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Cu-Fe_3C(Cr_3C_2) Bulk Nanocomposites Prepared by Mechanosynthesis Followed by Magnetic Pulse Compaction

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The Cu–Fe_3 and Cu–Cr_3C_2 bulk nanocomposites are prepared by consolidation of the mechanically alloyed powders. The structure and properties (density, Vickers microhardness and electrical conductivity) of them have been studied. It is shown that microhardness is equal to 236 HV and 470 HV for a Cu–5 vol.% carbide phase and for a Cu–30 vol.% carbide phase, respectively. The microhardness which can be influenced by the heat treatment temperature depends on the grain size of the Cu matrix. The electrical conductivity values of 38–44% IACS (International Annealing Copper Standard) at room temperature have been found.

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1. Introduction

Copper and copper alloys have been extensively used in a wide range of applications requiring high electrical and thermal conductivities and good mechanical properties for electric switches, contactor brushes, electrodes for welding and electrospark machining. Nanocrystalline copper has excellent electrical and thermal conductivity as well as high strength and hardness [1–5]. However, a serious drawback of nanocrystalline copper is the thermal instability of the grain size and of the microstructure of grain boundaries [6]. The microhardness of nanocrystalline copper decreases after annealing temperatures above 500 °C. The properties can be improved by incorporating of transition metals carbides. The most effective way to produce a bulk copper–carbide nanocomposite is mechanical alloying (MA) of a mixture of powders of copper, transition metal and graphite followed by compaction. The hardness of Cu–2 vol.% Cr_3C_2 composite produced by the consolidation of the mechanically alloyed powder is 5 times higher than that of a nanocrystalline copper produced by equal channel angular pressing [7]. For this composite, the electrical conductivity value is equal to 50% IACS. Such a material could be successfully used for outlets of household appliances, contact tips of submerged welding, electrodes of electrical spot welding et al. It should be noted that mechanical properties and electrical conductivity of nanocomposites consisting of the copper–chromium carbide with the other content or the copper–iron carbide are still not available.

Earlier studies [8–11] have shown that in the powder composites produced using graphite a large amount of carbide phase is formed during the milling process. A subsequent heat treatment at temperature above 400 °C leads to the carbide grain growth and copper recrystallization. It results in the microhardness decrease. But in the powder composites produced using liquid organic medium (xylene) as a carbon source the milling process results only in saturated solid solution formation and the heat treatment does not lead to the noticeable carbide and copper grains growth. The milling of powders in liquid organic media results in bulk composites with a highly dispersive and homogeneous structure and increased hardness and density [12–14].

In the present study, the structure and properties (density, Vickers hardness and electrical conductivity) of the Cu–Fe_3 and Cu–Cr_3C_2 nanocomposites are studied. The samples have a nominal composition of 5 and 30 vol.% carbide phase and were prepared by mechanical alloying using graphite or xylene followed by magnetic pulse compaction.

2. Synthesis and characterization

The Cu–Fe_3C and Cu–Cr_3C_2 samples with a nominal carbide content of 5 and 30 vol.% were prepared by mechanical alloying. As starting materials, high-purity powders of Cu (99.72 wt%, mean particle size 18 μm), Cr (99.92 wt%, mean particle size 17 μm), Fe (98 wt%, particle size 3–20 μm) and graphite were used. The mechanical alloying was performed in a planetary ball mill (Fritsch Pulverizette-7) under argon atmosphere at different milling time. The Cu +30 vol.% Fe_3C, Cu +30 vol.% Cr_3C_2, Cu +5 vol.% Fe_3C, Cu +5 vol.% Cr_3C_2 were prepared at milling times of 24 and 48 h. The solid-phase milling of the elemental components was performed under low excessive pressure of a purified argon atmosphere. The samples were marked as Fe30G24, Fe30G48, Cr30G24, respectively. The solid-liquid-phase milling of metallic powders was performed in the vials filled with xylene. In this case the samples were marked as Fe30X96, Cr30X24, Fe5X48, and Cr5X48, respectively.

The procedure and parameters of mechanical alloying are detailed in our previous publications [10, 11]. The mechanically alloyed powder was consolidated by magnetic pulse compaction with a load of 1.5 GPa [15, 16]. The powder was previously degassed. This procedure was executed by means of evacuation and heating up to temperature of 500 °C for 240 min. The consolidated samples with a diameter of 15 mm and a thickness of 1 mm had a density of more than 94% related to the theoretical one. Some compacted samples were additionally heat treated at temperatures of 600 and 800 °C for 1 h under argon. X-ray diffraction patterns were measured in the Bragg–Brentano geometry utilizing a DRON-3M diffractometer using Cu K_α radiation. The qualitative and quantitative analyses of the X-ray data were carried out using the software of the Moscow Institute of Steel and Alloys [17]. The average grain size was determined by the Warren–Averbach method with the (311) line being approximated by a Voigt function [18]. Auger spectra and secondary-electron images were recorded using the JAMP-10S spectrometer by applying an acceleration voltage of 10 kV, a current of 10^{-7} A, and a 300 nm electron probe. The hardness of compacted samples was determined from the Vickers microhardness measurements using a load of 0.49 N and a loading time of 10 s. The electrical conductivity was measured using the induction method at room temperature [19].

3. Results and discussion

3.1. Structure

Previously, we had determined the milling time required for the carbide formation during the milling process or after subsequent heat treatment at 600 and 800 °C. For the Cu–Cr–graphite and Cu–Cr–xylene systems, this time was 24 h, for the Cu–Fe–graphite system — 48 h, and for the Cu–Fe–xylene system — 96 h. The X-ray patterns (Fig. 1) of the Fe30G48 (a), and Cr30G24 and Cr30X24 (b) samples which were recorded after consolidation show the carbides precipitation. The X-ray patterns of the Cr30G24 does not show peaks for carbide phase because of its small grain size [10]. The grain size of the chromium carbide increases after the heat treatment at 600 and 800 °C, so that the peaks for carbide phase appear (Fig. 1b).

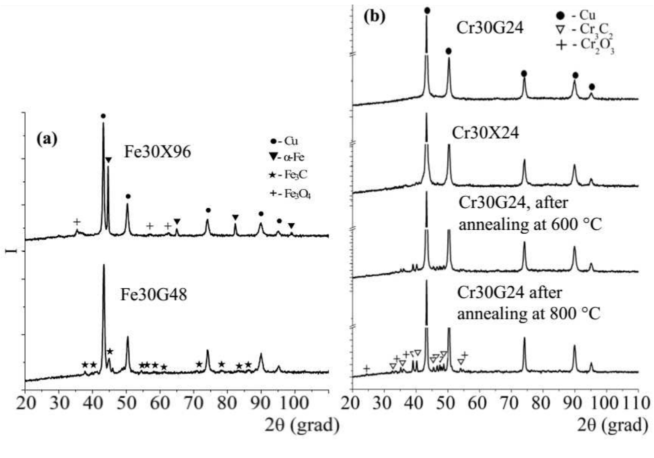

Fig. 1. X-ray diffraction patterns of (a) Fe-containing and (b) Cr-containing composites.

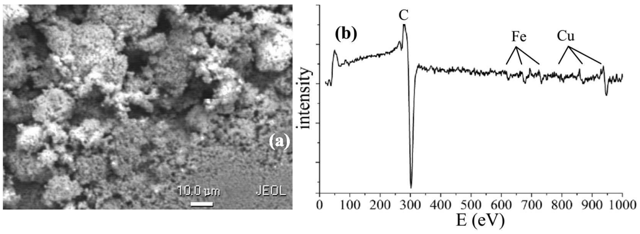

Fig. 2. (a) SEM image of the milled Cu–Fe–xylene powder and (b) corresponding Auger spectrum for $t_{\mathrm{MA}} = 96$ h.

The X-ray pattern of the Fe30X96 sample displays strong peaks for Cu and Fe phases. However, heat treatment at 600 and 800 °C of the Cu–Fe–xylene powder samples with $t_{\mathrm{MA}} = 96$ h allow us to obtain a cementite volume fraction of about 30% [11]. One might think that in the case of the Fe30X96 sample the carbide phase is not formed due to oxidation process. The powder is oxidized during heat treatment before and after magnetic pulse compaction. As it seen from Fig. 1, the X-ray patterns contain peaks for Cr_2O_3 or Fe_3O_4 phases. Using xylene for MA, the particle size rapidly decreases as the liquid facilitates the milling process. Small particle size of powder (≈ 1 μm), as seen from SEM image (Fig. 2a), milled for a long time (96 h), leads to oxidation of the particles surfaces at high temperature during heat treatment process. The particles surfaces of as-milled powder are enriched with carbon, as seen from the Auger spectrum (Fig. 2b). Carbon and hydrogen are the products of the catalytic decomposition of xylene [14]. Hydrogen is practically insoluble in copper and has a low solubility in iron. Hydrogen leaves the vessel as a gas. Carbon is predominantly oxidized during the heat treatment. The considerable oxidation of carbon and transitional metal (Fe, Cr) during the heat treatment process results in small amount of carbide phase. Obviously, chromium is a stronger carbide forming element than iron. In this case, the chromium quantitatively is less oxidized than iron because of higher barrier properties of its oxide film [20].

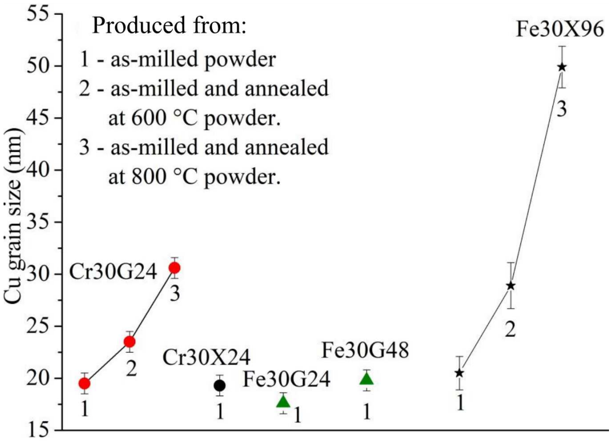

Fig. 3. Cu grain size of consolidated Fe-containing and Cr-containing composites.

All produced bulk composites have the Cu matrix which is characterized by a very fine nanocrystalline structure with a grain size of about 20 nm (determined with X-ray analysis) (Fig. 3). With increasing the annealing temperature the copper grain size rapidly grows (Fig. 3). All produced composites have a density of 92–97% of the theoretical value with exception of the Fe30X96 composite (Fig. 2c). Its density value is equal to 70%.

3.2. Vickers microhardness

The Vickers microhardness of consolidated samples is shown in Figs. 4 and 5. It can be seen from Figs. 4 and 5 that for the Fe-containing and Cr-containing composites consolidated at 500 °C the hardness value is equal to 300–470 HV for 30 vol.% of carbide and of 236 HV for 5 vol.% of carbide. The hardness considerably decreases with increasing the annealing temperature of the powders before consolidation, in spite of oxide phase formation. The microhardness value goes down with the carbide content decreasing and with the copper recrystallization. The microhardness of the Cr-containing composites is higher than that of the Fe-containing composites due to higher hardness values of chromium carbide and oxide. For the composites produced using xylene as a carbon source the hardness values are not so high. They reach 320–392 HV. But because of high copper plasticity, the milling of copper and transition metal powders in liquid organic media and subsequent heat treatment is the only way to produce the composites with a small amount of carbide phase.

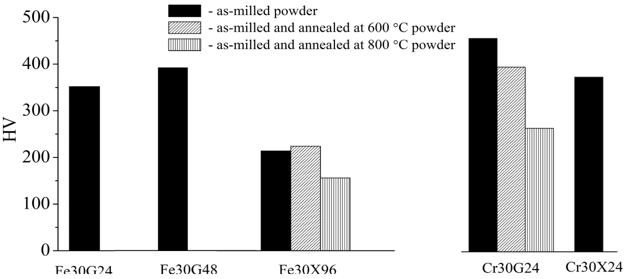

Fig. 4. Microhardness (HV) of Fe-containing and Cr-containing composites.

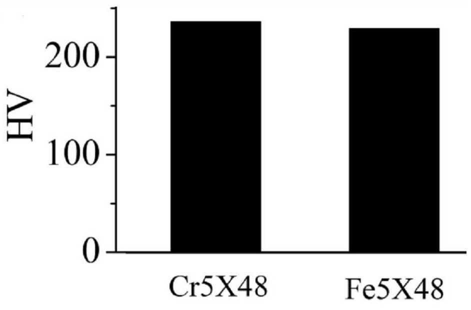

Fig. 5. Microhardness (HV) of powder and consolidated Fe5X48 and Cr5X48 composites.

3.3. Electrical conductivity

The measured electrical conductivity is shown in Fig. 6. The electrical conductivity of 38–44% IACS was found for composites. It is practically independent of production conditions. On the whole, it does not decrease greatly with increasing the carbide content in the range of 5–30 vol.%. The values of electrical conductivity and the hardness of composites produced are acceptable for commercial materials. The electrical conductivities of the composites are comparable with the properties of alloys produced by compocasting. For example, for the Cu–22 vol.% NbC, 31 vol.% TiC, 29 vol.% VC composites produced by compocasting the electrical conductivity values of 50%, 48%, 57% IACS, respectively, had been found. But the hardness of these composites does not exceed 160 HV [21].

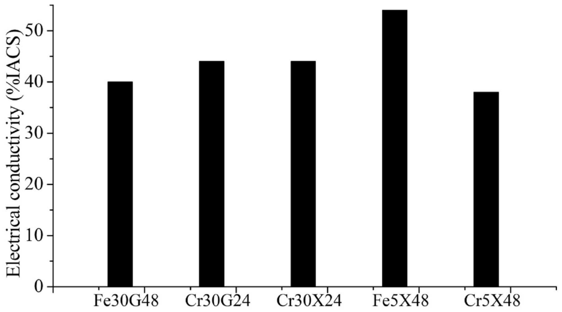

Fig. 6. Electrical conductivity (% IACS) Fe-containing and Cr-containing composites.

4. Conclusions

The results suggest that the mechanically alloyed Cu-Fe$_3$C and Cu-Cr$_3$C$_2$ powders containing 5 and 30 vol.% of carbide phase followed by consolidation using magnetic pulse compaction technique have a good potential as conductors with high hardness and conductivity. The measured relative densities of bulk composites are equal to 92–97%. The Vickers hardness reaches 470 HV for the Cu–30 vol.% Cr$_3$C$_2$ and 392 HV for the Cu–30 vol.% Fe$_3$C composites, and 236 HV for the composites containing the 5 vol.% carbide phase. The hardness of the composites decreases with increase of the annealing temperature. But the electrical conductivity is practically independent of the production conditions and of the carbide content in the range of 5–30 vol.%. The electrical conductivity of 38–44% IACS was found for these composites. The copper composites containing the 5 vol.% carbide phase can be only produced using liquid organic medium (xylene). For the Cu-Fe$_3$C and Cu-Cr$_3$C$_2$ composites, especially for the Cu-Fe$_3$C obtained using xylene careful removal of the oxygen impurity is required before consolidation.

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