Fabrication of Cu-W Nanocomposites by Integration of Self-Propagating High-Temperature Synthesis and Hot Explosive Consolidation Technologies

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Abstract

Manufacturing W-Cu composite nanopowders was performed via joint reduction of CuO and WO3 oxides with various ratios (W:Cu = 2:1, 1:1, 1:3, 1:13.5) using combined Mg–C reducer. Combustion synthesis was used to synthesize homogeneous composite powders of W-Cu and hot explosive consolidation (HEC) technique was utilized to fabricate dense compacts from ultrafine structured W-Cu powders. Compact samples obtained from nanometer sized SHS powders demonstrated weak relation between the susceptibility and the applied magnetic field in comparison with the W and Cu containing micrometer grain size of metals. The density, microstructural uniformity and mechanical properties of SHS&HEC prepared samples were also evaluated. Internal friction (Q−1) and Young modulus (E) of fabricated composites studied for all samples indicated that the temperature 1000 °C is optimal for full annealing of microscopic defects of structure and internal stresses. Improved characteristics for Young modulus and internal friction were obtained for the W:Cu = 1:13.5 composite. According to microhardness measurement results, W-Cu nanopowders obtained by SHS method and compacted by HEC technology were characterized by enhanced (up to 85%) microhardness.

Article info

Received: 15 March 2018
Received in revised form: 10 May 2018
Accepted: 23 June 2018

Keywords:
tungsten-copper nanocomposite SHS hot explosive consolidation microhardness mechanical properties

1. Introduction

The combination of two immiscible tungsten and copper phases in a W-Cu composite generates a pseudo-alloy which may cover the major needs of an advancing electronic technology and engineering. W-Cu belongs to a class of materials which the properties of one component enhance those of another due to synergistic complementing effect of mechanical and electrical properties of tungsten and copper [1–3]. Cu-W composites are widely used as heat sinks, electric resistance welding electrodes, heavy-duty electronic contacts, warhead materials, etc. [4–6]. High density and homogeneous microstructure push forward their physicochemical and thermoelectrical properties and are required to W-Cu materials with high performance. The fabrication of W-Cu materials that will outperform the properties of composites obtained via conventional methods is a peremptory challenge because of the great difference in melting points, lattice parameters and mutual insolubility between the two components. Various fabrication methods such as infiltration sintering, powder metallurgy, electroless plating, spark plasma infiltrating sintering were used to obtain W-Cu composites with improved characteristics [7–12]. Mechanical alloying (MA) and activated sintering in the presence of severe additives have been reported [13–16]. During MA strong grain
refinement leads to an increase of interfaces between phases, improves the strength of materials, however inevitably deteriorates the sintering process and electrical properties. To significantly enhance the performance of W-Cu composites the sinterability of the powders should be improved [9, 17–20]. The utilization of nanopowders may have an extremely important influence on the sinterability, moreover, will benefit the mechanical and thermal properties.

In our previous works, a novel strategy based on self-propagating high-temperature synthesis (SHS) or combustion synthesis (CS) method for the preparation of fine Mo-Cu and W-Cu composite powders was reported. It involves the joint reduction of CuO and WO$_3$ (MoO$_3$) oxides by using combined Mg+C reducer [21–24]. The use of such type reducer considers regulating the reaction temperature within a broad range and implementing the synthesis in controllable conditions.

Although various post-treatment procedures were suggested to increase the W-Cu green part’s density, they are still not executable to fabricate high density compacts. Recently, the superiority of consolidating materials with high density in a rather short time and lower temperature compared with traditional sintering techniques was demonstrated by hot explosive consolidation (HEC) method [25–28]. Explosive compaction of powders is a cost-effective fabrication process based on the propagation of shock waves produced by a detonating explosive. The waves transmit through a thin steel cylindrical container to powder consolidating the material due to induced high pressure. HEC is presumed applicable to fabricate high density shapes from ultrafine structured W-Cu composites.

In the present work, W-Cu nanocomposite powders of high homogeneity were synthesized (with various metals mole ratio, 2:1, 1:1, 1:3, 1:13.5) using SHS to facilitate the consolidation by HEC technology. The density, microstructural uniformity and mechanical properties of SHS&HEC prepared samples were evaluated.

2. Experimental

Copper (II) and tungsten (VI) oxides, carbon black and magnesium used as precursors in combustion experiments are displayed in Table 1. Cylindrical samples were prepared from the initial mixture of the reactants via uniaxial (P = 1 kN) pressing and placed in a CPR-3l reaction chamber. Reactor filled with nitrogen (purity 99.97%, oxygen content less than 0.02%) to the pressure up to 2.0 MPa.

Combustion reaction was initiated by a short-term annealing of tungsten coil. Temperature-time histories of the combustion process were recorded by thermocouple technique. The preparation of samples for the typical combustion experiment and registration of combustion parameters is thoroughly described in [24].

The combusted samples were grinded into a powder, subjected to acid leaching by 5–10% hydrochloric acid at 40 °C to eliminate MgO byproduct. X-ray diffraction (XRD) with monochromatic CuKα radiation (diffractometer DRON-3.0, Burevestnik, Russia) operated at 25 kV and 10 mA was used to determine phase composition of the initial reagents and final products. The identification from the XRD spectra was performed using the JCPDS database. The morphology, microstructure and composition of obtained powdered materials were studied by the help of BS-300 and LEICA440i scanning electron microscopes (SEM) equipped with Oxford EDS.

The SHS prepared Cu-W powder was poured into cylindrical steel tube container and pre-densification of powders by static pressure was performed with loading 1.5 t, before explosive consolidation. Then the compaction of powdered samples

| Reagent               | Source                 | Particle size, μm | Main impurities, %       |
|-----------------------|------------------------|-------------------|--------------------------|
| Tungsten oxide (WO$_3$) | High grade, Krasniy khimik, Ukraine | less than 40 | Al (0.001), As (0.001), Si (0.001), Ca (0.003), Co (0.002), Cr (0.001), Fe (0.001) |
| Copper oxide (CuO)    | High grade, STANCHEM, Poland | less than 40 | H$_2$O (0.04), Pb (0.0045), Fe (0.0053), Zn (0.055), chlorides (0.0084) |
| Magnesium powder (Mg) | MPF-3, Russia           | 150-300           | H$_2$O (0.01), Cl (0.005), Fe (0.05), |
| Carbon black          | P-803, Russia           | less than 1.0     | Ash (0.2), moisture (0.3) |
done by two stages: 1st - dynamic pre-densification of billets at room temperatures at different intensity of compression (5 GPa and 10 GPa) in the stainless steel tube container, with wall thickness 3 mm, 22 mm in diameter and length 122 mm (Fig. 1).

After explosive predensification at room temperature the hot explosive consolidation (HEC) was performed at certain temperatures in a range from 700 up to 1050 °C, up to melting point of copper at a high heating rate (about 10 to 20 K∙s⁻¹), reaching the required temperature within 0.3 to 1 min.

The cylindrical (axi-symmetric) scheme of dynamic loading was applied for the explosive compaction process. Industrial explosives and their mixtures with varying amounts of ammonium nitrate (Table 2) were used to initiate the shock waves.

The densities of consolidated samples were measured, carrying out measurements in water, after immersion of samples in paraffin.

Microhardness of samples was determined by Vickers indentation method using ПМТ-3 at loads 20 and 100 g. The hardness number (HV, kg∙mm⁻²) is determined by the load (F, kg) over the surface area of the indentation (mm²). For a number of samples the value of micro-hardness (H) was determined also by Khrushchev-Berkovich method using the formula \( H = \frac{1854 \times 100}{C^2} \), where \( C \) is the diagonal of impression of micrometer eyepiece at 100 g load [29].

Mechanical properties of fabricated samples were studied by measuring internal friction \( (Q^{-1}) \) and Young modulus \( (E) \) using the acoustic spectrometer (Andronikashvili Institute of Physics, Georgia). Measurements of resonance frequency \( v_r \) of the sample allow to build the curve of Young modulus change by the relation:

\[
\nu_r = \frac{k}{d} \sqrt{\frac{E}{\rho}} \frac{L}{d^2}
\]

where \( d \) is the sample thickness, \( L \) is the length of vibrating plate, \( \rho \) is the sample density and \( k \) is the constant factor. For this purpose rectangular plate with dimensions 1×3×22 mm cut from the cylindrical ingot. The cutting was made using electric spark mechanical tool. Firstly, a plate along the cylinder axis was cut out and then it was fixed in other clamp and then from the plate strips were cut with necessary dimensions.

The internal friction was calculated by the formula: \( Q^{-1} = 1/N \ln(A_1/A_2) \), where \( N \) is the number of sample oscillations at amplitude decreasing from the value \( A_1 \) to \( A_2 \). Differential amplitude discriminator was used for these tests counting the number of oscillations of sample in the range of amplitude change between two threshold values \( A_1 \) and \( A_2 \).

Inductance-capacitance (LC) oscillator was utilized to estimate the diamagnetic susceptibility of the samples under study. Measurements were performed for the samples inserted in to the LC inductor coil at the varying frequency. The real part of the magnetic susceptibility is proportional to the ratio of the square of the shift in frequency from resonance.

The morphology and microstructure of consolidated samples were examined using SEM (DSM-960, Opton, Germany), chemical composition and element distribution of composites were

| Explosive Material | Density 10³, kg∙m⁻³ | Detonation rate, V, m∙s⁻¹ | Pressure on St.3 P., 10⁹ N∙m⁻² |
|--------------------|---------------------|---------------------------|-------------------------------|
| Ammonite           | 1.0-1.2             | 3600-4800                 | 10                            |
| Ammonite + ammonium nitrate | 1.0      | 1700-2000                | 5                             |
| Hexogen            | 1.0                 | 6000-6050                 | 20                            |
controlled by the Auger Electron Spectroscopy (AES) method using instrument LAAS-200 (Riber, France). Various analytical techniques, including ICP mass spectrometer (ELAN 9000, Canada) and LECO-type element analyzer were applied do determine metallic and non-metallic impurities. To carry out metallographic examinations the hot explosive consolidated composite were removed from the steel jackets by mechanical treatment. Then these cylindrical samples were cut to small pieces and put in the mould with epoxy matrix, polished and prepared for further examinations.

3. Results and discussion

To optimize the reduction conditions according to ambient gas pressure and initial mixture composition, as well as to provide combined and accomplished reduction of CuO and WO$_3$ oxides the software package ISMAN-THERMO developed for multi-component systems was used [30]. Thermodynamic modeling was performed in the systems for the preparation of W-Cu alloys with different proportions of metals (W:Cu = 1:1, W:Cu = 2:1, W:Cu = 1:3 and W:Cu = 1:13.5).

According to the calculations’ results [30], as well as preliminary experimental and kinetic data, the complete reduction of copper and tungsten is possible within a certain range of reducer’s amounts and at high enough temperatures excluding the formation of WC and W$_2$C carbides [31–32].

Tungsten-copper bimetallic system (1) (Cu:W = 1:1) can be synthesized in behalf of variation the carbon amount in the range of 1.55 to 2.5 moles, while changing the amount of Mg between 1.3 and 2.2 moles [23]. The simultaneous reduction of copper and tungsten in the W-rich system (2) was achieved in the temperature range between 1000 to 2100 °C at certain amounts of carbon and magnesium (x = 2.7–4.2 moles & y = 2.7–4 moles, respectively). Furthermore, for the Cu-rich system (3), at the temperature interval 1050–1900 °C, the values for x parameter from 2.6 to 3.8 moles and for y from 1.8 to 2.8 moles were selected as optimum from the thermodynamic perspective to achieve combined and full reduction of metals [24]. Calculations for the copper-rich WO$_3$-13.5CuO-yMg-xC system have shown that within the considered intervals of y and x, multi-phase products of various compositions may be formed always in the presence of tungsten carbides as byproducts. Therefore the possibility of obtaining copper-rich Cu-W (with copper content exceeding 80 wt.%) composite powders was studied from the mixture WO$_3$-3Mg-zCu, i.e. by introduction of copper into the initial mixture in the form of metallic powder instead of copper oxide. Besides, in this case only magnesium was chosen as a reducer.

The optimized values of adiabatic combustion temperature and equilibrium composition of products were deduced depending on the ambient gas pressure. Thermodynamic consideration endorsed the utilization of ambient gas pressure ≥0.3 MPa to avoid vigorous gas release and evaporation of initial reagents and intermediates.

3.1. Combustion synthesis and characterization of W-Cu powders

The combustion experiments performed at pressure P = 0.3 MPa to avoid the formation of gaseous tungsten oxides, Mg and Cu. Based on thermodynamic calculations the combined magnesio-carbothermic reduction of CuO and WO$_3$ was investigated experimentally for the systems at fixed amount of Mg and varying the amount of carbon. Preliminary experiments supported by thermodynamic data assisted the reasonable choice of Mg amount to provide the reducing of the both metals at comparatively low temperatures. In the system (1) experiments were performed at Mg amount 1.3 mol [23]. In the system (2) with 2.7 mol amount of Mg. Combustion experiments performed in the tungsten-lean system (3) (3CuO-WO$_3$-yMg-xC) showed that 1 magnesium amount of 1.7 mol is admissible [24].

Series of combustion experiments aimed at exploring the qualitative and quantitative role of carbon on the combustion peculiarities and phase formation features of the products in all systems under study were performed. According to the overall representation of the results obtained, it was
shown that with the increasing carbon percentage decrease in combustion parameters was observed caused by increase in portion of low-exothermic interaction in the reactive mixture.

Combustion features, phase composition of the target materials and morphology characteristics depending on copper content \((z)\) were studied for the initial \(\text{WO}_3\)-3Mg-zCu mixture demonstrating smoothly decrease in combustion parameters when increasing the amount of copper in the initial mixture; and combustion limit was observed at copper content of 18 moles.

XRD analysis of the combustion solid products of the \(\text{WO}_3\)-CuO-1.3Mg-xC mixtures indicates that only at carbon content of 2.1–2.2 mol makes possible to obtain target products of combustion: W-Cu and MgO [23].

According to the XRD analysis results of system (2) at limiting amounts of carbon magnesium tungstate formed. The excess amount of carbon from 3.5 to 4 moles leads to complete reduction and formation of 2W-Cu composite powder. In the case of system (3), the simultaneous reduction of tungsten and copper was attained at a certain amounts of Mg and C reducers, \(y = 1.7\) moles and \(x = 4.7–4.8\) moles, respectively [24].

Consequently, in the system 4, combustion in the \(\text{WO}_3\)-3Mg-zCu mixture allowed to obtain desired product within the studied interval of \(z = 13.5–17.5\). W-13.5Cu composition was chosen as optimum on account of comparative homogeneity of the product.

Thus, in all systems magnesia was the only by-product which was leached by 5–10% HCl solution.

It was shown that the preparation of W-Cu alloys with 1:1, 2:1, 1:3, 1:13.5 molar ratios is possible at definite \(y/x\) ratio and \(z\) value at combustion temperature \(\sim 1150–1300\) °C which is near to the low temperature part of thermodynamically predicted area.

Microstructural examinations and XRD analysis certify the presence of fine snowflake-like particles of W-Cu composite powder up to 30–50 nm in size after the acid leaching of combustion products (1,2,3) (Fig. 2). The microstructure images of the combustion product of the \(\text{WO}_3\)-3Mg-13.5Cu mixture have indicated to their predominant homogeneity despite the fact that very small drops of molten copper were registered associated with the combustion temperatures exceeding melting point of copper.

![SEM micrographs and XRD patterns of W-Cu (a), 2W-Cu (b), W-3Cu (c) composite powders after acid treatment, \(P_{\text{N}_2} = 0.3\) MPa.](image-url)
After the determination of optimum parameters for the synthesis of W-Cu powders with molar ratio W:Cu = 1:1; W:Cu = 2:1; W:Cu = 1:3; W:Cu = 1:13.5 the experimental batches were manufactured according to selected optimum conditions for each batch. The synthesis was performed in the tubular reactor SHS-3L, constructed specially for such purposes. From each composition were synthesized about 500 g for further explosive compaction and physimechanical characterization.

Optimal parameters for synthesis of above mentioned experimental batches are as follows:

W:Cu with 1:1
Initial charge composition:
WO$_3$ + CuO + 1.3Mg + 2.7C; $T_c$ = 1300 °C

W:Cu with 2:1
Initial charge composition:
2WO$_3$ + CuO + 2.7Mg + 3.7C; $T_c$ = 1200 °C

W:Cu with 1:3
Initial charge composition:
WO$_3$ + 3CuO + 1.9Mg + 4.9C; $T_c$ = 1150 °C

W:Cu with 1:13.5
Initial charge composition:
WO$_3$ + 13.5Cu + 3Mg; $T_c$ = 1170 °C

After the combustion products cooled, exposed to grinding and leached by hydrochloric acid (HCl) for the separation of target material (W-Cu) from the byproduct (MgO). Optimal parameters for the acid leaching process were found out according to the dissolution temperature, acid concentration and treatment time. The leached target material is then dried in vacuum electric oven at 150 °C followed by XRD, SEM examinations and chemical analysis. For the evaluation of specific surface area of obtained powders adsorption analysis was performed (SSA for the composite (1) was ~1.4, (2) ~1.6, (3) ~3.5 and (4) ~0.7 m$^2$g$^{-1}$). According to XRD and ICPMS analysis results, after acid leaching magnesia was completely removed and the products contains only target metals with fine nanostructure.

3.2. HEC consolidation and characterization of compact samples

Optimal parameters for the consolidation of W-Cu composites (pressure, temperature, initial density) in cylindrical steel tubes with various dimensions was determined via predensification at room temperature applying (i) static pressure at different intensity of compression (1.5 t), and (ii) dynamic (explosive) densification at loading intensities 10 GPa at 950 and 1050 °C.

Microstructure examinations combined with spectral analysis indicated to homogeneous structure of the obtained W:Cu composites. These examinations have shown that the surface of the obtained samples is without any cracks, however some porosity and small amount of unknown phases were observed.

The results of the microhardness measurements indicate to close values (from 355 to 370 kg∙mm$^{-2}$) for samples with low contents of copper and the smallest value (120 kg∙mm$^{-2}$) for the alloy with maximum content of copper (82.5%) at T = 950 °C (Table 3).

HEC samples obtained from nanometer sized SHS powders exhibit strong diamagnetic susceptibility response. In comparison with the W or Cu containing micrometer sized grains they have a lower dependence of the susceptibility on the applied magnetic field.

Table 3
Results of microhardness measurements

| Sample composition       | Temperature of compaction, T, °C | Microhardness, vickers indentation load P = 20 g, HV kg∙mm$^{-2}$ |
|-------------------------|---------------------------------|---------------------------------------------------------------|
| W:Cu = 1:13.5 (82.5% Cu) | 1000                            | 122                                                          |
| W:Cu = 1:13.5 (82.5% Cu) | 930                             | 116                                                          |
| W:Cu = 1:13.5 (82.5% Cu) | 950                             | 120                                                          |
| W:Cu = 1:1 (25.7% Cu)    | 1050                            | 277                                                          |
| W:Cu = 1:1 (25.7% Cu)    | 950                             | 340                                                          |
| W:Cu = 1:1 (25.7% Cu)    | 950                             | 370                                                          |
| W:Cu = 1:1 (25.7% Cu)    | 950                             | 360                                                          |
| Cu:W = 1:2 (85% W)       | 950                             | 365                                                          |
Mechanical properties: internal friction \((Q^{-1})\) and Young modulus \((E)\) of fabricated composites were also studied for all samples. It was shown that within the temperature range 300–380 K on the internal friction \(Q^{-1}(T)\) curve two relaxation peaks at \(T = 340\) K and \(T = 370\) K were appeared, while the \(E(T)\) curve has a continuous concave shape in contrast to similar dependences for the most metals and alloys. For the same sample heated at 1000 °C similar critical dependences at 310 K and 370 K are characteristic not only for internal friction, but also for Young modulus. Besides, it is seen for all \(E(T)\) dependences that the relative change of Young modulus over total temperature range does not exceed 10%.

Comparing all three curves for Young modulus change it is evident (Fig. 3) that they exhibit identical behavior, but absolute values depending on annealing temperature are somewhat different: greater values are at the highest temperature (1000 °C), then at the minimal temperature (730 °C), and the smallest values are characteristic for the medium temperature (930 °C). Apparently, the Young modulus value depends not only on the annealing temperature, but also on sample history, i.e. synthesis conditions, presence of cracks and pores in the sample.

Comparative analysis of characteristics for samples prepared from \(W:Cu = 2:1\) and \(W:Cu = 1:3\) composites demonstrate that Young modulus for the first sample is several times larger as compared to that of the sample \(W:Cu = 1:3\). This is expected outcome allowing for the large fragility of the last one, because the density of this sample was measured to be considerably lower. This may be explained by the presence of much more voids and cracks in the sample \(W:Cu = 1:3\).

Similar behavior of Young modulus and internal friction was observed for these samples. With aim to clear out the nature of defect structure, involved in relaxation processes in the temperature range 300–380 K, temperature spectra of Young modulus and internal friction of the sample \(W:Cu = 1:13.5\), treated at 700 °C were recorded at deformations in 4 times above a standard. The relative deformation of sample in the experiments on acoustic spectrometer is defined via the deviation of its vibration frequencies and measured in kHz. A standard deviation in experiments was 2.5 kHz.

Improved characteristics for Young modulus and internal friction were obtained for the \(W:Cu = 1:13.5\) composite annealed at 1000 °C (Fig. 4). It is seen that above-mentioned peculiarities (critical temperature dependences) of Young modulus and internal friction completely disappeared. This indicates to the fact that structure defects, with the movement of which were related the above observed relaxation peaks, were completely treated. It was shown, that with rising the treatment temperature dependences of \(E(T)\) and \(Q^{-1}(T)\) become more smooth (without critical changes). The results indicated that for the \(W/Cu\) composites the temperature 1000 °C is optimal for full annealing of microscopic defects of structure and internal stresses.

The main characteristics of W-Cu pilot samples are as follows (Table 4). According to microhardness measurement results, W-Cu nanopowders obtained by SHS method and compacted by HEC technology show enhanced hardness up to 85%.
4. Conclusions

W-Cu composite nanomaterials were prepared from joint reduction of CuO and WO₃ oxides using coupling approach of combustion reactions. It was shown that the preparation of pilot batches of W-Cu alloys with 1:1, 2:1, 1:3, 1:13.5 molar ratios is possible from the WO₃-CuO-13.5Mg-xC and WO₃+13.5Cu+zMg mixtures at definite y/x ratio and z value. Moderate combustion temperature was in the range of 1150–1300 °C and near to the low temperature part of thermodynamically predicted area. Obtained ultrafine structured W-Cu powders were exposed to hot explosive consolidation (HEC) for the fabrication of dense compacts. The investigation of magnetic properties of compact samples displayed their ability of strong diamagnetic susceptibility. Internal friction (Q⁻¹) and Young modulus (E) measurements indicated that the optimal annealing temperature for all samples is ~1000 °C. According to microhardness and density measurement results W-Cu nanocomposites obtained by SHS method and compacted by HEC technology demonstrated enhanced microhardness (up to 85%) and in some cases density is near to theoretical value.

Acknowledgment

The authors gratefully acknowledge the financial support of the International Science and Technology Center (ISTC project # A-2123).

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Table 4
Main characteristics of various samples of different Cu content

| Composition, Cu:W | SHS & HEC prepared | Commercial [33] |
|-------------------|---------------------|----------------|
|                   | Sample density, g·cm⁻³ | Microhardness, V, kg·mm⁻² (P = 20 g) | Sample theoretical density, g·cm⁻³ | Microhardness, V, kg·mm⁻² (P = 20 g) |
| 1:13.5 (82.5%Cu)  | 10.31               | 120            | 10.28               | - |
| 3:1 (51.1%Cu)     | 11.22               | 160            | 11.85               | 115  |
| 1:1 (25.6%Cu)     | 11.34               | 360            | 14.50               | 195  |
| 1:2 (14.7%Cu)     | 12.70               | 365            | 15.90               | 240  |
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