Properties of dispersion hardened copper processed by internal oxidation in air

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Abstract

The prealloyed copper powders containing different amount of aluminium (1, 2.5 and 3.5 mass.%) were milled for 5 h in a planetary ball mill to form alumina particles by internal oxidation in air. The powders were compacted by hot pressing in argon at 800 °C for 3 h. In the next step compacts were heat treated in argon at 800 °C for 5 h in order to determine their thermal stability *via* microhardness measurements. Compacts from as-received Cu-1, 2.5 and 3.5 mass.% Al and non-alloyed electrolytic copper powders were also synthesized under the same condition. Compacts of milled powders before and after heat treatment exhibited considerably higher microhardness than compacts of non-alloyed electrolytic copper and as--received powders. The increase of microhardness and good thermal stability were ascribed to the small grain size and presence of fine and uniformly distributed alumina particles formed by internal oxidation during milling. The electrical conductivity of compacts was above the minimum requirement limit for Cu-based alloys.

K e y w o r d s: dispersion hardened copper, internal oxidation in air, high energy ball milling, grain size

1. Introduction

The mechanical alloying initially invented for the production of oxide dispersion strengthened (ODS) Ni-based superalloys by powder metallurgy was extended later to other ODS alloys. Mechanical alloying proved to be superior for processing of ODS Cu--based alloys with better high temperature capabilities in comparison with other processing techniques. The development of dispersion hardened Cu-Al_2O_3 alloys was based on high energy milling of copper powder with nanosized alumina powder particles [1–3]. In the recent years some attempt was made to produce these alloys by internal oxidation using high energy milling of prealloyed copper powders [3–5]. High energy milling is considered to be adventageous not only for formation of fine and uniformly distributed alumina dispersoids, but for obtaining very fine grain--sized microstructure in comparison with conventional internal oxidation processes.

Some earlier investigations have shown that during high energy milling in air of prealloyed copper powders it is possible to produce dispersion hardened Cu-Al_2O_3 alloys by internal oxidation [7, 8]. Due to the high diffusion rate in copper [9, 10], oxygen from air diffuses during milling process into prealloyed copper powder particles and aluminium oxidizes *in situ* forming very fine Al_2O_3 particles [7] and well within the range required for dispersion hardening [11]. In addition, the structure of milled prealloyed copper powders is characterized by very fine grain structure, ranging to nanometer scale, which influence on hardening must not be neglected. Other methods adopted for internal oxidation of the prealloyed powders usually involve surface oxidation of particles with formation of copper oxides, or mixing prealloyed powders and fine copper oxide powders [12]. Subsequent heating to temperatures at which copper oxide dissociates allows the diffusion of oxygen into particles and alumina formation *in situ*.

The purpose of this work was to estimate the effect of high energy milling in air on grain size and

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properties of dispersion hardened Cu-Al_2O_3 compacts produced from prealloyed copper powders containing different aluminium content. The electrical conductivity and thermal stability (expressed through microhardness measurements after high temperature heat treatment) may be regarded as the basic parameters for evaluation of properties of dispersion hardened Cu-Al_2O_3 compacts.

2. Experimental procedure

The inert gas atomized prealloyed copper powders containing different amount of aluminium, *i.e.* Cu-1, 2.5 and 3.5 mass.% Al were milled for 5 h in the planetary ball mill. The weight ratio of powders to steel balls was 1 : 35. After milling all powders were treated in hydrogen at 400 °C for 1 h in order to eliminate copper oxides. Compacts were obtained by hot-pressing in an argon atmosphere at 800 °C for 3 h under the pressure of 35 MPa. Compacts from as-received Cu-1, 2.5 and 3.5 mass.% Al and non-alloyed electrolytic copper powders were also synthesized under the same condition. Compacts from previously milled powder were annealed in argon at 800 °C for 5 h in order to measure the thermal stability. This process of annealing will be referred as the heat treatment in the further text.

Compacts before and after heat treatment were characterized by X-ray diffraction analysis (XRD), whereas the hardening was assessed in terms of microhardness measurements using a 50 g load.

X-ray diffraction analysis was performed using "Siemens D-500" X-ray powder diffractometer with CuK_α Ni filtered radiation. The grain size (D) was determined from the broadening (β) of the first four diffraction lines (111, 200, 220 and 311) using the approach developed by Williamson and Hall [13]:

$$\beta \cos\theta = \frac{k}{D} + \frac{k\Delta d}{d} \sin\Theta, \qquad (1)$$

where the shape factor $k = 0.9$ and radiation wave length $\lambda = 0.15405$ nm. $\Delta d/d$ represents the average lattice distortion.

The microstructure was characterized by light microscopy. At polished compacts the electrical conductivity (% IACS, $IACS_{20\,°C} = 0.5800\ \mu ohm^{-1} \cdot cm^{-1}$) was measured using "Sigmatest" apparatus, whereas the density of compacts (ρ) was determined by the Archimedes method. The theoretical density of compacts was calculated from the simple rule of mixtures, taking the fully dense values for copper ($8.96\ g \cdot cm^{-3}$) and alumina ($3.95\ g \cdot cm^{-3}$).

Density, microhardness and electrical conductivity measurements were conducted in five test rounds using at least three compact specimens with different chemical composition.

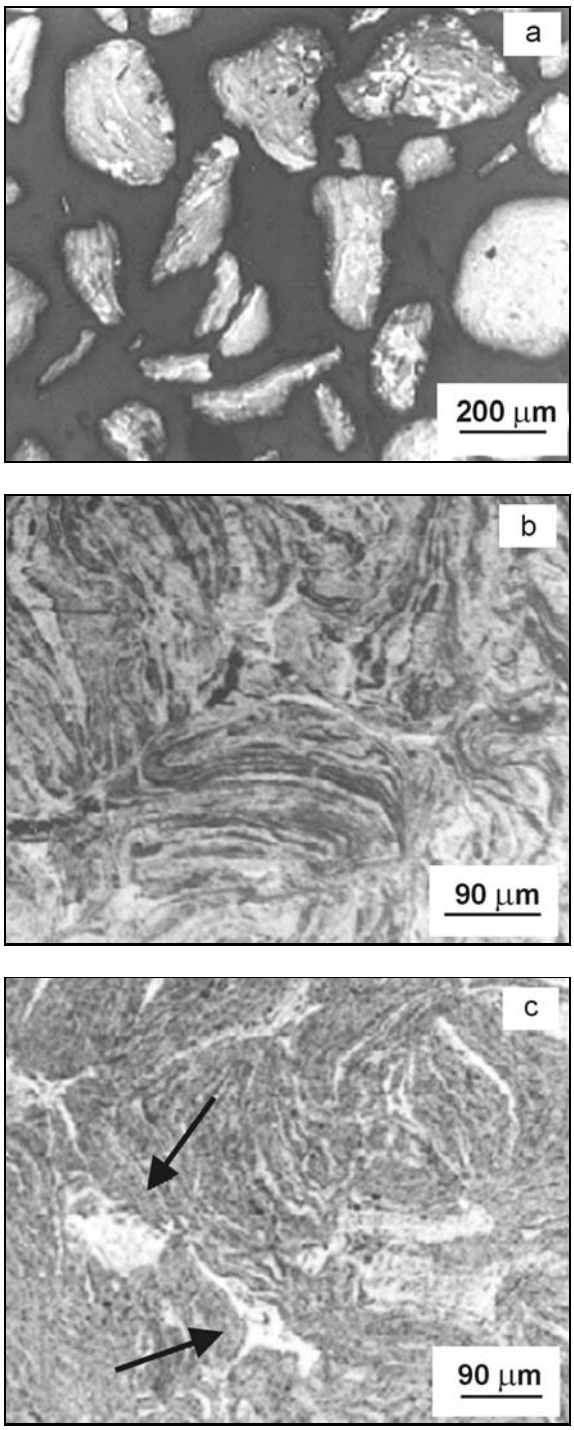

Fig. 1. Light microscope. Microstructure of Cu-1 mass.% Al milled powder particles (a) and compacts before (b) and after (c) heat treatment. The recrystallized grains are shown by arrows.

3. Results and discussion

Microstructure of Cu-1 mass.% Al milled powder particles and compacts before and after heat treatment is shown in Fig. 1. The morphology of individual

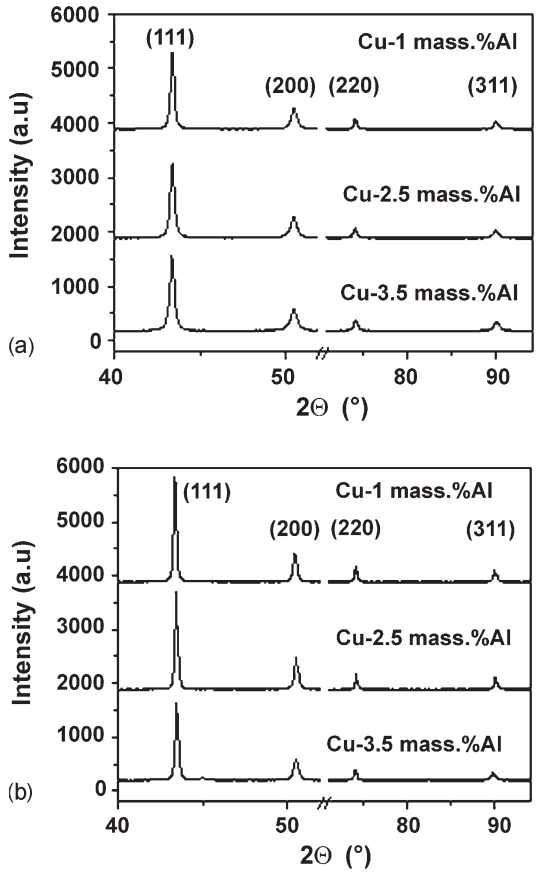

Fig. 2. XRD patterns of compacts before (a) and after (b) heat treatment.

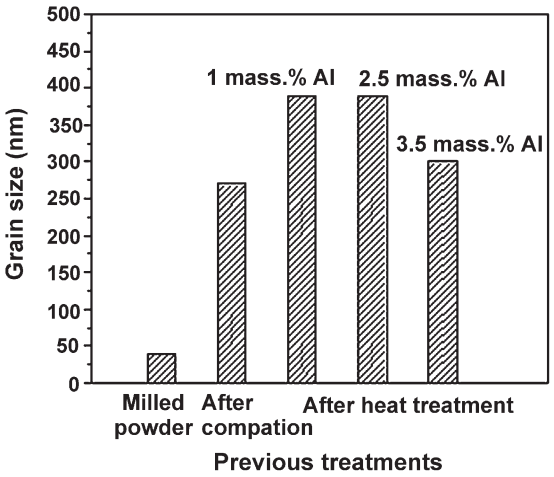

Fig. 3. Grain size vs. previous processing conditions.

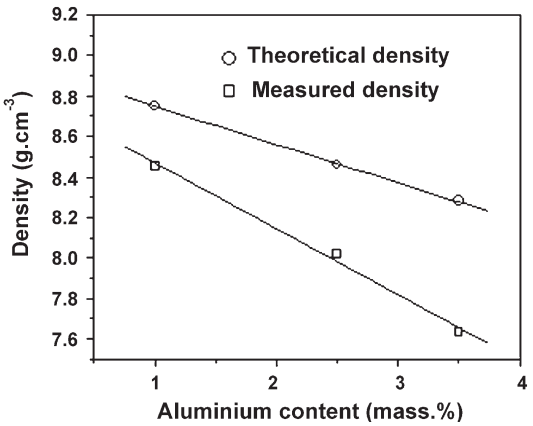

Fig. 4. Density vs. aluminium content in prealloyed powder.

powder particles (Fig. 1a) is significantly changed after milling, i.e. a highly deformed lamellar structure is formed. This lamellar structure is retained even after hot-pressing (Fig. 1b) and after the following heat treatment when some recrystallized copper grains may be seen (Fig. 1c). The microstructure of compacts processed from Cu-2.5 and 3.5 mass.% Al milled powders is very similar to the microstructure shown in Fig. 1.

The diffraction lines (111, 200, 220 and 311) of the XRD patterns of Cu-1, 2.5 and 3.5 mass.% Al compacts before and after heat treatment indicate that compacts are characterized by the similar microstructural features (Fig. 2). The diffraction lines from compacts before heat treatment (Fig. 2a) are weaker and broader indicating smaller grains compared to those after heat treatment (Fig. 2b). On the other side, after heat treatment the line peaks from Cu-1 and 2.5 mass.% Al compacts are stronger and narrower indicating larger grains than those in Cu-3.5 mass.% Al compacts (Fig. 2b).

The change of grain size of compacts calculated using Eq. (1) and as a function of previous processing conditions is shown in Fig. 3. Before heat treatment, compacts have very similar grain size of about 270 nm. It should be noted that the milled powders exhibited the grain size approximately 40 nm [7]. Heat treatment was accompanied by slight grain growth compared to compaction. The Cu-3.5 mass.% Al compact showed the highest resistance to grain growth indicating that the higher alumina content will cause better stabilization of fine grain structure. It could be assumed that in the presence of very small grain and due to the high number of alumina particles the most particles are distributed at grain boundaries contributing to the grain boundary hardening. After heat treatment Cu-1 and Cu-2.5 mass.% Al compacts retained similar grain size of approximately 390 nm, whereas Cu-3.5 mass.% Al compact had grain size of 300 nm.

The variation in the measured and theoretical density with respect to aluminium content in prealloyed powders is shown in Fig. 4. The measured density of Cu-1, 2.5 and 3.5 mass.% Al compacts (8.46, 8.02 and 7.63 $g \cdot cm^{-3}$, respectively) in comparison

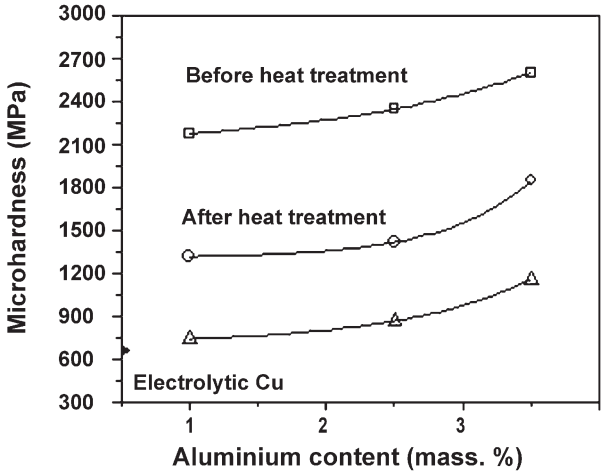

Fig. 5. Microhardness of compacts vs. aluminium content in prealloyed copper powder.

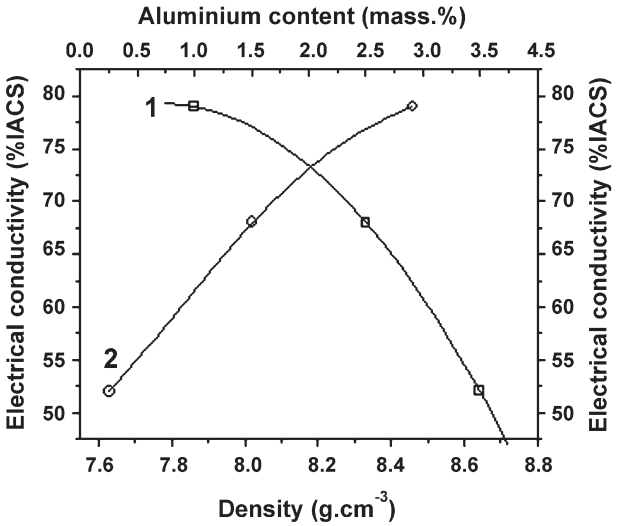

Fig. 6. Electrical conductivity of compacts vs. density and aluminium content in prealloyed copper powder.

with theoretical (8.75, 8.46 and 8.28 $g \cdot cm^{-3}$, respectively) was 96.7, 94.7 and 92.1 %, which indicates that the densification by hot-pressing of milled prealloyed powders was not completed. The theoretical density was calculated for 1.9, 4.7 and 6.6 mass.% Al_2O_3 after oxidation of 1, 2.5 and 3.5 mass.% Al of prealloyed copper powders, assuming that all amount of aluminium precipitates from the copper matrix [8]. The reason for such a poor consolidation could be related to the copper matrix hardening and dislocation generation by alumina particles [14].

The variation in microhardness with respect to the aluminium content in milled prealloyed powder compacts before and after heat treatment and as-received prealloyed powder compacts is shown in Fig. 5. The results show that high energy milling of the prealloyed compacts increases microhardness. The microhardness of compacts processed from non-alloyed electrolytic and as-received prealloyed Cu-1, 2.5 and 3.5 mass.% Al powders was 670 MPa and 745, 870 and 1160 MPa, respectively. Compacts of milled powders before and after heat treatment exhibited considerably higher microhardness than non-alloyed electrolytic and as-received prealloyed copper powders compacted under the same conditions. The microhardness of milled powders compacts is 3 to 4 times higher, whereas heat-treated compacts exhibit 2 to 3 higher microhardness than that of electrolytic and as-received compacts.

The highest microhardness (2600 MPa) and the best thermal stability (1850 MPa) were obtained for Cu-3.5 mass.% Al internally oxidized prealloyed copper powder compacts. The previous result [15] showed that the Cu-1 mass.% Al compact exhibited thermal stability at 600 °C. However, the results of this paper indicate that the thermal stability of Cu-1, 2.5 and 3.5 mass.% Al compacts may be maintained up to 800 °C.

The noticed increase in microhardness and good thermal stability were assumed to be due to the small grain size and the uniformly distributed fine alumina particles. According to the influence of aluminium content on hardening it may be supposed that higher microhardness could be expected with a further increase of aluminium content in prealloyed powder. This observation, however, is not in accordance to that made by Nadkarni & Synk [10] and Mehta et al. [6] who reported that alumina content above 0.65 mass.% did not result in additional hardening. Recently published results [5] suggest a strong influence of aluminium content on properties of Cu-Al_2O_3 composite prepared by internal oxidation.

The electrical conductivity of compacted Cu-1, 2.5 and 3.5 mass.% Al powders after 5 h of milling was 79, 68 and 52 % IACS, respectively. The conductivity decreases with aluminium content in prealloyed powders (Fig. 6, line 1) but it still may be regarded as high, considering that the requirement for the minimum of electrical conductivity for copper-based alloys for high temperature application is 50 % IACS [16]. The increase of alumina content means that between particles and copper matrix more interfaces, considered as a possible source of additional electron scatter, were formed thus reducing the conductivity of copper [17]. The electrical conductivity (Fig. 6, line 2) decreases also with the decreased density of compacts because pores disrupt the electron motion through the copper matrix in a similar way as alumina particles do. The higher conductivity of commercially available copper alloys ranging between 78 and 92 % IACS [10] is related to the lower content of aluminium (less than 0.7 mass.%) and the full density.

4. Summary

The effect of high energy milling on the grain size and some properties of Cu-1, 2.5 and 3.5 mass.% Al compacts processed from 5 h-high energy milled powders in air have been determined. Measurements of thermal stability and electrical conductivity were carried out as a function of alumina content and high temperature heat treatment at 800 ℃ for 5 h.

– The examined compacts are characterized by the small grain size. Before heat treatment all compacts possessed a similar grain size around 270 nm. After a slight grain growth during the heat treatment compacts of Cu-1 and 2.5 mass.% Al retained grain size of approximately 390 nm, whereas the grain size of Cu-3.5 mass.% Al compacts was 300 nm.

– Compacts of milled powders before and after heat treatment exhibited considerably higher microhardness than did non-alloyed electrolytic and as-received powders compacted under the same conditions.

– The highest microhardness and the best thermal stability at 800 ℃ were obtained for Cu-3.5 mass.% Al compacts.

– The increase in microhardness and good thermal stability was assumed to be due to the small grain size and the presence of fine and uniformly distributed alumina particles formed by internal oxidation during milling in air.

– The electrical conductivity of the compacts processed from Cu-1, 2.5 and 3.5 mass.% Al milled powders was 79, 68 and 52 % IACS, respectively. These values are higher than the minimum value of conductivity required for copper-based alloys for high temperature application.

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