

## Fabrication and properties of low oxygen grade Al<sub>2</sub>O<sub>3</sub> dispersion strengthened copper alloy<sup>①</sup>

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**Abstract:** The low oxygen grade Al<sub>2</sub>O<sub>3</sub> dispersion strengthened copper alloy without hydrogen-fired expansion was fabricated by the technique of vacuum hot press and hot extrusion. The mechanical and electrical properties measurements and microstructures observation on as-hot extruded, as-cold drawn and as-annealed Cu-Al<sub>2</sub>O<sub>3</sub> alloy were conducted. The results show that the addition of a suitable amount of boron in the alloy can lower the residual free oxygen content and then inhibit the hydrogen-fired expansion. The density,  $\sigma_b$ ,  $\sigma_{0.2}$ , hardness,  $\delta$  and electrical conductivity of the alloy reach 8.86 g/cm<sup>3</sup> (relative density of 99.6%), 340 MPa, 250 MPa, HB95, 24% and 93% (IACS) respectively after hot extruded with the extrusion ratio of 30:1. Its properties have no change after annealed at 900 °C for 1 h. Its strength increases after cold drawing, while its ductility and electrical conductivity drop gradually. Various properties of the cold drawn alloy can recover to those of as-extruded after annealed at 900 °C for 1 h without the occurrence of recrystallization.

**Key words:** hydrogen-fired expansion; free oxygen; dispersion strengthen; Cu-Al<sub>2</sub>O<sub>3</sub> alloy

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### 1 INTRODUCTION

Cu-Al<sub>2</sub>O<sub>3</sub> dispersion strengthened copper (DSC) alloy has been paid more and more attention to for its excellent combination of high strength, high electrical conductivity and resistance to softening at elevated temperatures<sup>[1-6]</sup>. It is of a vast range of application prospect as large power microwave tubes, integrated circuit leadframes, resistance welding electrodes, electric contacts and advanced aircraft wings<sup>[7-10]</sup>. However, it is prone to expand after annealed at elevated temperature in hydrogen. In addition, there exist some problems such as slow leaking, target poisoning as vacuum electronic devices<sup>[11, 12]</sup>. All these problems mentioned above have perplexed the research and production on dispersion strengthened copper alloy for a long time. But few reports on resolving these problems can be found up to now. In our previous work<sup>[13, 14]</sup>, it was suggested that hydrogen-fired expansion is associated with residual free oxygen in the alloy mostly presented in form of Cu<sub>2</sub>O. Cu<sub>2</sub>O can react with hydrogen to form vapor with high pressure and then cause cracks and cavity and result in expansion of the alloy. Therefore, in this work, boron was added in the alloy to reduce the residual Cu<sub>2</sub>O and form the thermally stable boron oxide (B<sub>2</sub>O<sub>3</sub>). The low oxygen grade Al<sub>2</sub>O<sub>3</sub> dispersion strengthened copper alloy without hydrogen-fired expansion was fabri-

cated by adding boron in it and the techniques of vacuum hot pressing and hot extruding. Meanwhile, its mechanical and electrical properties and microstructures were examined.

### 2 EXPERIMENTAL

Cu-0.12% Al (mass fraction) alloy was melted in the induction furnace and the melt was atomized into fine alloy powders (< 147 μm) using nitrogen gas. These alloy powders were then mixed with an appropriate quantity of Cu<sub>2</sub>O powders. The powder mixture was sealed in a container and then was internally oxidized at a given temperature. After the internal oxidation reaction had finished, the mixture was hydrogen-reduced. These reduced powders were mixed with a suitable amount of boron powders in order to reduce the residual cuprous oxides and then were vacuum hot-pressed to be a  $d = 60$  mm × 60 mm cylindrical ingot at 950 °C for 3 h. The ingot was canned with a copper tube and evacuated and sealed and then hot extruded to give a bar with an extrusion ratio of 30:1 at 930 °C. The extruded bar was cold drawn to 92% (about 25% per pass) and then annealed at 900 °C for 1 h.

The vacuum hot-pressing test was performed on the HIGH-MULTI 10000 vacuum hot-pressing machine for 3 h at 950 °C under a pressure of 27 MPa and vacuum of  $1.33 \times 10^{-2}$  Pa. The hot extrusion test

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was performed on the oil hydraulic press at 930 °C in nitrogen atmosphere with the dies heated to 450 °C and lubricated with graphite and oil. Densities were measured by loss of weight in water. The concentration of the residual free oxygen was analyzed by TC-436 nitrogen/oxygen device. Electrical conductivity measurements were conducted on a QJ19 double bridge at room temperature (20 °C). Metallographs were observed on Neophot-21 microscope. Tensile tests were carried out on an INSTRON testing machine at room temperature at a strain speed of 2 mm/min. Tensile fracture observations were performed on KYKY-2800 scanning electron microscope (SEM). Fine microstructures of thin foils were examined on a H-800 transmission electron microscope (TEM) operated at 200 kV.

### 3 RESULTS AND DISCUSSION

#### 3.1 Hydrogen-fired expansion and oxygen content

The free oxygen in DSC presents mainly in the form of Cu<sub>2</sub>O and solid solute oxygen (O<sub>(ss)</sub>). Table 1 compiles the possible reactions during hot pressing and hydrogen firing and their corresponding ΔG<sub>m</sub>. It can be found from Table 1 that ΔG<sub>m1</sub><sup>⊖</sup> < 0 within 900–1 000 °C. It indicates that boron can reduce Cu<sub>2</sub>O and form the thermal stable B<sub>2</sub>O<sub>3</sub>. In the case of annealing in hydrogen at 900 °C to 1 000 °C, ΔG<sub>m3</sub><sup>⊖</sup> and ΔG<sub>m4</sub><sup>⊖</sup> > 0, indicating that Al<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub> are stable and can not react with H<sub>2</sub>. ΔG<sub>m1</sub><sup>⊖</sup> < 0 suggests that the hydrogen which has diffused into copper matrix may react with Cu<sub>2</sub>O and form high pressure vapor. The inflating vapor can weaken the structure of copper at the grain boundaries and generate microcavities and cracks and result in expansion. The addition of a suitable amount of boron in the alloy can inhibit the occurrence of reaction (2) during annealing in hydrogen. Table 2 lists the radial hydrogen-fired expansion values of Cu-Al<sub>2</sub>O<sub>3</sub> alloys after annealed in hydrogen for 1 h at 900 °C. It shows that both of the boron-added as-pressed and as-extruded DSC alloys

do not expand after annealed in hydrogen.

The residual free oxygen content in the boron-added DSC alloy is shown in Fig. 1. The oxygen concentration in the alloy is only 10 × 10<sup>-6</sup> which is obtained by integration of curve 1. This value reaches the standard of the oxygen content in oxygen-free copper. But the residual free oxygen concentration in the DSC alloy without added boron is up to 280 × 10<sup>-6</sup> and the value of hydrogen-fired expansion for d 22 mm bar reaches 0.07 mm<sup>[14]</sup>. It is revealed that the adding of boron in the DSC alloy can lower the residual free oxygen content in the alloy and inhibit hydrogen-fired expansion.

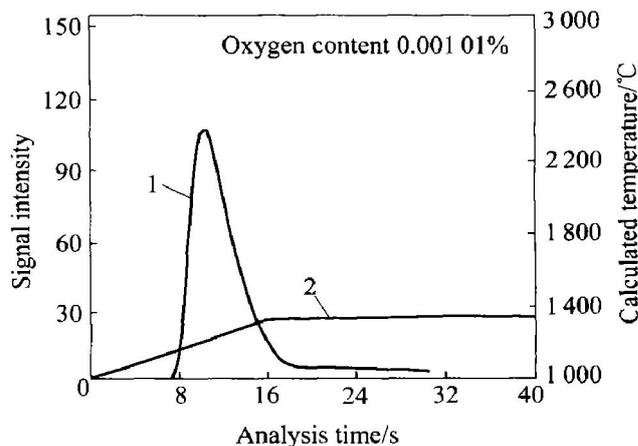


Fig. 1 Analysis curve of oxygen content  
1—Relative signal intensity curve;  
2—Temperature curve

#### 3.2 Properties and microstructures of Cu-Al<sub>2</sub>O<sub>3</sub> alloy

The properties of Cu-Al<sub>2</sub>O<sub>3</sub> alloys under different treatments are summarized in Table 3. The density of the alloy ingot is up to 8.83 g/cm<sup>3</sup> (relative density of 98.9%) after vacuum hot-pressed. Fig. 2(a) shows the typical microstructure of as-pressed DSC alloy. The microstructure of the as-pressed alloy is very dense and powders are bonded very tightly and few cavities can be seen. This shows that the powder compact has been fully sintered. In addition, owing to the deformation

Table 1 Values of reaction free energy change ΔG<sub>m</sub><sup>⊖</sup>

Reaction formula	Calculation equation of ΔG <sub>m</sub> <sup>⊖</sup>	ΔG <sub>m</sub> <sup>⊖</sup> at 900 °C to 1 000 °C / (J•mol <sup>-1</sup> )
3Cu <sub>2</sub> O(s) + 2B(s) = 6Cu(s) + B <sub>2</sub> O <sub>3</sub> (s) (1)	ΔG <sub>m1</sub> <sup>⊖</sup> = -761 900 + 36.74T	< 0
Cu <sub>2</sub> O(s) + H <sub>2</sub> (g) = 2Cu(s) + H <sub>2</sub> O(g) (2)	ΔG <sub>m2</sub> <sup>⊖</sup> = -72 170 - 11.87T	< 0
Al <sub>2</sub> O <sub>3</sub> (s) + 3H <sub>2</sub> (g) = 2Al(l) + 3H <sub>2</sub> O(g) (3)	ΔG <sub>m3</sub> <sup>⊖</sup> = 947 050 - 151.63T	> 0
B <sub>2</sub> O <sub>3</sub> (s) + 3H <sub>2</sub> (g) = 2B(s) + 3H <sub>2</sub> O(g) (4)	ΔG <sub>m4</sub> <sup>⊖</sup> = 545 390 - 81.34T	> 0

\* Thermodynamic data in Table 1 are cited from Ref. [15].

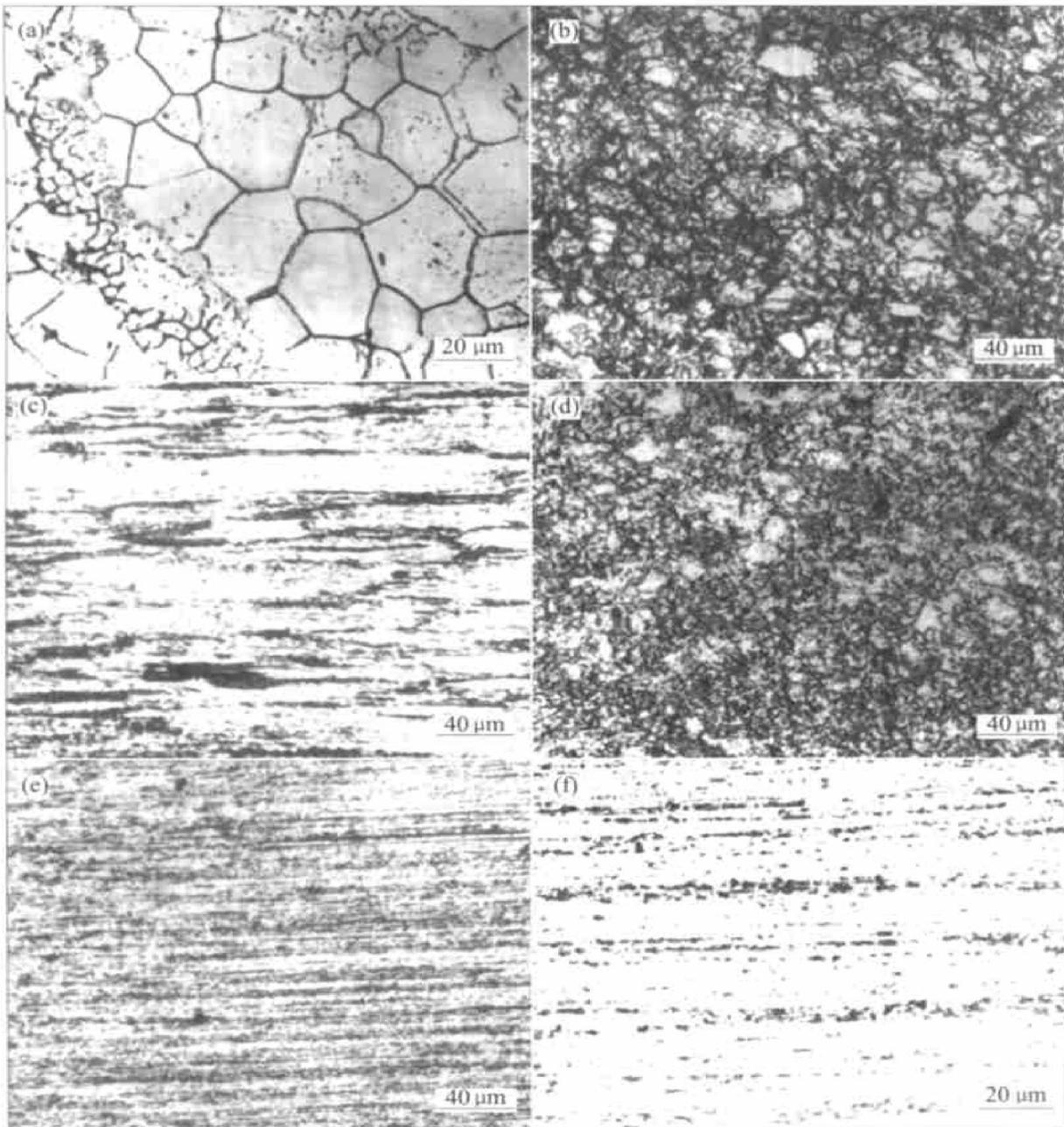
**Table 2** Hydrogen-fired expansion values of Cu-Al<sub>2</sub>O<sub>3</sub> alloy annealed at 900 °C for 1 h

Specimen	Diameter before hydrogen fired/mm	Diameter after hydrogen fired/mm	Expansion amount/mm
As hot pressed	59.685	59.685	0
As hot extruded	9.835	9.835	0

**Table 3** Properties of Cu-Al<sub>2</sub>O<sub>3</sub> alloy under different treatment conditions

Treatment condition	$\sigma_b$ /MPa	$\sigma_{0.2}$ /MPa	$\delta$ /%	HB	Electrical conductivity(IACS)/%	Relative density/%
As hot pressed	277	184	10	78	–	98.9
As hot extruded	340	250	24	95	93.0	99.6
As hot extruded plus annealed	335	250	23	95	94.0	99.6
As cold drawn	490	485	10	128	91.4	–
As cold drawn plus annealed	345	240	23	94	94.0	–

Annealing temperature is 900 °C, and annealing time is 1 h.

**Fig. 2** Typical Microstructures of Cu-Al<sub>2</sub>O<sub>3</sub> alloy

- (a) —As vacuum hot pressed(transverse); (b) —As extruded(transverse); (c) —As extruded(longitudinal);  
 (d) —As drawn with 92% cold work (transverse); (e) —As drawn with 92% cold work(longitudinal);  
 (f) —As annealed with 92% cold work(900 °C 1 h, longitudinal)

around the powder boundary, the dynamic recrystallization has occurred and formed fine grains.

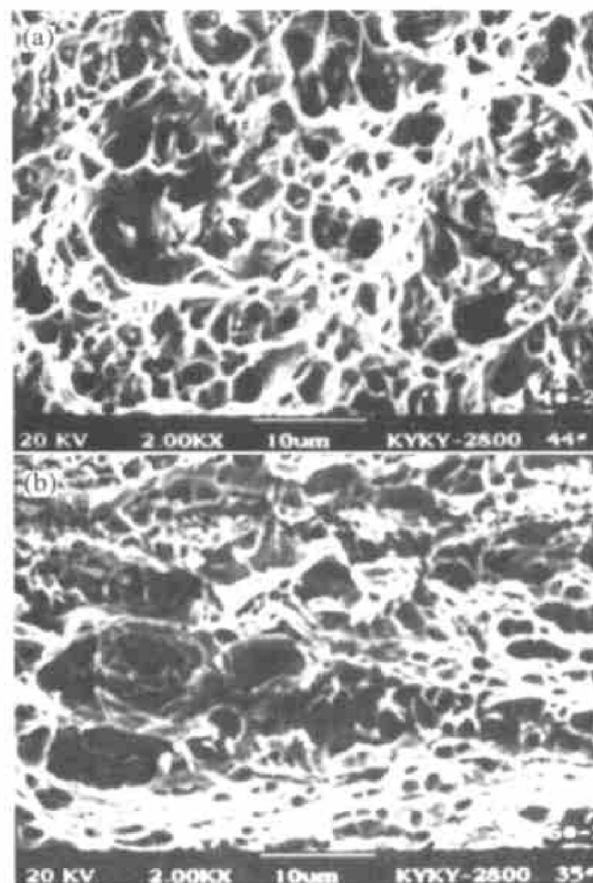
The density of the alloy further rises to 8.86 g/cm<sup>3</sup> (relative density of 99.6%) after hot extruded with the extrusion ratio of 30:1. The  $\sigma_b$ ,  $\sigma_{0.2}$ , HB,  $\delta$  and electrical conductivity reach 340 MPa, 250 MPa, 95, 24% and 93% (IACS) respectively (Table 3). The properties of the extruded alloy almost have no change after annealed for 1 h at 900 °C. Figs. 2 (b) and 2(c) show the microstructures of as-extruded alloy in traverse and longitudinal directions. The alloy is close to full density and has become a crystalline compound in transverse direction (Fig. 2(b)). Some large Al<sub>2</sub>O<sub>3</sub> particles stringers distribute on the boundaries of alloy powders (Figs. 2(c) and (f)). Because of the high specific surface free energy of nitrogen atomized Cu-Al alloy powders, solute Al would segregate inevitably on the surfaces and at the grain boundaries to lower the systematic free energy during the preparation of Cu-Al alloy powders<sup>[16]</sup>. This effect leads to the formation of continuous oxide Al<sub>2</sub>O<sub>3</sub> films during the subsequent internal oxidation. When the internally oxidized powder is vacuum hot pressed and extruded, these oxide films are broken down due to the attrition and flowing of the metal, and thus form discontinuous Al<sub>2</sub>O<sub>3</sub> stringers. Besides, these grains are obviously elongated, however they are not broken and keep relatively stable in size in the longitudinal direction (Fig. 2(c)). No dynamic recrystallization has occurred.

After cold drawn to 92% deformation,  $\sigma_b$ ,  $\sigma_{0.2}$  and hardness (HB) increase markedly to 490 MPa, 485 MPa and 128 respectively, while  $\delta$  and electrical conductivity decrease to 10% and 91.4% (IACS). Fig. 2(d) and Fig. 2(e) show the typical microstructures of as-cold drawn bar. It can be seen that the microstructures markedly become finer and the boundaries of alloy powder become more ambiguous and broad. The grains are sharply elongated and straightened, resulting in the fine fibrous texture. Meanwhile, the Al<sub>2</sub>O<sub>3</sub> stringers become finer and the Al<sub>2</sub>O<sub>3</sub> particles enter the powder granules and distribute more homogeneously accompanied by the metal flowing, indicating that the ductile flowing of the metal during cold draw can cause the attrition among the powder granules and further break the Al<sub>2</sub>O<sub>3</sub> oxide film on the granule surfaces and improve the bonding of powders. After annealed in hydrogen for 1 h at 900 °C, the properties of cold drawn alloy recover to the those of as-hot extruded and no recrystallization can be found in their optical metallograph (Fig. 2(f)).

### 3.3 Tensile fracture surfaces of Cu-Al<sub>2</sub>O<sub>3</sub>

The tensile fracture surface SEM images of Cu-Al<sub>2</sub>O<sub>3</sub> in extruded condition are shown in Fig. 3. It is

illustrated that there are no obvious original cracks on the fracture surface in the longitudinal or transverse direction. A great number of large and deep dimples distribute uniformly on the fracture surface, which features indication of the toughness failure. It can be also seen from Fig. 3(a) that although the granules are occasionally separated and ruptured as a whole, the tear ridges leave behind inside these dimples. This demonstrates that the powder has been bonded well.

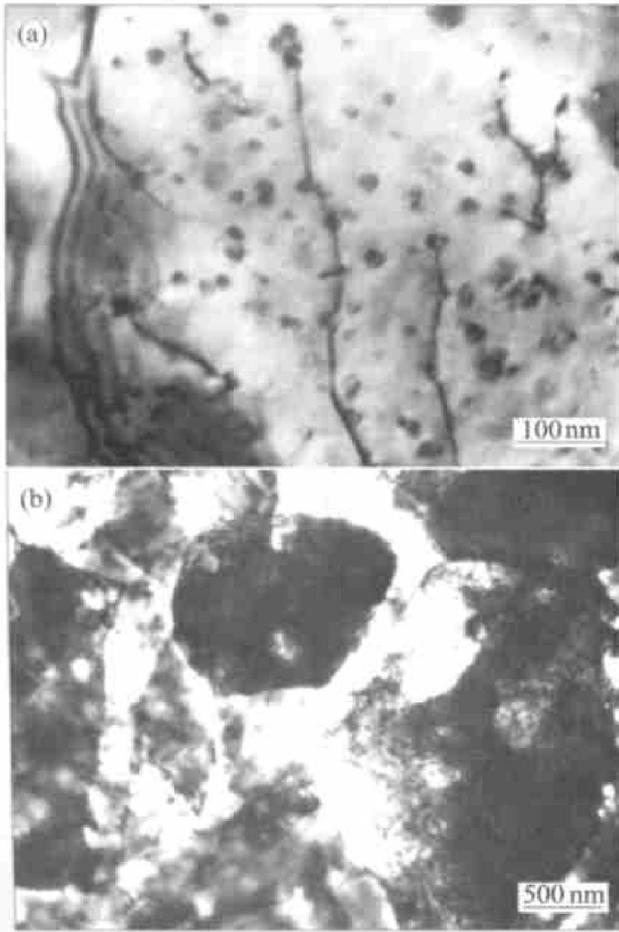


**Fig. 3** SEM images of tensile fracture surface of Cu-Al<sub>2</sub>O<sub>3</sub> alloy

- (a) —As hot extruded (transverse);  
(b) —As hot extruded (longitudinal)

### 3.4 TEM observation of microstructure

The TEM images of the Cu-Al<sub>2</sub>O<sub>3</sub> alloy annealed for 1 h at 900 °C are shown in Fig. 4. As shown in Fig. 4(a), a large number of Al<sub>2</sub>O<sub>3</sub> particles disperse uniformly in the copper matrix. Most of Al<sub>2</sub>O<sub>3</sub> particles present in the form of sphere or ellipsoid with an average size of about 18 nm and mean interparticle spacing of about 100 nm. It is well known that the mean free path of electron in copper is about 50 nm. Therefore, these Al<sub>2</sub>O<sub>3</sub> particles with so large interparticle spacing do not cause strong scattering of electrons that the electrical conductivity of dispersion strengthened copper is up to 94% (IACS). It can be also found from Fig. 4(a) that dislocations are pinned by particles. These Al<sub>2</sub>O<sub>3</sub> particles inside the grains can strengthen the copper matrix by the Orowan



**Fig. 4** TEM BF images of Cu-Al<sub>2</sub>O<sub>3</sub> alloy annealed at 900 °C for 1 h  
 (a) —Dispersed Al<sub>2</sub>O<sub>3</sub> particles in copper matrix;  
 (b) —Subgrains

mechanism. Because Al<sub>2</sub>O<sub>3</sub> is very hard and thermally stable and does not coarsen markedly even at the temperature close to the melting point of copper<sup>[9, 17]</sup>, it can impede efficiently the movement of dislocations and grain boundaries and thereby enhance the yield strength and strength of the alloy at elevated temperature. In addition, it can increase the critical nucleus radius and inhibit nucleation during recrystallizing and then raise the recrystallizing temperature, so that there is no obvious recrystallization in the microstructure of an annealed Cu-Al<sub>2</sub>O<sub>3</sub> alloy and the mechanical properties of the extruded alloy have no change after annealed at 900 °C for 1 h. Fig. 4(b) shows the subgrains formed during annealing with a size of 2 - 3 μm. These substructures can strengthen the Cu-Al<sub>2</sub>O<sub>3</sub> alloy too. These strengthening mechanisms make dispersion strengthened copper retain about 10 times yield strength and 1.5 times tensile strength of pure copper after annealed at 900 °C, while  $\sigma_b$  and  $\sigma_{0.2}$  of oxygen-free copper are about 200 MPa and 25 MPa respectively after annealed at 900 °C<sup>[2]</sup>. It is unfortunate to mention that B<sub>2</sub>O<sub>3</sub> can not be identified during the TEM observation owing to trace amount, and then the roles played by the B<sub>2</sub>O<sub>3</sub> on the mechan-

ical and electric properties and recrystallization of Cu-Al<sub>2</sub>O<sub>3</sub> alloy have not been established in the present work and wait for further study.

#### 4 CONCLUSIONS

1) The addition of a suitable amounts of boron in the Cu-Al<sub>2</sub>O<sub>3</sub> alloy can lower the residual free oxygen content and then inhibit the hydrogen-fired expansion.

2) The density,  $\sigma_b$ ,  $\sigma_{0.2}$ , hardness,  $\delta$  and electrical conductivity of the alloy reach 8.86 g/cm<sup>3</sup> (relative density of 99.6%), 340 MPa, 250 MPa, 95HB, 24% and 93% IACS respectively after hot extruded with the extrusion ratio of 30:1. Its properties keep unchanged after annealed for 1 h at 900 °C.

3) After cold drawn to 92%,  $\sigma_b$ ,  $\sigma_{0.2}$  and HB increase to 490 MPa, 485 MPa, 128 respectively, while  $\delta$  and electrical conductivity decrease to 10% and 91.4% (IACS). The microstructure becomes finer and the boundaries are more ambiguous and broad. The properties of alloy recover to those of as-extruded and there exists no recrystallization in microstructure after annealed at 900 °C for 1 h.

4) A great number of large and deep dimples distribute on the fracture surface of as-extruded, which feature indication of obvious ductility nature of fracture.

5) A large number of Al<sub>2</sub>O<sub>3</sub> particles with mean size of 18 nm and interparticle spacing of 100 nm disperse uniformly in the copper matrix. These Al<sub>2</sub>O<sub>3</sub> particles mostly present in the form of sphere or ellipsoid with an average size of 18 nm and mean interparticle spacing of 100 nm. They prevent efficiently the movement of dislocations and grain boundaries, thus improving the strength of the alloy at room and elevated temperature and retard recrystallization.

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