

The properties of high-energy milled pre-alloyed copper powders containing 1 wt.% Al

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(Received 30 November 2005, revised 2 April 2006)

Abstract: The microstructural and morphological changes of inert gas atomized pre-alloyed Cu-1 wt. % Al powders subjected to high-energy milling were studied. The microhardness of hot-pressed compacts was measured as a function of milling time. The thermal stability during exposure at 800 °C and the electrical conductivity of compacts were also examined. During the high-energy milling, severe deformation led to refinement of the powder particle grain size (from 550 nm to about 55 nm) and a decrease in the lattice parameter (0.10 %), indicating precipitation of aluminium from the copper matrix. The microhardness of compacts obtained from 5 h-milled powders was 2160 MPa. After exposure at 800 °C for 5 h, these compacts still exhibited a high microhardness value (1325 MPa), indicating good thermal stability. The increase of microhardness and good thermal stability is attributed to the small grain size (270 and 390 nm before and after high temperature exposure, respectively). The room temperature electrical conductivity of compacts processed from 5 h-milled powder was 79 % IACS.

Keywords: Cu-1 wt.% Al pre-alloyed powders, high-energy milling, grain size, hardening, electrical conductivity.

INTRODUCTION

It is well known that copper dispersion-strengthened by aluminium oxide (Al_2O_3) particles produced by powder metallurgy processes is characterized by a unique combination of high strength and good electrical and thermal conductivity at room as well as at elevated temperatures. Aluminium oxide dispersoids are insoluble in the copper matrix and possess high hardness and stability at high temperatures.¹ Recently, because of these properties, the application of dispersion-strengthened copper has been expanded in several areas, especially in the electronics industry and nuclear technology. The properties of dispersion-strengthened copper are the consequence of fine aluminium oxide dispersoids in a copper ma-

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doi: 10.2298/JSC0701045R

trix. Aluminium oxide dispersoids contribute to the strengthening of the copper matrix in a way that provides resistance to dislocation motion according to the Orowan theory.² While several methods of introducing fine aluminium oxide particles in the copper matrix have been extensively investigated, mechanical alloying and internal oxidation seem to be the most universally applicable. Internal oxidation produces *in situ* the finest aluminium oxide particles and most uniform particle distribution.¹ Earlier investigations have shown that by using high-energy milling in air of pre-alloyed copper powders, it is possible to produce dispersion-strengthened Cu-Al₂O₃ alloys by internal oxidation with oxygen from the air.³

The goal of the present investigation was to introduce fine aluminium oxide particles through high-energy milling in air of pre-alloyed copper powder containing 1 wt.% Al, to consolidate the powder milled up to 20 h and to determine the properties of compacted material.

EXPERIMENTAL

Inert gas atomized pre-alloyed copper powder containing 1 wt.% aluminium was milled for 3, 5, 10, 15 and 20 h in a planetary ball mill. The weight ratio of powder to steel balls was 1:35. The high-energy milling was performed in air in order to enable the formation of aluminium oxide dispersoids by internal oxidation with oxygen from the air. Following milling, the powder was treated in hydrogen at 400 °C for 1 h in order to eliminate copper oxides formed at the surface during milling. Compacts (10 mm in diameter and 10 mm in height) were obtained by hot-pressing in an argon atmosphere at 800 °C for 3 h under a pressure of 35 MPa. Compacts from as-received Cu-1 wt.% Al and electrolytic copper powders were also prepared under the same conditions. The compacts obtained from 5 h-milled powder were additionally subjected to high temperature exposure in argon at 800 °C for 1 and 5 h, with the goal to examine their thermal stability.

The microstructure of the powder and compacts was characterized by X-ray diffraction analysis (XRD), optical and scanning electron microscopy (SEM). The effect of hardening was assessed by microhardness measurements using a 50 g load. X-Ray diffraction analysis was performed using a Siemens D-500 diffractometer with CuK_α Ni-filtered radiation. The lattice parameter was refined by the least square method. The average lattice distortion, *i.e.*, the relative deviation of the lattice parameters from their mean value ($\Delta d/d$)⁴ and the grain size (D) were determined from the broadening (β) of the first four X-ray peaks (111, 200, 220 and 311), using the approach developed by Williamson and Hall:⁵

$$\beta \cos \theta = \frac{k\lambda}{D} + \frac{k\Delta d}{d} \sin \theta \quad (1)$$

where $k = 0.9$ is the shape factor and $\lambda = 0.15405$ nm is the radiation wavelength. The density (ρ) of the compacts was determined by the Archimedes method, whereas the theoretical density was calculated from the simple rule of mixtures, taking the theoretical values of copper (8.96 g cm⁻³) and aluminium oxide (3.95 g cm⁻³). The room temperature electrical conductivity (% IACS) of polished compacts was determined using the Siemens conductometer Sigmatest.

RESULTS AND DISCUSSION

During high-energy milling, severe deformation (lattice distortion and grain size refinement) leads to X-ray peak broadening with milling time (Fig. 1).^{4,5} The effect of milling time on the grain size and lattice distortion of the examined powder particles is presented in Fig. 2. As can be seen, the most intensive change oc-

curs in the early stage of milling. The grain size decreases from about 550 nm before milling to about 55 nm after 5 h of milling. In the period from 5 h to 20 h, the grain size remains practically constant, about 30 nm. On the contrary, the lattice distortion strongly increases during 5 h of milling. At longer milling times, the change of the lattice distortion becomes less evident. This result is in agreement with some earlier observations, that the deformation of particles occurs during the early stages of milling.⁵

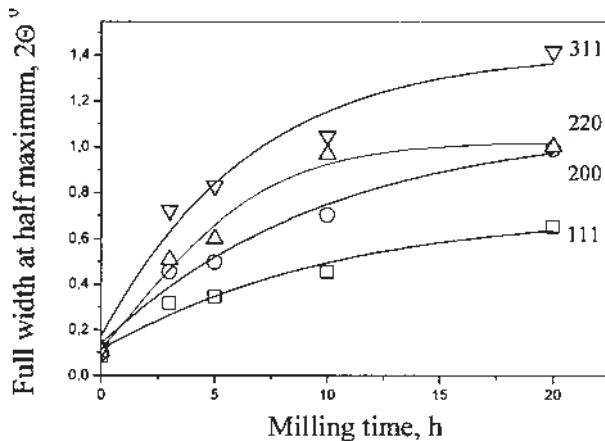


Fig. 1 Full width at half maximum (FWHM) vs. milling time for Cu-1 wt.% Al powders.

Figure 3 shows the decrease in the lattice parameter with milling time, indicating precipitation of aluminium from the copper matrix. Precipitated aluminium is oxidized *in situ* by oxygen from air, forming aluminium oxide dispersoids. Earlier investigations showed that these dispersoids are very fine³ and well within the range required for dispersion hardening.⁶ The decrease in the lattice parameter is rapid at the very beginning of the milling process but only slowly decreases with prolonged milling. This behaviour is due to facilitation of the oxidation process through the severe deformation of the copper matrix at the very beginning of the milling process. The difference in the

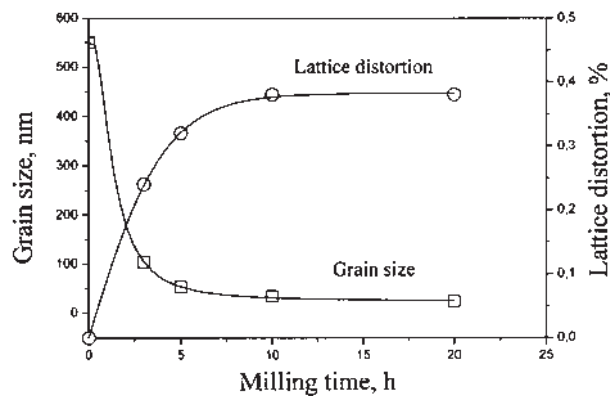


Fig. 2 Effect of milling time of the grain size and lattice distortion of Cu-1 wt.% Al powders.

lattice parameters of pre-alloyed Cu-1 wt.% Al powders before ($a_{\text{Cu-1 wt.\% Al}} = 0.36197$ nm) and after 20 h of milling ($a_{\text{Cu-1 wt.\% Al}} = 0.36163$ nm) is 0.10 %. This difference, similar to the difference (0.16 %) in the theoretical lattice parameters of the pre-alloyed powder ($a_{\text{Cu-1 wt.\% Al}} = 0.36210$ nm) and the copper powder ($a_{\text{Cu}} = 0.36152$ nm) indicates that after 20 h of milling almost all the aluminum had precipitated from the copper matrix. Assuming that the complete amount of aluminium was oxidized, it can be calculated that by internal oxidation of 1 wt.% aluminium, 1.9 wt.% of aluminium oxide was produced in the copper matrix.

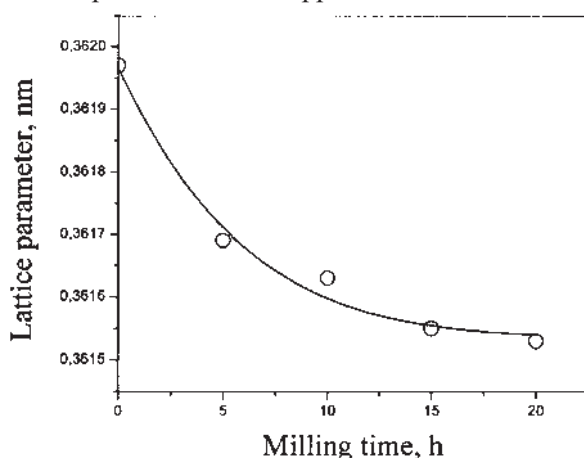


Fig. 3 Lattice parameter vs., milling time for Cu-1 wt.% Al powders.

During high-energy milling, powder particles change their Morphology as the consequence of repeated deformation, fracturing and welding.⁷ SEM micrographs show Cu-1 wt.% Al powder particles before milling (Fig. 4a) and the development of the powder morphology with increasing milling time (Figs. 4b–d). The particle size increases up to 10 h of milling due to the dominance of welding,⁷ whereas the particles are rather flattened because of the strong plastic deformation occurring in the early stage of the milling process (Fig. 4b). After 20 h of milling, the particle size had decreased since fracturing predominates in the milling process⁷ and the particles appear to be rather uniform in size (Fig. 4c). The presence of some coarse particles (Fig. 4c–e) indicates that after 20 h of milling, coalescence had occurred to some extent.

In contrast to the microstructure of the as-received Cu-1 wt.% Al powder particles, milled powder particles exhibit a lamellar microstructure. Lamellae present individual plastically deformed powder particles and they are typical for high-energy milled powder. The lamellar structure of Cu-1 wt.% Al particles is retained after compaction. Figure 5 shows the microstructure (optical microscopy) of Cu-1 wt.% Al particles before milling (Fig. 5a), after 10 h of milling (Fig. 5b) and after hot-pressing (Fig. 5c).

The microhardness of the compacts as a function of milling time is shown in Fig. 6. The microhardness increased in the first 5 h of milling, while with prolonged milling, the values of the microhardness remained nearly constant. The in-

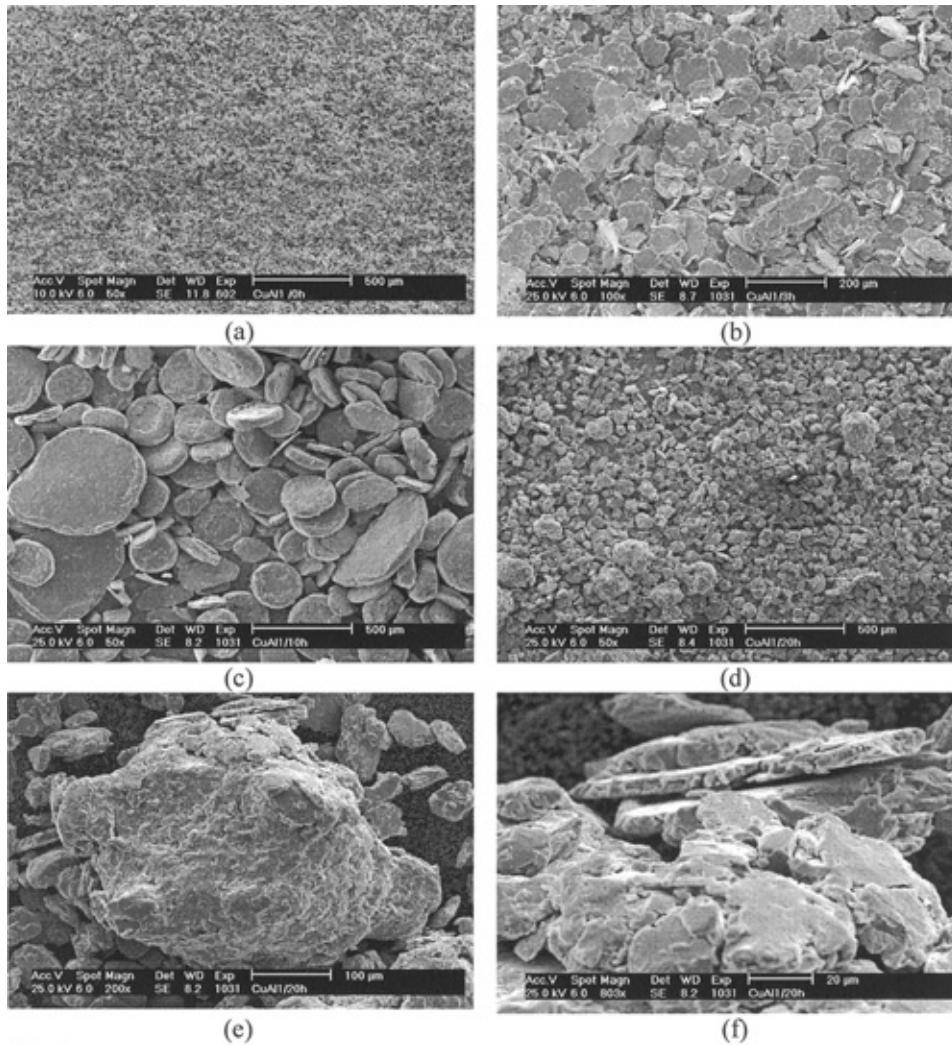


Fig. 4 Morphology of Cu-1 wt.% Al particles as a function of milling time: (a) before milling; (b) 3 h, (c) 10 h, (d) 20 h, (e) detail of Fig. 4d, (f) detail of Fig. 4e.

crease in microhardness may be attributed to two processes: intensive refinement of the grain size (see Fig. 2) and aluminium oxide precipitation in the form of fine particles from the pre-alloyed copper matrix.³ The rapid decrease of the lattice parameter (see Fig. 3) is a consequence of precipitation of aluminium from the copper solid solution and successive formation of fine aluminium oxide in the copper matrix. The microhardness of compacts obtained from as-received Cu-1 wt.% Al powders (745 MPa) increased up to 2160 MPa after 5 h of milling, which is 3 times higher than that of compacts produced from electrolytic copper powder (670 MPa) compacted under the same conditions. This result shows that an aluminium oxide

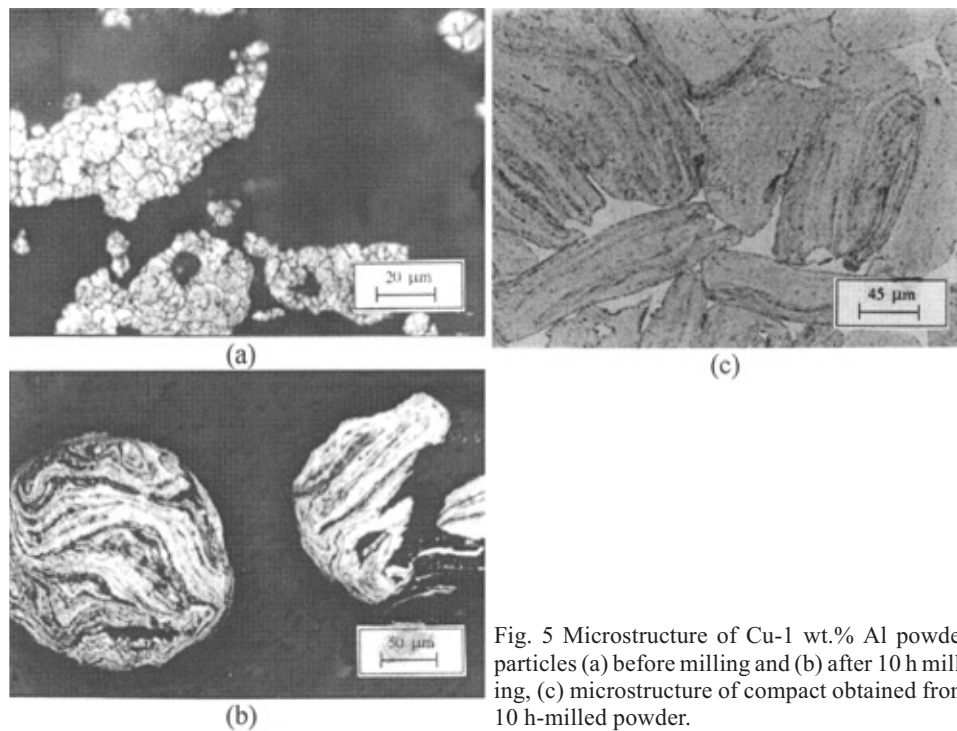


Fig. 5 Microstructure of Cu-1 wt.% Al powder particles (a) before milling and (b) after 10 h milling, (c) microstructure of compact obtained from 10 h-milled powder.

content of 1.9 wt.%, formed through oxidation of 1 wt.% Al, has a very strong effect on the hardening of the copper matrix, in contrast with observations of Mehta⁸ and Nadkarni¹ who reported that an aluminium oxide content above 0.65 wt.% did not result in an increased hardening.

The grain size of 5 h-milled powders and compacts before and after 5 h of exposure at 800 °C was calculated (XRD patterns are given in Fig. 7). The different

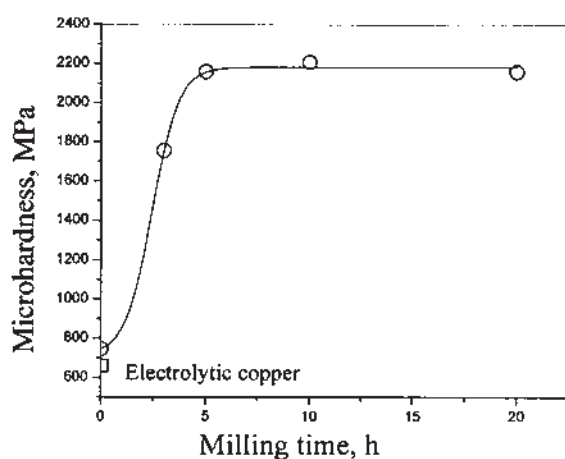


Fig. 6 Effect of milling time of the microhardness of Cu-1 wt.% Al compacts.

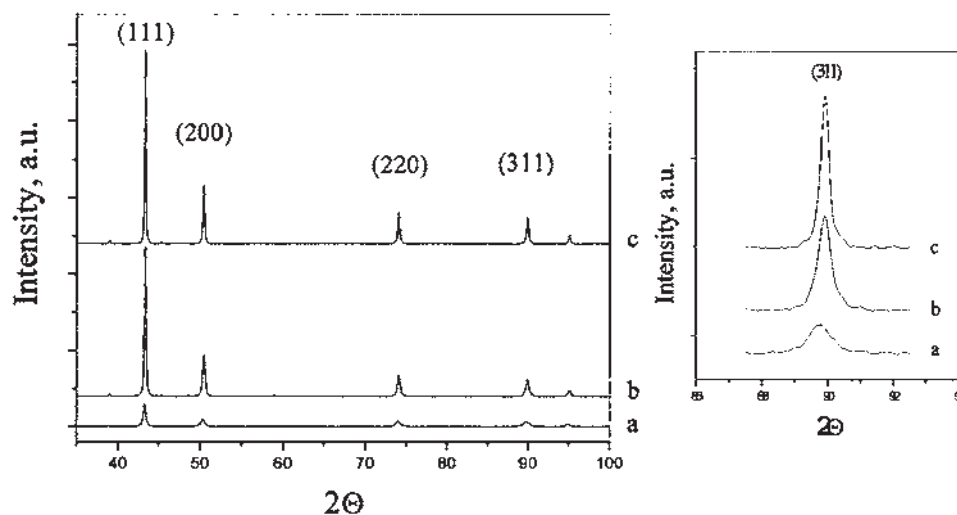


Fig. 7 XRD Patterns of compact obtained from Cu-1 wt.% Al powders milled for 5 h (a) and compacts before (b) and after high temperature exposure at 800 °C for 5 h (c). The enlarged full width at half maximum (FWHM) of the (311) diffraction peak is shown in the detail.

FWHM (full width at half maximum) of the diffraction peaks of Cu-1 wt.% Al (see detail of Fig. 7) indicates different grain sizes of 55, 270 and 390 nm, respectively. These results suggest that grain growth occurs during hot-pressing, but during exposure to high temperatures, the grain growth is much slower.

In order to assess their high temperature thermal stability, compacts of Cu-1 wt.% Al were exposed to a temperature of 800 °C for 1 and 5 h. The results given in Table I reveal that the microhardness decreased to some extent with increasing time of exposure (from 1720 to 1325 MPa, after 1 and 5 h of exposure, respectively). Since the microhardness retains a high value after 5 h of exposure, it may be concluded that compacts obtained from 5 h-milled Cu-1 wt.% Al powders exhibit good thermal stability. Also, the microhardness after 5 h is more than 2.5 times greater than the microhardness of compacts obtained from electrolytic copper powder (670 MPa).

TABLE I. Effect of high temperature (800 °C) exposure on the microhardness of Cu-1 wt. % Al compacts obtained from 5 h-milled powders

Temperature/Time	25 °C	800 °C/1 h	800 °C/5 h
Microhardness	2160 MPa	1720 MPa	1325 MPa

Taking into account the results on the grain size and thermal stability, it may be supposed that the good thermal stability of the compacts is related to a relatively slow grain growth at 800 °C. Small dispersoids not only increase the microhardness by strengthening the copper matrix, but also, if formed at grain boundaries,

they impede grain growth, thus postponing recrystallization and preventing grain growth by pinning grain boundaries.⁹

The density of the compacts, as one of their important properties, was also measured. The results indicate that the densification by hot-pressing of milled pre-alloyed powder was not completed. The measured density of the compacts processed from 5 h-milled powder (8.46 g cm^{-3}) was 96.7 % of the theoretical value (8.75 g cm^{-3}). It was reported that the measured density of extruded materials is higher than 99.3 %.¹⁰ It should be noted that in this study the theoretical density was calculated for 1.9 wt.% Al_2O_3 after oxidation of 1 wt.% Al of pre-alloyed copper powder, assuming that all of the aluminium precipitates from the copper matrix.

The room temperature electrical conductivity of compacts obtained from 5 h-milled powder was 79 % IACS. The presence of aluminium oxide interfaces between the aluminium oxide particles and the copper matrix are considered as a possible source of additional electron scatter, thus reducing the conductivity of the copper matrix.¹¹ Since the required lower limit of conductivity for copper-based alloys for higher temperature applications is 50 % IACS,¹² while the conductivity of commercially available copper alloys ranges between 78 and 92 % IACS,⁹ the measured conductivity value might be accepted as being satisfactory.

CONCLUSIONS

The microstructural and morphological changes of high-energy milled pre-alloyed Cu-1 wt.% Al powders was studied. The microhardness of compacted milled powders was followed as a function of milling time. The high temperature thermal stability and electrical conductivity of compacts were also examined. The main conclusions are as follows:

- During high-energy milling of pre-alloyed Cu-1 wt.% Al powders, severe deformation leads to particle grain size refinement (from 550 nm to about 55 nm) and to a decrease in the lattice parameter, indicating precipitation of aluminium from the copper lattice.
- The lamellar structure formed at the beginning of the milling process is retained during compaction.
- The microhardness of the compacts obtained from as-received Cu-1 wt.% Al pre-alloyed copper powders was 745 MPa, whereas the compacts obtained from 5 h-milled powders show a steep increase in microhardness up to 2160 MPa, a value 3 times higher than that of as-received electrolytic copper powders (670 MPa) compacted under the same conditions.
- Compacts obtained from 5 h-milled Cu-1 wt.% Al pre-alloyed powders after exposure for 1 and 5 h at 800 °C have microhardness values of 1720 and 1325 MPa, respectively, indicating good thermal stability.
- The increase of the microhardness and good high thermal stability may be related to the relatively slow grain growth (270 and 390 nm before and after exposure at 800 °C, respectively).

– The room temperature electrical conductivity of compacts obtained from 5 h-milled powder was 79 % IACS, which is in the range of the conductivity of commercially available copper alloys for higher temperature applications.

Acknowledgement: The authors wish to thank the Ministry of Science and Environmental Protection of the Republic of Serbia for financial support through the project No. HE1967.

I Z V O D

ОСОБИНЕ ПРАХА БАКРА ПРЕДЛЕГИРАНОГ СА 1 МАС. % АЛ И ТРЕТИРАНОГ У ВИСОКОЕНЕРГЕТСКОМ МЛИНУ

ВИШЕСЛАВА РАЈКОВИЋ, ДУШАН БОЖИЋ И АЛЕКСАНДАР ДЕВЕЧЕРСКИ

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У раду су испитане промене облика и структуре честица које настају при млевењу праха предлегираног бакра са 1 мас. % Аl у високоенергетском млину. Микротврдоћа компакта добијених од претходно млевених прахова је одређена у зависности од времена млевења, а термичка стабилност испитивана је после 1 и 5 h излагања компаката на 800 °С. Такође је одређена и електрична проводност компактираног праха. Услед велике деформације при млевењу прахова у високоенергетском млину дошло је до знатног уситњавања зрна са 550 на око 55 nm. Смањење параметра решетке (0.10 %) указује да је услед оксидације при млевењу предлегираног праха дошло до издвајања алуминијума из решетке бакра. Разлика у микротврдоћи компакта од предлегираног праха претходно млевеног 5 h пре (2160 МПа) и после (1325 МПа) 5 h излагања на 800 °С указује на добру термичку стабилност материјала. Висока микротврдоћа и добра термичка стабилност су последица како ситног зрна компакта (270 nm) тако и успореног раста зрна (до 390 nm) у току излагања компакта повишеној температури. Електрична проводност компакта на собној температури је 79 % IACS.

(Примљено 30. новембра 2005, ревидирано 2. априла 2006)

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