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Structures, properties and responses to heat treatment of deformation processed Cu-15%Cr composite powders prepared by mechanical milling①

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[Abstract] Cu-15%Cr composite powders were produced from elemental powders by mechanical milling technique. The structures, properties and thermal stability of the composite powders were characterized by scanning and transmission electron microscopy (SEM and TEM, respectively), electron probe microanalysis(EPMA), X-ray diffractometry and microhardness testing. The results show that powders are first flattened into thin discs at the initial stage of milling and then evolved into spheroid on further milling. Lamellar structure in powders is produced after intermediate milling. The Cr laminas degenerate into particles uniformizing in Cu matrix with excessive milling. The microhardness values and internal strain sharply increase with increasing milling time. Nano-sized Cu grains were found by TEM analysis. The microstructural observations suggested that the composite powders have high thermal stability and both spherodisation and thermal grooving contribute to the instability of Cr laminas.

[Key words] Cu-Cr alloy; deformation processed composite; mechanical milling
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1 INTRODUCTION

The interest in developing high strength with high conductivity copper-based alloys has led to a constant effort on modifying the alloying preparation to improve their strength. Microstructural refinement and composite strengthening are effective methods for high strength and mechanical milling offers a possibility of producing alloys with a refined microstructure and composite structure[1,2].

Historically, mechanical milling offers a possibility of producing alloys with a refined microstructure[3]. Cu-TiB_2, Cu-Ta, Cu-Mo and Cu-Nb are examples of dispersoids-containing copper alloys fabricated by mechanical milling[4]. This technique has also been employed in the alloying of immiscible systems with positive heat of mixing, which cannot be accomplished by the conventional melting and casting processes, such as Cu-Cr[5] and Cu-W[6,7].

For the sake of dispersion or solution of the second phase in matrix, all of the just-described alloys fabricated are based on a long time for milling. It has been proved that lamellar composites are often developed at the first stage of mechanical milling and such structure associates with superior properties[1,2]. The present work studies the microstructures and properties of mechanically milled Cu-15%Cr composite powders for different durations less than 10 h. Their responses to heat treatment are also studied in order to evaluate the thermal stability of these alloys in consolidation.

2 EXPERIMENTAL

Commercial elemental Cu powders and Cr powders with a medium particle size of 50 μm and 100 μm, respectively, were used as starting materials. The mixture with composition of Cu-15% Cr was milled in an attritor mill. An impeller rotation rate of 400 r/pm and a ball-to-powder mass ratio of 10:1 were used. 1% stearic acid was added as a process control agent to prevent excessive cold welding of the particles during milling, and the milling was under Ar atmosphere. Running cold water was circulated in the cooling jacket.

After each time of mechanical milling, a little amount of powder (about 5 g) was collected for X-ray, microstructure, microhardness and heat treatment analysis. X-ray diffractometer with Cu K_α radiation was employed to study the evolution of the structure of the alloyed powder particles. Microhardness measurements were made on polished resin mounted powders using a Vickers indentor with 0.98 N load and 15 s duration. The morphologies of the as-milled powders were analyzed by an SEM S570. TEM samples were prepared by consolidating the powders in a copper tube to form a solid compact, which were then ground and thinned using ion beam milling. Measurements of Cu grain size were carried

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out using a 120 kV Philips TEM and an optical microscope. Heat treatment of the powders was carried in a vacuum furnace.

3 RESULTS AND DISCUSSION

3.1 Morphologies of particles and structural evolution as-milled condition

Figs. 1(a) and (b) show the morphologies of the Cu-15% Cr powders milled for 2 h and 10 h, respectively. In Fig. 1(a) the particles are thin and flat in shape, which were formed by microdeformation. No significant increase in particle size was observed at the initial milling stage. This result differs from what were mentioned in other references[8, 9], and it can be attributed to the effect of stearic acid. After milling for 10 h, no flattened particles could be observed, the powders became to spherical in shape. The increase in the hardness of the particles because of strain hardening is the reason for fracturing to sphere. But the particles still had size on the order of tens of micrometer because of the excellent ductility of Cu. Although there is evidence of stearic acid impeding cold-welding of powders, lamellar phase morphologies were quickly formed after milling for 2 h, as shown in Fig. 1(c). As milling for 10 h, The Cr laminae degenerated into short particles uniformized in Cu matrix, which is shown in Fig. 1(d). This can be explained by the brittleness of Cr. At the initial stage, Cr phase was elongated by forging and shearing in milling. As a brittle refractory metal, Cr phase is not susceptible to extensive room-temperature plastic deformation and easy to be fractured to particles.

The X-ray diffractions of the milled composite powders show that the Cu peaks broadened in width and decreased in height with milling time which means that the grains are fragmented or refined and the lattice is disordered. Because of the anisotropy of Cu[10], the grain size was measured by optical microscope and TEM instead of Hall-Williamson formulary based on XRD and only Cu(200) reflection was measured here to calculate the internal elastic strain. 10% W powder was used as reference for locating Cu peaks of reflection. The change in lattice parameter of Cu with milling time as measured by XRD is illustrated in Fig. 2. After milling for 10 h, the microstrain obtained was 0.274%, which indicates that the lattice is disordered severely with milling time.

Fig. 3 shows a TEM bright micrograph of Cu grains milled for 3 h. Nano-structured Cu grains are observed with high concentration of dislocations. Although the grain boundary is vague for the severe plastic deformation, it can be determined that the average size of Cu grain is within nano-size. The grain size as a function of milling durations is also shown in Fig. 2. It is found that the grain size of Cu decreases very rapidly at the initial milling stage and then becomes steady on further milling. After milling for 3 h, Cu grain size was reduced to about 50 nm from the initial 2.3 μm.

Fig. 4 shows the microhardness results. The microhardness value had a significant increase until milling for 5 h and was followed by a slightly increase. Fig. 4 reveals that the microhardness of powders after milling for 10 h is 3.724 GPa, which is about four times of that of

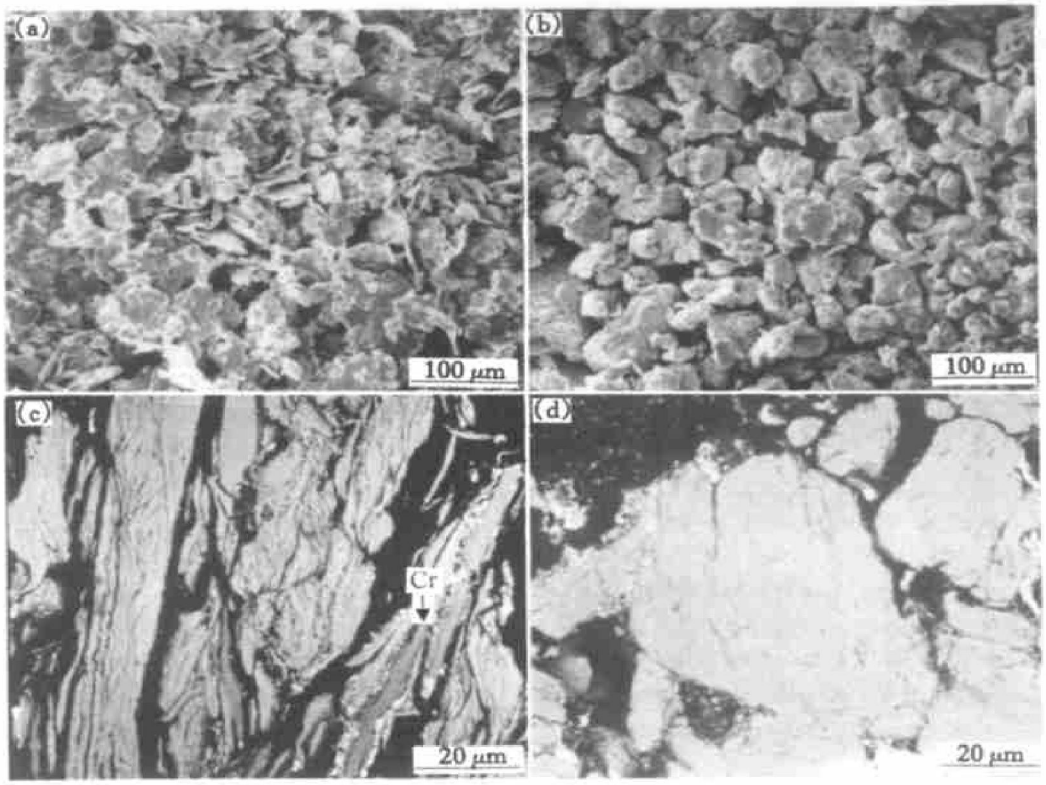

Fig. 1 Microstructures of Cu-15% Cr milled powders
(a), (c) —2 h; (b), (d) —10 h

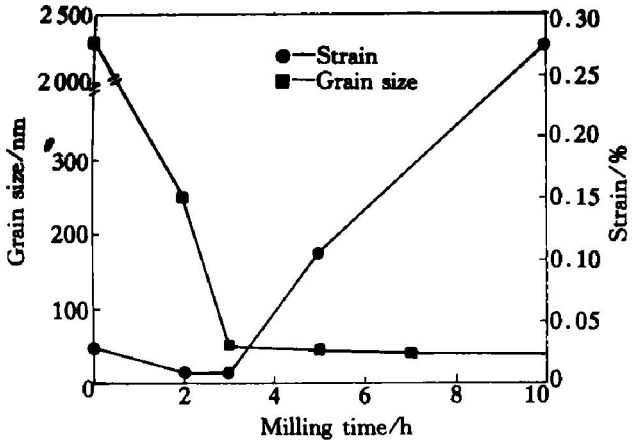

Fig. 2 Effect of milling time on grain size and microstrain of Cu for composite powders

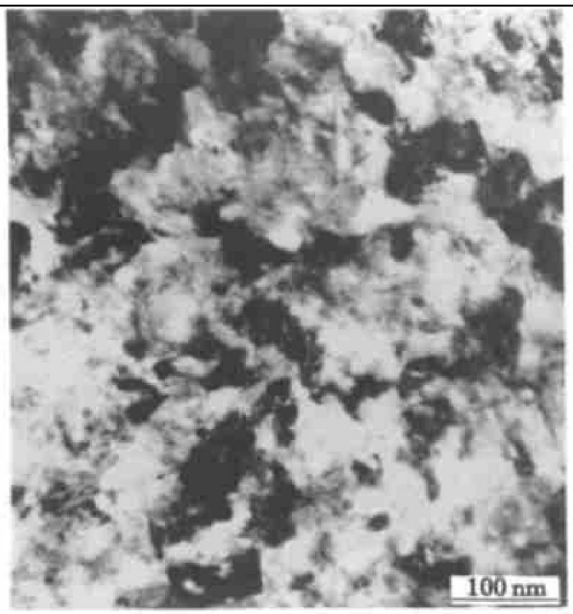

Fig. 3 TEM micrograph of Cu in composite powders milled for 3 h

unmilled elemental composites. This result is in agreement with the structure change. The increase in microhardness is due to the high dislocation density, the refined subgrains, the increased solute content of Cr and many other structural defects.

3.2 Effect of heat treatment

Consolidation of milled powders inevitably necessitates their exposure to elevated temperatures. During this exposure, microstructural changes will occur. In addition to recovery/recrystallization of the heavily cold-worked material, the microstructural morphology is altered. Lamellae often evolve into spheres, and the structure coarsens in general. These changes usually affect the properties of material.

Fig. 5 shows the microstructures of alloys milled for 3 h and heat treated at 450 ℃, 950 ℃ for 1 h. After heat treatment at 450 ℃ for 1 h, only small dispersed Cr particles evolved into ellipsoids or

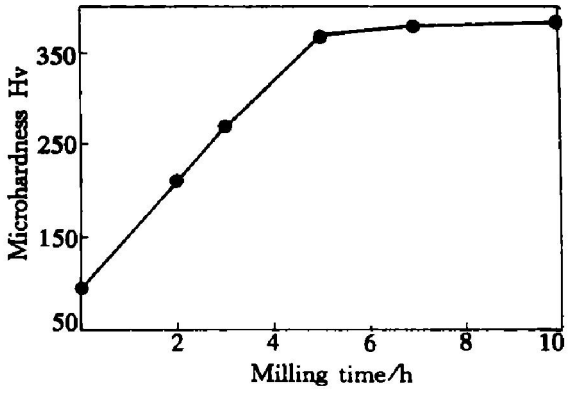

Fig. 4 Effect of milling time on Vickers microhardness of composite powders

spheres, as shown in Fig. 5(a). After heat treated at 950 ℃ for 1 h, Cr lamellae in narrow edges, which are less than 2 μm, exhibited spheroidization and the Cr phase began to break up into smaller segments. It is interesting to note that rough boundaries form on the Cr lamellae edges, as shown in Fig. 5(b), this should be explained by thermal grooving[11, 12]. Establishment of the equilibrium dihedral angle at the triple point between the interphase and the internal boundaries produces groove. With the effect of surface tension, Cr transfers from the groove to the broad faces of the Cr lamellae, and then the boundary groove is dependent to maintain the equilibrium dihedral angle at the junction. Eventually, the rough boundary forms.

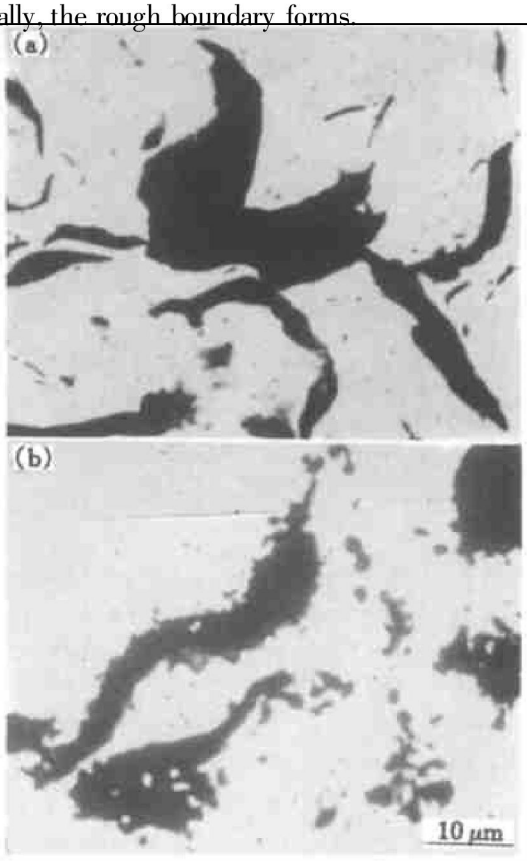

Fig. 5 Microstructures of composite powders milled for 3 h and heat treated at different temperatures
(a) —450 ℃, 1 h; (b) —950 ℃, 1 h

Fig. 6 shows the TEM micrographs of the powders milled for 3 h and heat-treated as prior-described. Coarsening of Cu grains was evident but the Cu grains were still with submicro-crystallite. The grains were found to be about 0.3 μm and 0.4 μm for the powders heat treated at 450 ℃ and 950 ℃ for 1 h, respectively, as observed in Fig. 6. At 450 ℃, small Cr particles with an average size of 10 nm were found in Cu grains, which might precipitate from Cu and then ripen to about 50~ 150 nm after heat treated at 950 ℃ for 1 h.

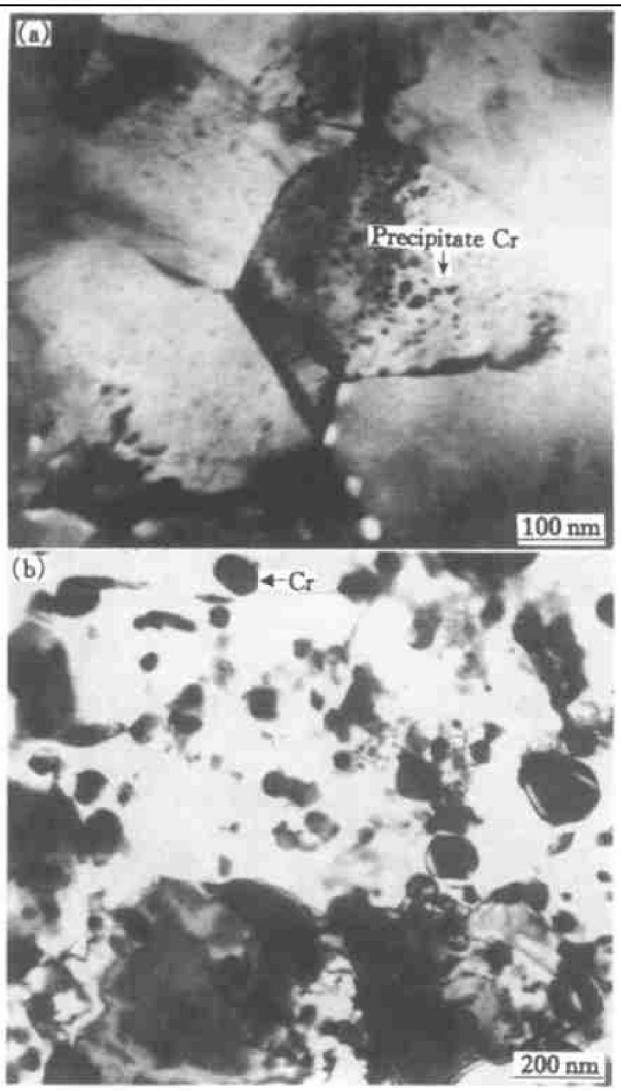

Fig. 6 TEM micrographs of Cu in composite powders milled for 3 h and heat treated at different temperatures
(a) —450 ℃, 1 h; (b) —950 ℃, 1 h

4 CONCLUSIONS

Cu-15% Cr composite lamella powder is successfully produced by mechanical milling. The hardness and microstrain of composite powder are significantly increased with milling time. The Cr laminae degenerate into short particles with excessive milling. Nano-sized Cu grains are produced after milling for 3 h, as confirmed by TEM. Heat treatment shows that both spherodisation and thermal grooving contribute to the instability of Cr lamellae in deformation processed composite powder. During heat treatment, very fine Cr particles precipitate from Cu and coarsening of the particles follows. The Cu grains are with submicro-size and lamellae structure have no significant change. These show that the deformation processed composite powders have high thermal stability and the composite powders might have potential for the development of conductivity alloys with high properties.

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