**Article ID:** 1003 - 6326(2000)02 - 0209 - 04

# Fabrication of high strength conductivity submicron crystalline Cu-5%Cr alloy by mechanical alloying①

HU Lian-xi(胡连喜), WANG Xiao-lin(王晓林), WANG Er-de(王尔德)
*School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, P. R. China*

**Abstract:** Cu-5%Cr alloy bulk material with submicron grains were fabricated by mechanical alloying and subsequent hot hydrostatic extrusion. The microstructure, mechanical properties and electrical conductivity of the alloy were experimentally investigated, and the influence of the extrusion temperature on its microstructure and properties was made clear. Also, the strengthening mechanism of the alloy was discussed. It was revealed that the microstructure of the alloy is very fine, with an average grain size being about 100 ~ 120 nm, and thus possesses significant fine-grain strengthening effect, leading to very high mechanical strength of 800 ~ 1 000 MPa. Meanwhile, the alloy also possesses quite good electrical conductivity and moderate tensile elongation, with the former in the range of 55% ~ 70%(IACS) and the latter about 5% respectively.

**Key words:** mechanical alloying; submicron crystalline; Cu-Cr alloys; hydrostatic extrusion **Document code:** A

## 1 INTRODUCTION

Copper alloys with high strength and high electrical conductivity are gaining increasing interest due to their wide application background as various electrode materials[1,2]. These alloys are normally precipitation or dispersion hardened alloys because alternatively strengthening mechanisms such as solid solution strengthening or cold work hardening reduce electrical conductivity. So far, precipitation hardened copper alloys such as Cu-Cr, Cu-Zr, and Cu-Cr-Zr alloys prepared by rapid solidification have been investigated[3~7]. Also, copper alloys strengthened with carbide, boride, or oxide dispersions have been fabricated by mechanical alloying[8~11]. However, little research has been done on grain refining and its effect on the mechanical and electrical properties of these alloys. To pursue an effective way to obtain copper alloys with high strength and high electrical conductivity, bulk Cu-5%Cr alloy material with submicron grains have been fabricated by mechanical alloying and hot hydrostatic extrusion, and its mechanical and electrical properties have been experimentally investigated. This research work is reported in the present paper.

## 2 EXPERIMENTAL

Commercial copper and chromium elemental powders, with the purity of 99.9% and the average powder size of 74 μm respectively, were used as the starting materials. Mechanical alloying of the powder mixture with a copper to chromium ratio of 95∶5 (in mass) was performed in a ball-attritor with a stirring speed of 350 r/min and under the protection of pure argon gas. The ball to powder ratio (in mass) was 10∶1 and each batch of powders was 2 kg. The Cu-5%Cr alloy powders prepared by mechanical alloying were then degassed and compacted into *d*40 mm cylindrical billets by hot pressing at 400 ℃ for 0.5 h under a vacuum of $10^{-2}$ Pa. The hot pressed billets were finally consolidated into *d*10 mm rods by hot hydrostatic extrusion. The extrusion temperature of the billets was selected within the range of 500 ~ 800 ℃, and the heating time of the billets before extrusion was 15 ~ 20 min.

The progress of mechanical alloying and the grain size of the mechanically alloyed powders were characterized by X-ray diffractometry (XRD).

The mechanical properties of the as-extruded Cu-5%Cr alloy were measured by means of tension test using *d*5 mm standard cylindrical specimens with a gauge span of 20 mm. Tensile tests were carried out with an Instron material-test machine, and the tension velocity was 0.5 mm/min. The electrical conductivity, %(IACS), of the alloy was determined by measuring the electrical resistance using the four-probe method. The microstructure of the alloy was characterized by electron probe X-ray microanalysis (EPMA) and transmission electron microscopy (TEM).

## 3 RESULTS AND DISCUSSION

### 3.1 Microstructure

Fig.1 shows the XRD patterns of Cu-5%Cr powders milled for different times. It was observed that, with increasing milling time, the diffraction

① **Received date:** Jan.19, 1999; **accepted date:** Apr.1, 1999

peaks of Cu became broader and the peak height decreased, suggesting a continuous decrease in the grain size of Cu. Indeed, calculations based on the measurements of the half width of the most intensive diffraction peak demonstrated that the grain size of Cu decreases down to less than 100 nm after the powders being milled for 45 h. Also, It was observed that the diffraction peaks of Cr weakens gradually with increasing the milling time, indicating that the amount of solution of the solute element Cr in matrix Cu increases with increasing the milling time.

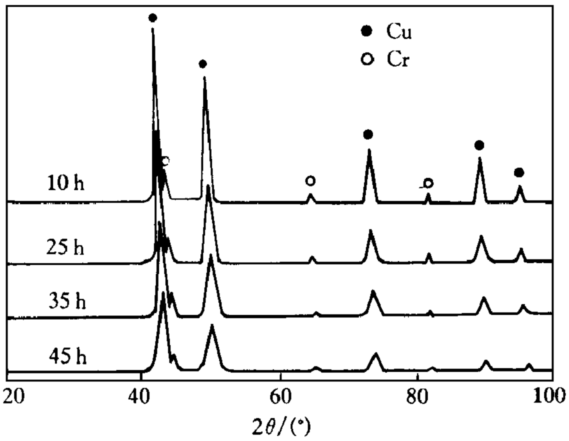


**Fig.1** XRD patterns of Cu-5 %Cr alloy powders milled for different hours

Fig.2 shows the backscattered electron images of the Cu-5 %Cr alloy consolidated, by hot hydrostatic extrusion at 600 ℃, from powders milled for 25 h and 45 h, respectively. It can be seen that the non-dissolved initial Cr particles in the alloy milled for 25 h are much coarser and less uniformly distributed than that in the alloy milled for 45 h. That is to say, increasing the milling time can not only increase the amount of solution of the solute element Cr in Cu, but also make the non-dissolved Cr particles become finer and more uniformly distributed.

Fig.3 shows the TEM images of the Cu-5 %Cr alloy powders milled for 45 h after consolidated at various temperatures. It can be seen that the alloy possesses very fine microstructure, with the grain size being in the range of 100 ~ 120 nm. This indicates that the submicron grains of the mechanically alloyed Cu-5 %Cr alloy possess good hot stability. However, the precipitation of the solute element Cr from Cu is dependent, to a large extent, on the extrusion temperature. When the extrusion temperature was below 600 ℃, no non-coherent Cr precipitates were observed (Fig.3(a)). When the extrusion temperature was up to 700 ℃, non-coherent Cr precipitates were observed (Fig.3(b)). When the extrusion temperature was higher than 750 ℃, precipitation of the Cr particles became serious, and the higher the temperature, the larger and the more the precipitated Cr particles (Fig.3 (c), (d)).

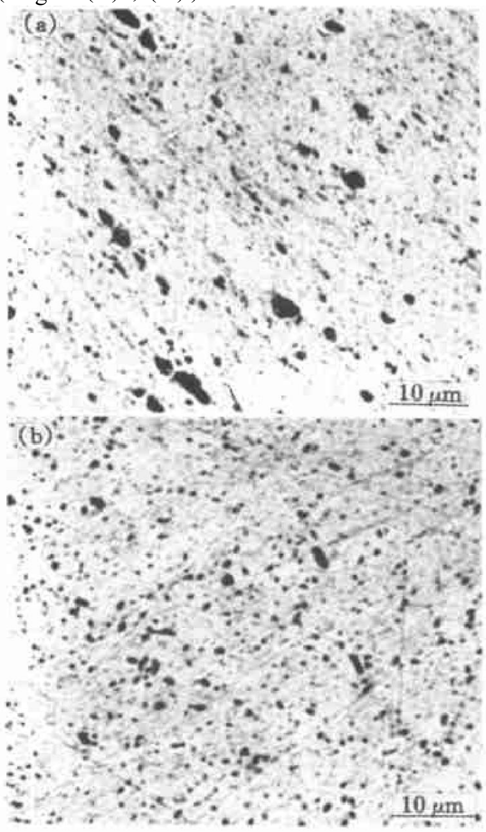


**Fig.2** Backscattered electron images of as-extruded Cu-5 %Cr alloy

(a) —Milled for 25 h; (b) —Milled for 45 h

### 3.2 Mechanical properties and electrical conductivity

Fig.4 shows the dependence of the room-temperature tensile mechanical properties of the as-extruded Cu-5 %Cr alloy on the extrusion temperature. When the extrusion temperature is lower than 700 ℃, the alloy possesses very high tensile strength (⩾950 MPa), with the maximum tensile strength reaching 1 000 MPa, and the corresponding extrusion temperature being 600 ℃. For the alloy extruded at temperature lower than 700 ℃, although the elongation increases with the increase of the extrusion temperature, it is still on a rather low level, with its value being in the range of 2 % ~ 4 %. When the extrusion temperature is higher than 700 ℃, the tensile strength of the alloy decreases, but the elongation increases significantly with increasing temperature. In the case that the alloy is extruded at 800 ℃, its tensile strength decreases down to 800 MPa, yet its elongation is raised to about 8 %. It is known[5] that the tensile strength of the rapidly solidified Cu-5 %Cr alloy after peak age hardening is no more than 760 MPa, and the corresponding elongation only reaches about 2 %. By comparison, it is obvious that the Cu-5 %Cr alloy prepared by mechanical alloying presents

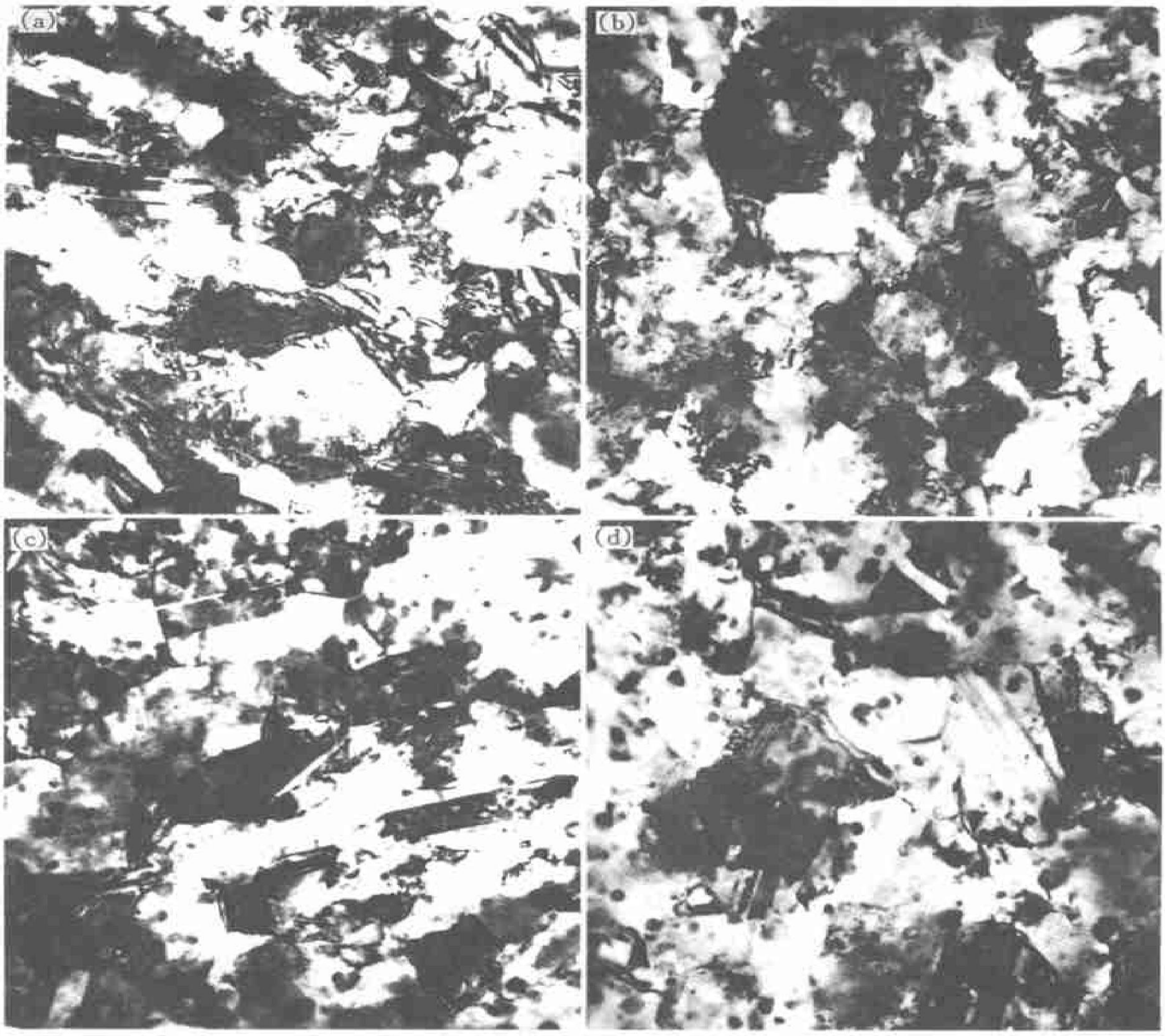

**Fig.3** TEM images of Cu-5 %Cr alloy extruded at different temperatures
(a) —600 ℃; (b) —700 ℃; (c) —750 ℃; (d) —800 ℃

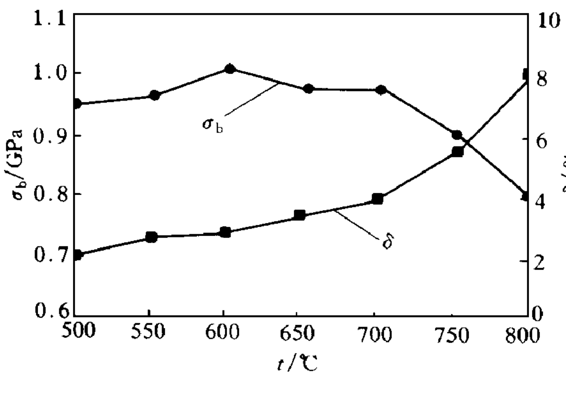


**Fig.4** Room-temperature mechanical properties of as-extruded Cu-5 %Cr alloy

much more excellent mechanical properties.

It has been shown[5] by Morris et al that the rapidly solidified Cu-5 %Cr alloy presents the highest tensile strength after it is annealed at 450 ℃ for 1 h due to its peak age hardening. For annealing at temperature higher than 450 ℃, the strength of the alloy decreases rapidly with the increase of the annealing temperature owing to the precipitation and growth of the non-coherent Cr particles. However, the submicron crystalline Cu-5 %Cr alloy prepared by mechanical alloying still possesses very high tensile strength even though it is consolidated at temperature up to 700 ℃; this can be attributed mainly to the fine-grain strengthening effect of the submicron Cu grains, together with the dispersion strengthening effect of the non-dissolved initial Cr particles and the precipitation hardening effect of the Cr precipitates. In the case of extrusion at 600 ℃, the alloy possesses the maximum tensile strength. This may be attributed to the possible shifting of the peak precipitation hardening temperature from 450 ℃ for 1 h annealing to 600 ℃ for 15 ~ 20 min short heating before extrusion. For extrusion below 700 ℃, the elongation of the alloy increases with increasing extrusion temperature due to the fact that enhancing the consolidation temperature helps to improve the bonding of the powders. However, for extrusion at temperature above 700 ℃, the tensile strength of the alloy decreases significantly, while the elongation increases rapidly with increasing extrusion temperature because of the breakdown of the coherency of the precipitated Cr phases with the matrix and the coarsening of the precipitates and non-dissolved initial Cr particles.

Fig.5 shows the dependence of the electrical conductivity of the Cu-5 %Cr alloy milled for 45 h at the extrusion temperature. When the extrusion temperature is below 700 ℃, the alloy possesses relatively low electrical conductivity of about 55 %(IACS), with the alloy extruded at 600 ℃ presenting the lowest electrical conductivity. When the extrusion temperature is above 700 ℃, the electrical conductivity of the alloy increases rapidly with increasing extrusion temperature, reaching about 70 %(IACS) for extrusion at 800 ℃. The reason for the lower electrical conductivity of the alloy extruded at temperature below 700 ℃ lies in that most of the precipitates during heating before extrusion have coherence relationship with the matrix and the amount of solution of the solute element Cr in Cu is still large, which causes serious scattering of electrons and leads to decrease of the electrical conductivity[12]. It is because of the serious precipitation segregation of the concentration of the solute element Cr in Cu that causes an abrupt decrease of the electrical conductivity of the alloy when it is extruded at 600 ℃. When the extrusion temperature is above 700 ℃, the electrical conductivity of the alloy increases rapidly with increasing extrusion temperature due to the breakdown of the coherency of the precipitates with the matrix and the coarsening of the precipitates.

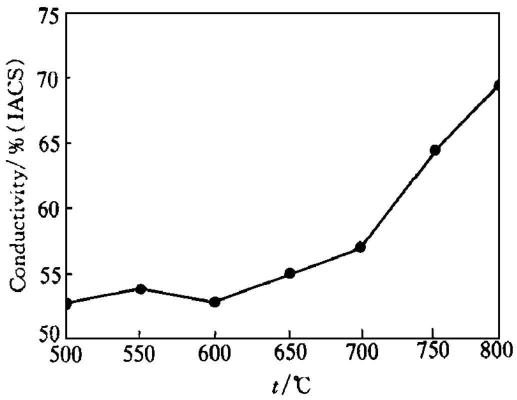


**Fig.5** Electrical conductivity of as-extruded Cu-5 %Cr alloy

## 4 CONCLUSIONS

1) Bulk material of Cu-5 %Cr alloy with submicron crystalline grains is successfully fabricated by mechanical alloying and hot hydrostatic extrusion. This material possesses very high strength and good electrical conductivity, with the tensile strength reaching 800 ~ 1 000 MPa and the conductivity 55 % ~ 70 %(IACS) respectively. Meanwhile, the elongation of the material is maintained at a moderate level of about 5 %.

2) The submicron crystalline Cu-5 % Cr alloy prepared by mechanical alloying possesses good hot stability. The grain growth of the alloy powders during consolidation at temperature below 800 ℃ is quite limited. The grain size of the alloy after consolidation remains to be 100 ~ 120 nm, giving rise to significant fine-grain strengthening effect. The fine-grain strengthening is considered to be the main strengthening mechanism of this material.

## REFERENCES

[1] Ghosh G, Miyake J and Fine M E. The systems-based design of high-strength, high-conductivity alloys [J]. JOM, 1997, 49(3): 56.
[2] ZHEN Yan-jun, YAO Jia-xin and LI Guo-jun. The present situation and future prospect of the research on high-strength high-conductivity copper-based alloys [J]. Materials Reviews, (in Chinese), 1997, 11(6): 52.
[3] Sarin K V and Grant N J. Cu-Zr and Cu-Zr-Cr alloys prepared from rapidly quenched powders [J]. Metall Trans, 1972, A3: 875.
[4] Arnberg L, et al. A new high strength, high conductivity Cu-0.5 %Zr alloy produced by rapid solidification technology [J]. Materials Science and Engineering, 1986, A83: 115.
[5] Morris M A and Morris D G. Microstructures and mechanical properties of rapidly solidified Cu-Cr alloys [J]. Acta Metall, 1987, (10): 2511.
[6] Wright R N. Age-hardening behavior of dynamically consolidated rapidly solidified Cu-2 %Zr powder [J]. Materials Science and Engineering, 1989, A114: 167.
[7] Morris M A, et al. Recrystallization mechanisms in a Cu-Cr-Zr alloy with a bimodal distribution of particles [J]. Materials Science and Engineering, 1994, A188: 225.
[8] Teruo Takahashi, et al. Alumina-dispersion-strengthened copper manufactured by mechanical alloying [J]. Powder and Powder Metallurgy, (in Japanese), 1989, 36: 404.
[9] Teruo Takahashi, et al. Mechanical properties of TiC- and ZrC-dispersion-strengthened copper prepared by mechanical alloying process [J]. Powder and Powder Metallurgy, (in Japanese), 1992, 39: 202.
[10] Toshimasa Morooka, et al. Particle-dispersion-strengthened Cu-Ti-B alloy powder prepared by mechanical alloying [J]. Powder and Powder Metallurgy, (in Japanese), 1992, 39: 202.
[11] Teruo Takahashi. Development of oxide- and carbide-dispersion-strengthened coppers by mechanical alloying [J]. Powder and Powder Metallurgy, (in Japanese), 1992, 39: 529.
[12] SONG Xue-meng. Analysis of physical properties of metals [M], (in Chinese), Beijing: Mechanical Industry Press, 1981.

**(Edited by HUANG Jin-song)**