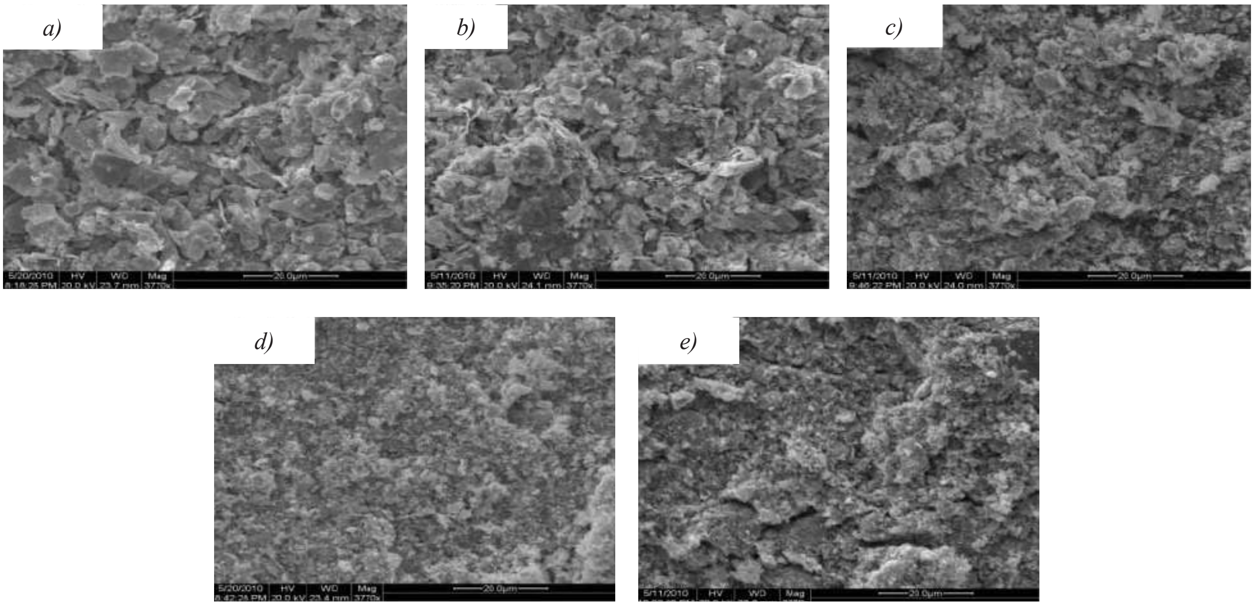

Fig. 1. Morphology of the Cu-5%Ni-6%C composite powders for different milling duration:
a — 10 h; *b* — 20 h; *c* — 30 h; *d* — 40 h; *e* — 50 h

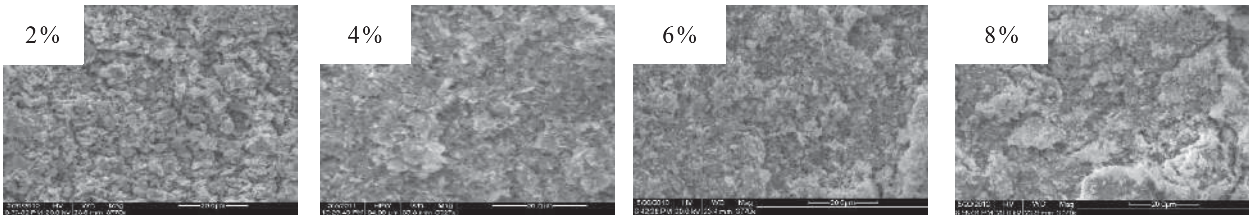

Fig. 2. SEM images of the Cu-5%Ni-xC ($x = 2\%, 4\%, 6\%, 8\%$) composite powders

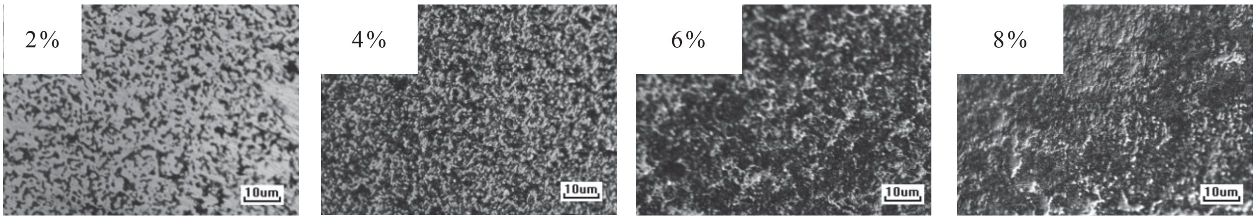

Fig. 3. Metallographic diagram of the Cu-5%Ni-xC ($x = 2\%, 4\%, 6\%, 8\%$) composite powder sintered at 800 °C

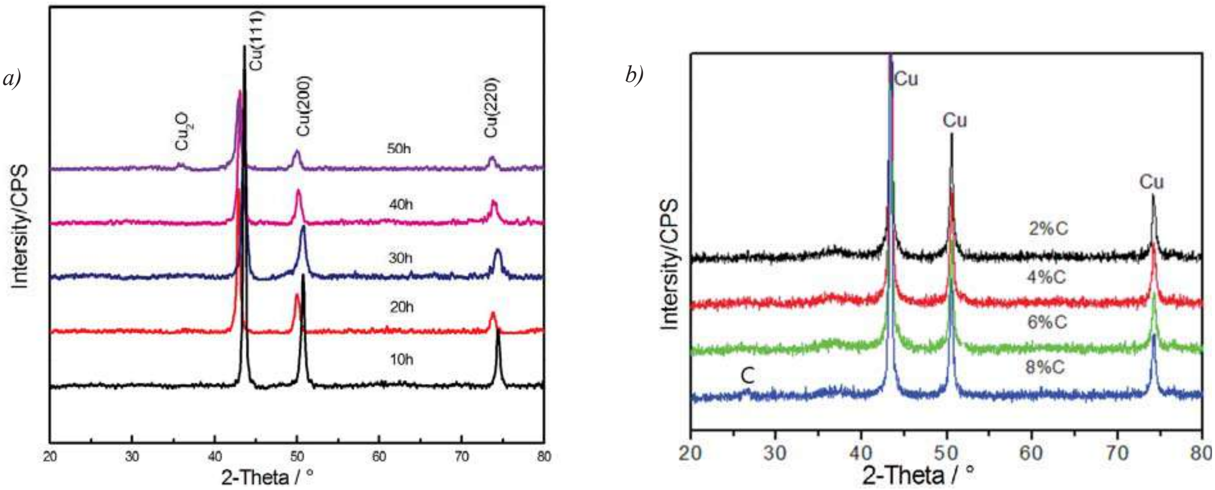

Fig. 4. XRD pattern of the Cu-5%Ni-6%C composite powders at milling: *a* — at different duration; *b* — for 40 h

That provides solute atom (C) segregation to the free surface, the grain boundary and the subgrain boundary, and carbon precipitation from the solid solution.

2.3. Hardness of Cu-Ni-C

The effect of the pressing pressure and the C content on the microhardness of the Cu-5% Ni-xC ($x = 2\%$, 4%, 6%, 8%) composite materials sintered at 800 °C is shown in Fig. 5. As can be seen, when the C content is constant, the microhardness of the composite material increases with the increase of pressure. The microhardness is no longer increased after it reaches the maximum value. When $x = 4\%$, the microhardness of the sample pressed at 10 MPa is 30 HV, and the microhardness is 75 HV when the pressing pressure increases (30 MPa). However, the microhardness of the sample is no longer increased when the pressing pressure is increased to a certain extent. In addition, the microhardness value of the sintered samples with the lower carbon content ($x = 2\%$, $x = 4\%$) is higher than that for a higher carbon content. The microhardness of Cu-5% Ni-xC decreases with the increase of carbon content. That is due to the lower hardness of the graphite, and adding carbon results in the decrease of hardness. Moreover, as evidenced by the metallographic diagram, the density of sintered samples decreases with the increase of the C content, which may also lead to the decrease of microhardness of the samples.

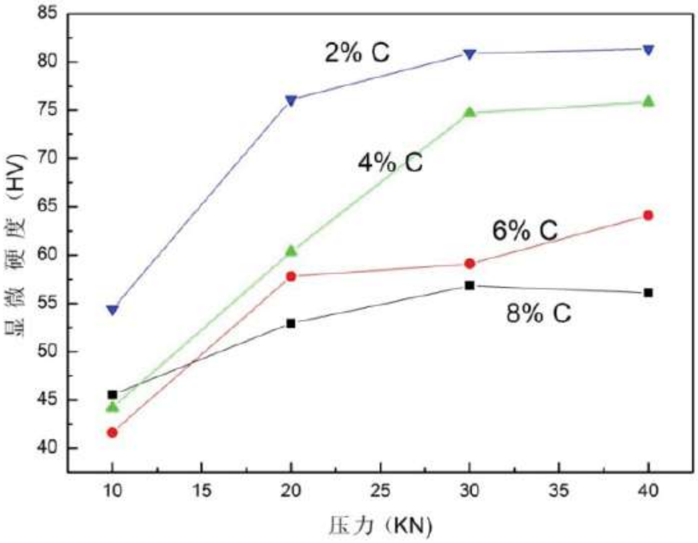

Fig. 5. Microhardness of the Cu-5% Ni-xC ($x = 2\%$, 4%, 6%, 8%) composite materials

CONCLUSIONS. The Cu-5% Ni-xC ($x = 2\%$, 4%, 6%, 8% wt.) composite powders were prepared by mechanical alloying (MA), and Cu-Ni-C composite materials were sintered by atmosphere sintering. The effect of the C content on their microstructure and mechanical properties was discussed and the following conclusions were obtained.

1. The results of SEM showed that the particle size of composite powders decreased with the increase of milling time and the C content. Carbon is dispersed in the composite powder more uniformly. The cold welding and fracture reach a dynamic balance and the powder particle size is close to the limit value for the composite powders ball milling for 40 h. The particle sizes of composite powders at ball milling for 40 h are 1 – 2 μm. In addition, the C content has an optimal value (6%), and the particle size of the composite powder is minimized. The best grinding duration is 40 hours, and the best carbon value is 6%.

2. After milling, the pure Cu phase with face-centered cubic structure is formed. The Cu diffraction peak intensity decreases, and the diffraction peak is widened and moved to the lower degree when the ball mill time and the C content are increased.

3. The metallographic diagram of the Cu-Ni-C composites is more fine and uniform with the increase of the C content for the samples sintered at 800 °C. However, adding carbon was not conducive to densification of sintered samples. Furthermore, the microhardness of Cu-5% Ni-xC decreases with the increase of the carbon content.

In the future, other properties (such as those related to friction and wear) will be investigated and the mechanism of carbon impact will be discussed.

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