Nanostructured Cu–Cr–W pseudoalloys by combined use of high-energy ball milling and spark plasma sintering

N F Shkodich¹, K V Kuskov², I D Kovalev¹ and Yu B Scheck¹

¹Merzhanov Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka, 142432 Russia
²National University of Science and Technology MISIS, Moscow, 119049 Russia

Abstract. Nanostructured pseudoalloys of immiscible Cu, Cr and W metals were prepared by combined use of high-energy ball milling (HEBM) and spark plasma sintering (SPS). Mechanical alloying in an Activator-2S planetary ball mill for 150 min provides a uniform distribution of refractory Cr and W particles in a moldable Cu matrix on a submicron and nanoscale level. Activated W–Cu–Cr powders were SPS-consolidated at 800–1000°C and 50 MPa for 10 min. The effect of preparation conditions on the microstructure, crystal structure, and properties (density, hardness, electric resistivity) of synthesized nanostructured W–Cu–Cr pseudoalloys was studied. The consolidated W–Cu–Cr composites showed a hardness of up to 9.5 GPa and an electric conductivity of 27–28% IACS, which makes them promising for use as an interrupter contact material.

1. Introduction

Over the past years, an increasingly growing attention has been given to tailoring the pseudoalloys of immiscible metals with strongly different melting points, which exhibit unique electric and thermophysical properties [1–3]. Combination of a refractory metal with a low-melting electro/thermo-conducting one opens up a way to designing novel materials for various applications in modern engineering. So copper-based pseudoalloys find their application in interrupter contacts, arc-resistant electrodes, heat-removing elements in microelectronic devices, etc. [4].

Among other metals, tungsten seems most attractive as a basis of items and materials for high temperature/pressure applications due to its exceedingly high refractoriness and mechanical strength. In addition, heavy-weight tungsten (19.3 g/cm³) exhibit a high absorption coefficient for γ-radiation, which makes this metal promising for use in protection against ionizing radiation. Despite the fact that the melting point of chromium (2180 K) is lower than that of tungsten (3695 K), Cr is rather promising for use in electrical engineering in view of its high-temperature strength, corrosion resistance, chemical inertness, and hardness.

Despite a wide range of existing materials suitable for use in various electrical contacts, the problem of highly reliable electrical contacts for use as current interrupters in electric power networks still remains far from its resolution [5–7]. As for Cu–Cr composite materials, these turned out to be especially suitable for vacuum current interrupters in the range of 12–30 kV and higher; within the range below 1 kV, Cu–W contactors are used [8, 9]. Due to incongruous properties of pure refractory components, W and Cr, contact materials suitable for use in the remaining gap between 1 and 12 kV are very difficult to fabricate and thus meet ever growing requirements to vacuum contacts. To ensure reliable contact, such materials must have specific structure, properties, and durability.

In order to further improve the performance of Cu–Cr alloys, it was suggested to add still another
metal X and thus obtain ternary Cu–Cr–X alloy [10–14]. The addition of 2.0 wt % W was found to improve the voltage resistance of contacts; adding 0.05–4.00 wt % Te improved the fusion-welding resistance of contact surfaces; adding 3.00–4.00 wt % Fe increased the solubility of Cr in Cu; and the addition of Ni improved the dielectric strength.

To ensure better mechanical strength of tailored alloys, the latter ones must be uniform and fine-grained. Such materials can in principle be prepared by high-energy ball milling (HEBM) and subsequent spark plasma sintering (SPS). In conventional powder metallurgy (sintering, hot pressing) this is hard to achieve since prolonged holding at high temperature leads to the loss of nanocrystallinity because of melting. In particular, this technique was recently used to fabricate nanostructured Cu–Cr pseudoalloy with a high Cr content [15].

In this communication, we report on fabrication of fine-grained Cu–Cr–W pseudoalloys by combined use of high-energy ball milling and spark plasma sintering.

2. Materials and Methods

Commercial powders of Cu (99.97% pure, particle size $d < 60 \mu m$), Cr (99.7%, $d = 10–30 \mu m$), and W (99.98%, $d < 6 \mu m$) were mixed in Cu/Cr/W ratios (by weight) of 55–40–5 (mix 1) and 20–10–70 (mix 2). The blends were processed in a water-cooled planetary ball mill Activator-2S using stainless-steel cylindrical vials and balls 7–9 mm in diameter. In all cases, the ball/mill ratio was 20 : 1. The drum was evacuated and then filled with Ar gas at 4 bar. The HEBM was carried out at a rotating speed of sun wheel/grinding chamber of 694 (900)/1388 rpm. Milling time ($\tau$) was varied between 5 and 150 min. The milled powders were then consolidated by spark plasma sintering (SPS) in vacuum (Labox 650, Sinter Land, Japan). The activated powder was placed into a cylindrical graphite die (inner diameter 15 mm) and uniaxially loaded at 50 MPa. Then the sample was heated at a rate of $500^\circ C/min$ up to some preset sintering temperature in the range 800–1000$^\circ C$ by passing rectangular pulses of electric current through the sample and the die. The dwell time at sintering temperature was 5–10 min. The consolidated samples had a shape of thin (2–3 mm) disks 15 mm in diameter.

Crystal structure, local composition of initial, milled powders and consolidated samples were characterized by XRD (DRON-3M diffractometer, Cu-$K_\alpha$ radiation, $2\theta =20–80^\circ$), SEM (Zeiss Ultra+, Carl Zeiss) and EDS (Oxford Inca spectrometer).

Microhardness $H_V$ of the composites was measured with a Vickers indenter. Electrical resistivity of the materials was measured by four-point probe method using a Cryotel apparatus (Cryotechnics & Electronics Ltd., Russia).

3. Results and Discussion

Figure 1 presents the XRD patterns of Cu–Cr–W mixtures taken before and after HEBM for different milling time $\tau$. Gradual broadening of diffraction peaks of activated powders is seen to be accompanied by a decrease in their intensity. This can be caused by a decrease in crystallite size, increase in defects density, and lattice strains. As for milled Cu–Cr–W powder mixture with a high tungsten content (70 wt %), an increase in milling time (to 30–120 min) leads to vanishing the (111), (200) and (220) peaks of Cu and the (110) and (220) peaks of Cr. Furthermore, during HEBM the W peaks shifted toward larger angles, thus indicating a change in the W lattice. Such a behavior of the XRD peaks coincides with the formation of nanoscale W–Cu–Cr structure. In a softer mode of mechanical treatment (694 rpm), the structural changes proceed slower than at 900 rpm of the sun wheel (figure 1b).

As for milled Cu–Cr–W (5 wt % W) powder mixture, an increase in HEBM time up to 30 min leads to a decrease in the intensity of W, Cu, Cr diffraction peaks, while the main peaks of Cu (111) and Cr (110) partially overlap. Starting from $\tau = 60$ min, a common diffraction peak appears at $2\theta = 41–42^\circ$, while the other reflexes become strongly broadened.

The activated powders were consolidated by SPS method at 800–1000$^\circ C$. 
Figure 1. XRD patterns of Cu–Cr–W mixtures taken before and after HEBM for different time $\tau$ (indicated): (a) mix 2 (70% W) and (b) mix 1 (5% W).

The SEM results for mix 1 in figure 2 suggest that the composite Cu–Cr–W derived from non-activated powder (figure 2a) is comprised of Cr particles (dark grey areas), rounded W particulates (white) embedded in a Cu matrix (grey). Copper particles are seen to be partially sintered while the chromium and tungsten ones exhibit no sintering with copper.

The composite derived from the mix 1 activated for 150 min (figures 2b, 2c) represents the Cu matrix uniformly doped with nanograins of tungsten (20–100 nm) and chromium (20–50 nm). It is worth noting that the Cu–Cr–W structures formed during HEBM are retained after SPS-consolidation.

Figure 2. SEM images of Cu–Cr–W composites derived from staring (a) and activated mix 1 ($\tau = 150$ min) SPS-consolidated at 800°C.
The Vickers hardness and relative density of W–Cu–Cr pseudoalloys derived from mix 1 and mix 2 are presented in table 1.

| Composition and milling conditions | H_V, GPa | \( \rho_{rel} \) |
|------------------------------------|----------|----------------|
| Mix 2 60 min, 694 rpm, 900°C       | 3.14±0.27| 0.75           |
| Mix 2 60 min, 694 rpm, 950°C       | 6.35±0.12| 0.91           |
| Mix 2 60 min, 900 rpm, 900°C       | 5.72±0.83| 0.7            |
| Mix 2 60 min, 900 rpm, 1000°C      | 9.5±0.72 | 0.82           |
| Mix 1 0 min, 694 rpm, 800°C        | 1.02±0.05| 0.62           |
| Mix 1 150 min, 694 rpm, 800°C      | 5.5±0.09 | 0.79           |
| Tungsten                           | 3.43*    |                |
| Copper                              | 0.369*   |                |
| Chromium                            | 1.06*    |                |

As follows from table 1, the Vickers microhardness \( (H_V) \) of produced Cu–Cr–W pseudoalloys exceeds that of Cu, Cr, and W by a factor of 30, 9 and 3, respectively.

HEBM leads to a fivefold increase in the microhardness of consolidated Cu–Cr–W pseudoalloys (mix 1) compared to the alloys derived from non-activated powders. The maximum value of \( H_V = 9.5±0.72 \) GPa was attained for consolidated composites derived from mix 2 at 900 rpm and 1000°C. Also it was demonstrated that energy-intensive mechanical treatment (900 rpm) is a more effective way to increasing the microhardness of Cu–Cr–W materials.

As is seen in table 1, relative density \( \rho_{rel} \) attains its maximum (0.91) in case of mix 2 sintered at 950°C. Further rise in sintering temperature up to 1000°C leads to a decrease in \( H_V \). This can be explained by a competition of two factors: material porosity and grain size. The initial increase in \( H_V \) can be explained by a decrease in overall sample porosity. But since at low porosities the Hall–Petch effect is prevailing, the hardness of polycrystalline material can be expected to decrease with an increase in the grain size. This can be associated with the process of grain growth at this temperature.

Electrical conductivity of our Cu–Cr–W composite is higher than 25% of International Annealed Copper Standard, which is tolerable for its use as an interrupter contact material.

Our results suggest that the combined use of high-energy ball milling (HEBM) and spark plasma sintering (SPS) can be readily recommended as a technological basis for fabrication of nanocrystalline Cu–Cr–W pseudoalloys.

Acknowledgments
This work was financially supported by the Russian Foundation for Basic Research (project no. 18-38-00843mol_a).

References
[1] Myshkin N K, Konchits V V and Braunovich M 1984 Elektricheskie kontakty (Electric Contacts) (Intellekt, Moscow) in Russian
[2] Slade P 1984 IEEE Trans. 7 25
[3] Binary Alloy Phase Diagrams ed Massalski T B, Okamoto H, Subramanian P R 1990 (ASM International Materials Park, Ohio)
[4] Avramov Yu S and Shlyapin A B 1999 New Composites of Immissible Components: Preparation, Structure, Properties (Moscow) in Russian
[5] Davis J R Copper and copper alloys Ohio: ASM International materials Park 2001
[6] Garay J F, Glade S C and Anselmi-Tamburini U 2004 Appl. Phys. Lett. 85 573
[7] Gordiev Yu I, Zeer G M and Zelenkova A K 2010 Izv Vyssh. Uchebn. Zaved. Poroshk. Metall. Funkts. Pokr. 4 47
[8] Mula S, Sahani P, Pratihar S K, Mal S and Koch C C 2011 Mater. Sci. Eng. A 528 4348
[9] Maneshian M N and Simchi F 2008 J. Alloys Comp. 463 153
[10] Zhang F B, Wang Z D and Chen Q 2012 Plasma Sci. Technol. 14 71
[11] Turchanin M A, Bondar A A, Dreval L A, Abdulov A R and Agraval P G 2014 Powder Metall. Met. Ceram. 53 70
[12] Xiu S H, Yang R, Xue J and Wang J X 2009 Trans. Nonferr. Metal. Soc. 19(S2) 444
[13] Espevik S, Rapp R A, Daniel P L and Hirth J P 1980 Oxid. Met. 14 85
[14] Wei X, Yu D M, Sun Z B, Yang Z M, Song X P and Ding B J 2014 Vacuum 109 162
[15] Shkodich N F, Rogachev A S and Vadchenko S G 2014 J. Alloys Comp. 617 39