COPPER ALLOYS WITH IMPROVED PROPERTIES: STANDARD INGOT METALLURGY *VS.* POWDER METALLURGY

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Abstract

Three copper-based alloys: two composites reinforced with Al_2O_3 particles and processed through powder metallurgy (P/M) route, i.e. by internal oxidation (Cu-2.5Al composite) and by mechanical alloying (Cu-4.7Al_2O_3) and Cu-0.4Cr-0.08Zr alloy produced by ingot metallurgy (vacuum melting and casting) were the object of this investigation. Light microscope and scanning electron microscope (SEM) equipped with electron X-ray spectrometer (EDS) were used for microstructural characterization. Microhardness and electrical conductivity were also measured. Compared to composite materials, Cu-0.4Cr-0.08Zr alloy possesses highest electrical conductivity in the range from 20 to 800°C, whereas the lowest conductivity shows composite Cu-2.5Al processed by internal oxidation. In spite to somewhat lower electrical conductivity (probably due to inadequate density), Cu-2.5Al composite exhibits thermal stability enabling its application at much higher temperatures than materials processed by mechanical alloying or by vacuum melting and casting.
Key words: Mechanical alloying, Internal oxidation, Al_2O_3 particles, Chromium-rich particles, Thermal stability

Introduction

Age hardened copper alloys such as Cu–Cr, Cu–Zr and Cu–Cr–Zr obtain high strength and hardness through the precipitation of tiny coherent particles from a supersaturated copper matrix [1]. Due to their good mechanical properties and high electrical conductivity, these alloys in the last decade have attracted widespread attention for application in electrical/thermal conducting field such as electrodes for resistance welding, trolley wire of electric railway, and electrical brush.

In general, application of low alloyed copper-based alloys with high electrical conductivity may be regarded as follows:

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- ▪ Different types of high electrical conductivity alloys have been developed. Most common are Cu-Cr and Cu-Zr alloys,
- ▪ small amounts of the third element additions are required to achieve optimum properties in these binary alloys,
- ▪ the chemical composition and especially technology of their processing are protected by patents or clasified documents.

The process of electrical-resistance welding reached full development in the production of aviation assemblies, car chassis and bodies, metallic furniture and other applications. This welding process uses pure copper (not advisable!) and copper-based alloys as the electrode material. Electrical-resistance spot welding involves passing a high current at a low voltage through a circuit closed by the pieces to be welded. The generated heat is sufficient to produce local fusion of the pieces under pressure, leading to an autogenously forged union. The drawing of of resistance spot welding is shown in Figure 1.
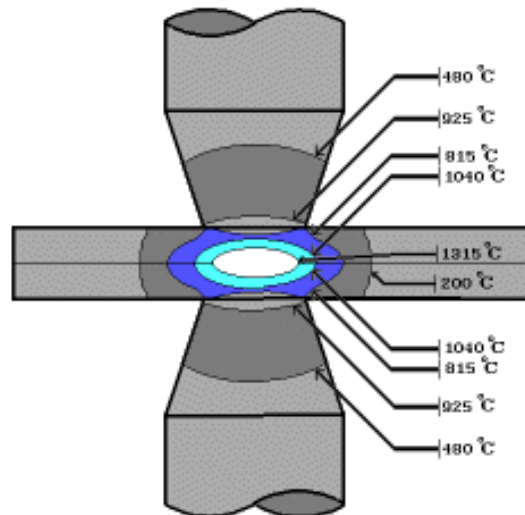

Figure 1 Set up of spot welded material inserted between a pair of electrodes with a span of temperatures developed during spot welding.

Thus, electrode materials must exhibit high electrical and thermal conductivities combined with high strength and low wear rate at elevated temperatures.

What are disadvantages of these alloys

Two deficiencies, characteristic for the precipitation hardened materials, which limit the further application of these alloys are:

- − At elevated temperatures the precipitated phases may grow and dissolve again in the copper matrix, therefore the mechanical properties of these alloys are significantly reduced,
- − lack of enough load bearing components on the surface and in the subsurface region results in the relatively low wear resistance of these alloys.

New copper-based alloys

Particulate reinforced copper matrix composites have been regarded as new promising candidates of electrical and thermal conduction functional materials in the last few years. Previous works has proved that addition of hard particles such as SiC, Al_2O_3, TiB_2 and TiC [2-4] can significantly improve the mechanical properties of copper matrix materials while maintaining high electrical and thermal conductivity. The incorporation of ceramic particles as reinforcement may also enhance the high-temperature mechanical properties, oxidation and wear resistance, without severe deterioration of thermal and electrical conductivity of the copper matrix. On account of the low price, Al_2O_3 particles have been mostly selected as the reinforcement phase [5-7]. The uniform distribution of Al_2O_3 particles can be accomplished by the process of internal oxidation [8, 9] or by mechanical alloying [10, 11].

Strengthening of the copper matrix
a. Internal oxidation

During high-energy milling aluminum dissolved in the copper matrix, as more noble than copper, oxidizes first reacting with oxygen from the air and forming nano-sized Al_2O_3 particles.

b. Mechanical alloying

Both nano- and micro-sized Al_2O_3 particles may be used as a strengthener during the process of mechanical alloying. High-energy milled powders are characterized by very fine, nano-scaled grain structure, which may be retained even during compaction and at temperatures near the melting point. This fine-grained structure contributes to copper matrix strengthening together with Al_2O_3 particles.

Three copper-based alloys, *i.e.* two composites reinforced with Al_2O_3 particles and fabricated through powder metallurgy (P/M) route and Cu–Cr–Zr alloy processed by standard melting and casting procedure were studied. The main objective was to investigate the effect of processing on microstructure, hardness, electrical conductivity and thermal stability of these materials during high temperature annealing.

Experimental
Material and processing

Processing parameters for production of samples used in experiments are shown in Table 1.

Table 1 Processing parameters.

Material	Processing	Product
P/M –internal oxidation	Prealloyed Cu-2.5Al powder	Cu-4.7Al_2O_3 (after internal oxidation)
P/M – mechanical milling	Copper powder + 5Al_2O_3	Cu-5Al_2O_3
Vacuum melting and casting	Oxygen free high conductivity copper (OFHC) + (Cu-10Cr + Cu-30Zr) master alloys	Cu-0.4Cr-0.08Zr

Powders were separately milled in air for 5 h in the planetary ball mill. Following milling, powders were treated in hydrogen atmosphere at 400°C for 1 h in order to eliminate copper oxides formed at the surface during milling. Compaction executed by hot-pressing was carried out in an argon atmosphere at 800°C for 1 h under the pressure of 35 MPa. Milling in air of prealloyed copper powder promoted formation of 4.7 wt.% of finely dispersed Al_2O_3 particles by internal oxidation.

Ingots of Cu-0.4Cr-0.08Zr alloy with 40 mm in diameter and 180 mm in height were produced by melting and casting in a laboratory vacuum furnace. Thermo-mechanical treatment (TMT) was executed in the following manner: hot rolling (to the predetermined diameter) at the temperature between 800 and 850°C→solution annealing at 960°C for 1h→water quenching→cold rolling (degree of plastic deformation was 50%)→aging (temperature of aging and time of aging were 425°C and 2h, respectively).

The shape and dimensions of samples are shown in Figure 2.

Figure 2 Samples obtained by P/M and ingot metallurgy D_{PM} =10m, H_{PM} =10mm; D_{ING} =15mm, H_{ING} =18mm.

Thermal stability

All samples were subjected to high temperature exposure in argon for 4 h in the range of temperatures from 300-950°C.

Methods of characterization

The microstructure of samples was characterized by light microscope "Zeiss Axiovert 25" and scanning electron microscope (SEM) "JEOL JSM-6610LV" equipped with electron dispersive X-ray spectroscope (EDS). Samples for microstructural investigations were polished applying the standard procedure, whereas a mixture of 5 g FeCl3 and 50 ml HCl in 100 ml distilled water was used for etching. The reinforcing of copper matrix was estimated by the microhardness measurements applying load of 50 g. The density of samples was determined by the Archimedes method. The electrical conductivity, expressed in % IACS (IACS20 °C = 0.5800 mΩ−1cm−1) was measured at 60 kHz on polished compacts using "Sigmatest 2.0 6.8." apparatus with electrode diameter of 14 mm.

Results and discussion

Properties of investigated materials before thermal conductivity tests are given in Table 2.

Table 2 Designations and properties of samples before thermal stability tests.

Designation	Type of process	Samples	Density, gcm^{-3}	Percent of theoretical density, %	Microhardness HV_{50g}	Electrical conductivity (%IACS)
Cu-2.5Al	Internal oxidation	Cylinder/ compact	8.02	94.79	250	67
Cu-5Al$_2$O$_3$	Mechanical alloying	Cylinder/ compact	7.92	93.84	155	87
Cu-0.4Cr-0.08Zr	Vacuum metallurgy + TMT	Cylinder/ ingot	8.93	100	150	90

Values of Table 2 clearly demonstrate that the highest microhardness – 250HV$_{50g}$ was obtained in Cu-2.5Al composite processed by internal oxidation. On the other side, Cu-0.4Cr-0.08Zr alloy processed by vacuum melting exibited the highest electrical conductivity – 90%IACS.

Microstructural examination

The microstructure of a composite processed by internal oxidation from 5 h-milled Cu-2.5Al powder is shown in Figure 3.
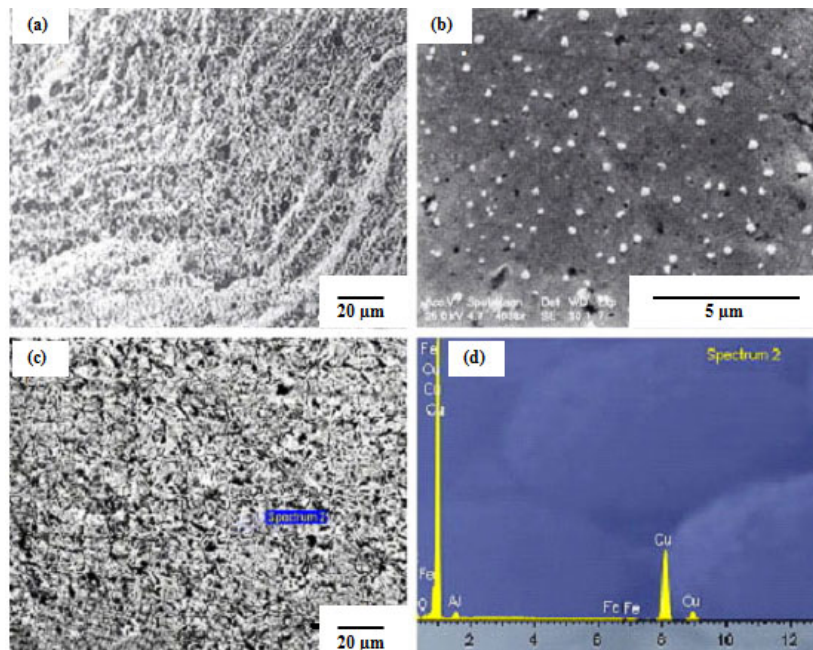

Figure 3 Microstructure of composite processed by internal oxidation from 5 h-milled Cu-2.5Al powder. (a) Light microscope; (b) SEM BSE image; (c, d) SEM and EDS spectrum of a small particle, respectively.

Small particles with the size less than 100 nm may be seen in copper matrix (Figure 3b). The presence of aluminium and oxygen in small particles was detected (Figure 3d) implying that their chemical composition is Al_2O_3.

The microstructure of composite obtained from 5 h milled Cu-5Al_2O_3 powder and processed by mechanical alloying is shown in Figure 4.

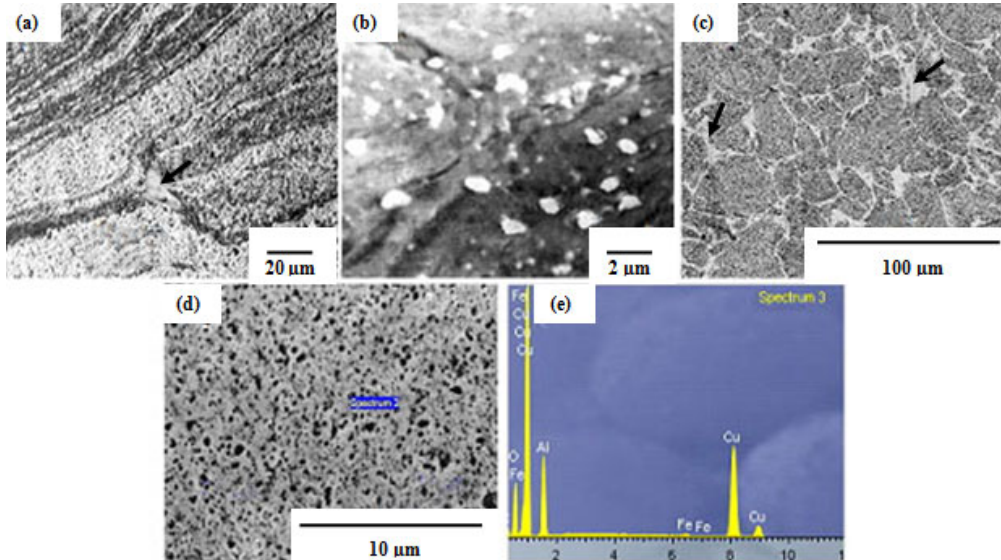*Figure 4 Microstructure of composite processed from 5 h-milled Cu-5Al₂O₃ powder. (a) Light microscope; (b, c) SEM BSE image; (d, e) SEM and EDS spectrum of a small particle, respectively. Arrows in Figure 4(a, c) denote the recrystallized regions.*

Lamellar structure is preserved in compact after hot-pressing (Figure 4a). The size of Al_2O_3 particles was approximately 750 nm in diameter (Figure 4b). Recrystallization (Figure 4c) was more pronounced than in Cu-2.5Al compact indicating that coarse Al_2O_3 particles are less efficient in preventing grain growth than smaller particles.

Microstructure of Cu-0.4Cr-0.08Zr alloy processed by vacuum melding and casting and after TMT is shown in Figure 5.
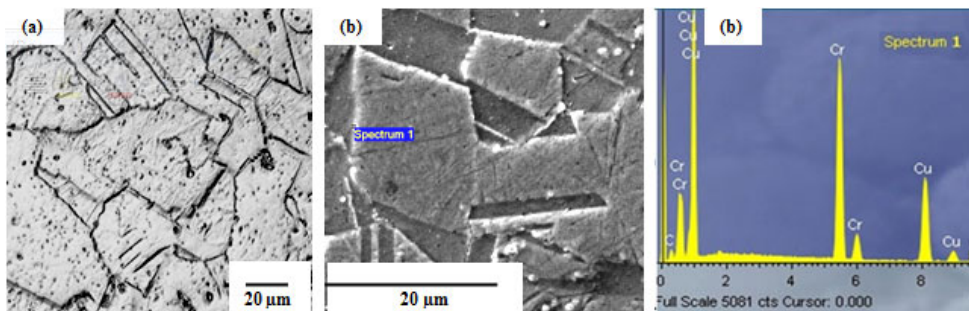

Figure 5 Microstructure of Cu-0.4Cr-0.08Zr alloy after TMT. (a) Light microscope; (b,c) SEM analysis: BSE image and EDS spectrum of a particle inside the grain, respectively.

Supersaturated solid solution of Cu-Cr-Zr alloys is strengthened during aging with very fine Cu_5Zr [12] precipitates. Globular and rod-like particles rich in chromium are actually a product of eutectic reaction during solidification and they do not play any role in strengthening.

Thermal stability

The effect of high temperature exposure in the range 300-950°C for 4h on microhardness of composites and Cu-0.4Cr-0.08Zr alloy is presented in Figure 6.
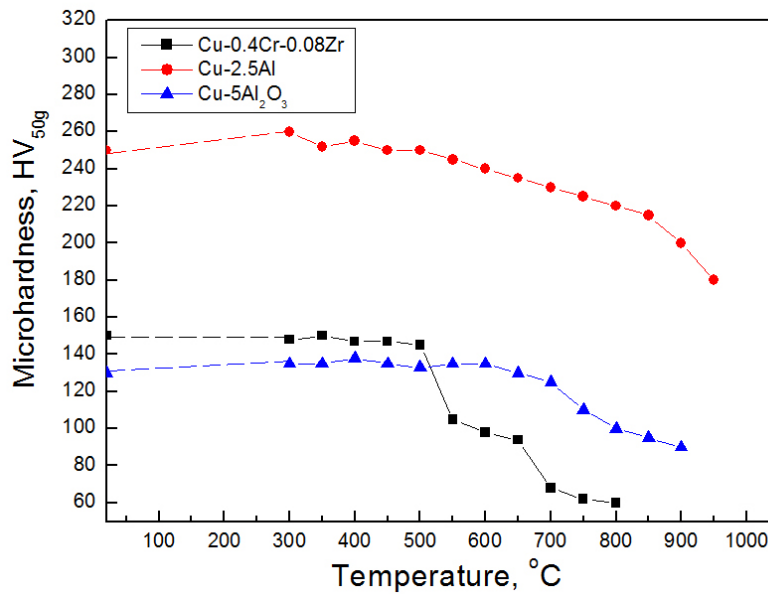

Figure 6 Microhardness as a function of high temperature exposure.

Composites behave much better than the alloy processed by the „classical" method. The highest level of microhardness shows Cu-2.5Al composite processed by internal oxidation.

According to the standard [13] thermal stability is determined by the highest temperature at which the hardness decreases for 15% in relation to the initial hardness. Values of T_s, corresponding to softening temperature, and obtained from diagrams in Figure 6 are given in Table 3. Actually, T_s determines the limit of applicability of a material at high temperatures

Table 3 Thermal stability T_s as a function of processing.

Material	Type of process	T_s, °C
Cu-2.5Al	Internal oxidation	925
Cu-5Al$_2$O$_3$	Mechanical alloying	680
Cu-0.4Cr-0.08Zr	Vacuum melting and casting	525

Highest microhardness is the consequence of the role of nano-particles and fine grained structure which also maintain high thermal stability of Cu-2.5Al composite. It may be assumed that nano-sized Al_2O_3 particles some of which are distributed at the grain boundaries and dislocations will slow down the grain growth in Cu-2.5Al composite [14]. Recrystallization is moved to temperatures even above 800°C.

The lower microhardness (nearly two times) compared to Cu-2.5Al is the direct consequence of increase of grain size in Cu-5Al$_2$O$_3$ composite suggesting that the role of micro-sized commercial Al_2O_3 particles in obstructing grain growth is less efficient.

It is evident that Cu-0.4Cr-0.08Zr alloy could not survive this competition. Although fine Cu$_5$Zr are formed at grain boundaries their ability to prevent dislocation motion and grain growth is less efficient than nano- and micro-sized Al_2O_3 particles. In this way recrystallization becomes active around 550°C.

It is obvious that composites may be used at higher temperatures than „classically" processed alloy. Internal oxidation provides much higher T_s compared to two other materials.

Optical microscopy (Figures 7-9) was applied to clarify phenomena occurring in the microstructure of samples subjected to high temperature annealing.
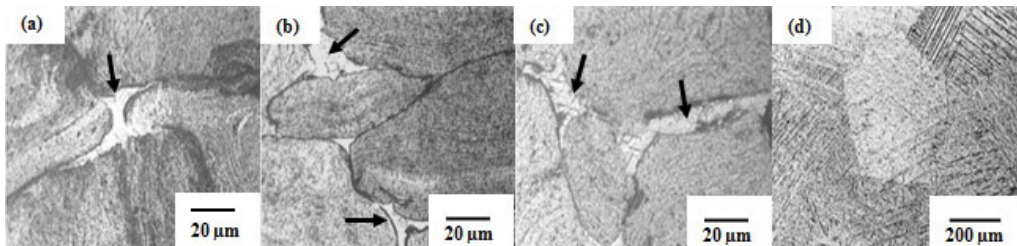

Figure 7 Light microscrope. Cu-2.5Al composite. Microstructure after high temperature exposure for 4h at: (a) 850°C; (b) 900°C; (c and d) at 950°C–minimum hardness. Arrows denote recrystallized regions.

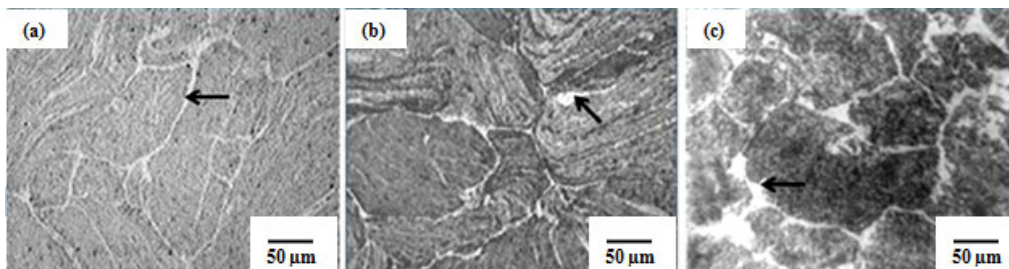Fully recrystallized microstructure (Figure 7d) leads to a significant microhardness drop.

Figure 8 Light micrograph. Cu-5Al$_2$O$_3$ composite. Microstructure after high temperature exposure for 4h at: (a) 70 ^{o}C; (b) 800°C ; 900°C. Arrows denote recrystallized areas.

Recrystallization is probably the main mechanism causing the decrease in microhardnes.
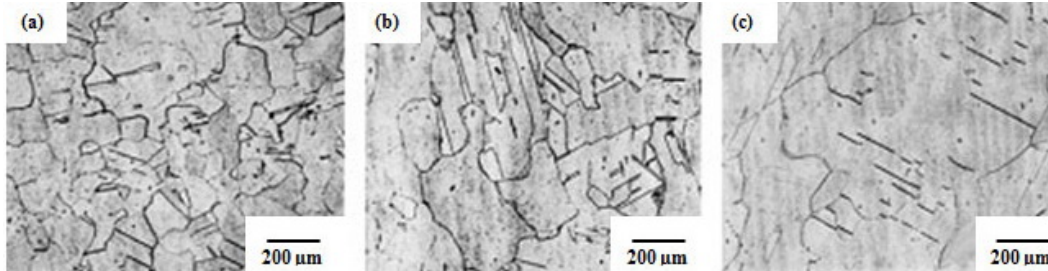

Figure 9 Light micrograph. Cu-0.4Cr-0.05Zr. Microstructure after high temperature exposure for 4h at: (a) 400°C; (b) 600°C; (c) 700°C.

Decrease in microhardness above 500°C is the consequence of recrystallization. The grain size was significantly increased.

Electrical conductivity

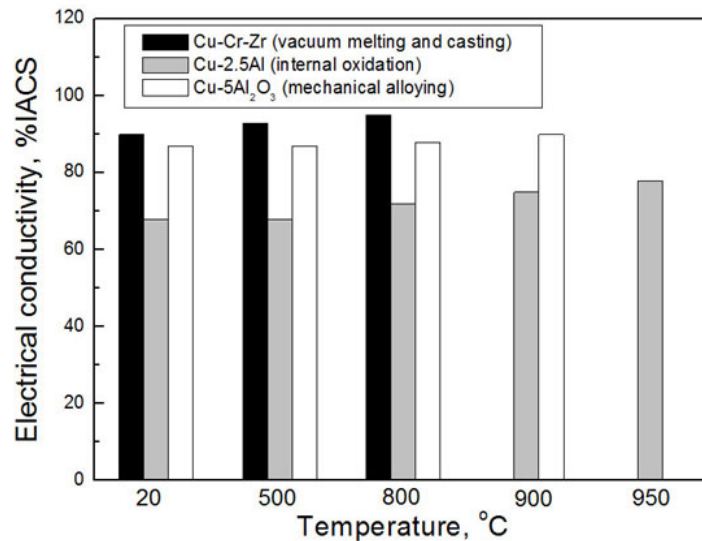The change of electrical conductivity with temperature of different materials is given in Figure 10.

Figure 10 Dependence of electrical conductivity on temperature.

Compared to composite materials the values from Figure 10 explicitly indicate that Cu-0.4Cr-0.08Zr alloy possesses the highest electrical conductivity in the range from 20 to 800oC, whereas the lowest conductivity shows composite Cu-2.5Al processed by internal oxidation.

Conclusions

In conclusion values of microhardness and electrical conductivity at T_s temperature are shown in Table 4.

Table 4 Values of microhardness and electrical conductivity at T_s temperature of investigated materials.

Material	Properties		
	T_s, ^{o}C	Microhardness, HV_{50g}	El. conductivity, %IACS
Cu-2.5Al	925	200	77
Cu-5Al$_2$O$_3$	680	135	88
Cu-0.4Cr-0.08Zr	525	108	93

Although with somewhat lower electrical conductivity (probably due to inadequate density), Cu-2.5Al composite processed by internal oxidation exhibits superior properties enabling its application at much higher temperatures than materials processed by mechanical alloying or by vacuum melting and casting.

Acknowledgement

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