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Mg-CARBOTHERMAL REDUCTION OF SILVER TUNGSTATE IN COMBUSTION MODE AND SYNTHESIS OF W-Ag PSEUDOALLOY

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W-Ag pseudoalloy was synthesized via reduction of silver tungstate precursor with Mg+C combined reducer in the combustion mode by applying reactions thermo-kinetic coupling approach. It has been revealed that growth of the C/Mg ratio leads to decrease of both the combustion temperature and its velocity conditioned by the growth in the portion of low-caloric reaction of carbothermic reduction. The latter allows to control thermal regime of the reaction for the preparation of fine-grained W-Ag pseudoalloy. Optimum conditions for preparation of W-Ag composite powder were determined.

Figs. 7, table 1, references 20.

Introduction

In recent years, tungsten (W)-based heavy alloys have received increased use in both commercial and industrial areas. Most heavy alloys consist of W particles embedded in matrix of other metals or their alloys such as iron, nickel, silver or copper [1]. In particular, W-Ag alloys can be used as heat dissipation materials in the microelectronic devices that are prone to failure at high operating temperatures, for example, as diverter plates in fusion reactors. They combine the arc erosion and welding resistance of tungsten with the excellent thermal and electrical conductivities of silver. The thermal expansion coefficient of composites can be adjusted by changing their composition to match those of ceramic materials used as substrates in semiconductor devices [2-4]. Powder metallurgy is the technique utilized to manufacture W-Ag alloys, but due to the mutual insolubility of W and Ag and poor wettability of liquid Ag on W, sintering cannot easily produce dense and homogeneous structures [5-6].

Experimental studies relating to the mechanical properties of samples formed from nanocrystalline precursor powders show that these ultra-fine grained materials are fundamentally different from their normal, coarse-grained counterparts [2].

As there is no alloying between the silver and tungsten the properties of the composites depend on direct proportion of their composition, the size, morphology, and distribution of phases within the composite with finer particles giving improved performance [7].

In this work a new pathway for the preparation of W-Ag composite nanopowder/pseudoalloy by energy-saving combustion synthesis (CS) method [8-10] is reported. Silver tungstate is suggested to be used as an initial precursor. In our previous work [11], Ag+WO₃ mixture prepared by solution combustion synthesis method for obtaining W-Ag pseudoalloy was used. But in this case both the metals are in the same crystalline structure (Ag₂WO₄), thus the formation of more homogeneous composite is expected.

For reduction of silver tungstate a combined Mg+C reducer was used, which allows to control the reaction temperature in a wide range at the synthesis of W-Ag material. This approach is known as reactions thermo-kinetic coupling [12,13] and its essence consists in the coupling of a low exothermic reduction reaction with a high caloric one with a possible change of the reaction pathway [17-20].

It is worthy to note, that silver tungstate can exhibit three different structural phases; α -, β -, or γ -Ag₂WO₄. Among these polymorphs α -Ag₂WO₄ is the most thermodynamically stable, belonging to orthorhombic symmetry. In its molecule all W atoms are six-coordinated and form WO₆ octahedra. These WO₆, W₂O₆, and W₃O₆ octahedra are connected by sharing edges and grouped altogether at a particular position (Fig. 1). Nevertheless, the number of different sites occupied by the Ag atoms in Ag₂WO₄ is six [14-15].

Experimental part

The following raw materials were used in experiments: sodium tungstate (Na₂WO₄·2H₂O, chemically pure grade), silver nitrate (AgNO₃, 7761-88-8, Czechia), magnesium (MPF-3, Russia, pure grade, particle size 0.15 *mm* < μ < 0.3 *mm*), carbon (P-803, Russia, μ < 0.1 μ m).

Chemical precipitation synthesis route was employed for the preparation of α -Ag₂WO₄ nanoparticles. This method possesses good stoichiometric control and production of ultrafine particles with high purity and improved compositional homogeneity in a relatively short processing time at lower temperatures. Nanocrystalline silver tungstate samples were prepared by reacting aqueous solutions of silver nitrate and sodium tungstate. These solutions were mixed slowly in 2:1 molar ratio with contineous stirring at room temperature for 20 *min*, keeping the pH value at constant magnitude 7. The



Fig. 1. Ball and stick model of the crystal structure of the α -Ag₂WO₄.





precipitate formed was centrifuged, filtered and washed by ethanol, then several times by distilled water. The product was dried at 70° C for 4 *h*. The final product was light yellow in color.

After drying, the product was homogenized in a ceramic mortar with Mg/C mixture for 10 *minutes* and cylindrical samples with 1-1.5 $g \cdot cm^{-3}$ density, 20-25 *mm* height and 20 *mm* in diameter were prepared. The prepared samples were placed in a reaction chamber CPR-3L (Fig. 2) which was sealed, evacuated, purged with nitrogen (purity 99.97 %, oxygen content less than 0.02%) and filled to the desired pressure (0.5 *MPa*).

The combustion process was initiated with short heating of a tungsten spiral (18 *V*, 2 *s*) from the upper surface of the sample. The combustion temperature (T_c) and combustion velocity (U_c) were measured using two C-type tungstenrhenium thermocouples (W-5Re/W-20Re), each 100 μm in diameter. The thermocouples were inserted into the sample at a depth of 10 *mm* with a distance 10 *mm* between each other. The standard measurement errors for T_c and U_c were \pm 20°C and 5% respectively. The output signals of thermocouples were transformed by a multichannel acquisition system and recorded by a computer with a frequency up to 2 *KHz*. The average of maxima for two temperature profiles was calculated as the combustion temperature (T_c). The average value of the combustion velocity was calculated by the formula: U_c = L·(Δt)⁻¹, where L is the distance between the thermocouples, Δt is the time distance between the signals of thermocouples.

Phase composition of the samples was analyzed by X-ray diffraction (XRD; D5005, Bruker, USA) using CuK α 1 radiation ($\lambda = 1.5406$ Å) with a step of 0.02° (2 θ) and a count time of 0.4 *s*. To identify the products from the XRD spectra, the data were processed using the JCPDS database.

Results and discussion

Characterization of nanostructured precursor

It is well known that the selection of the starting materials can highly contribute to enhancing the structure and properties of the final products. Based on that, fine precursor representing silver tungstate, was prepared by chemical precipitation method using silver nitrate and sodium tungstate as raw materials.

$$2\operatorname{Ag}(\operatorname{NO}_3) + \operatorname{Na}_2\operatorname{WO}_4 \cdot 2\operatorname{H}_2\operatorname{O} = \operatorname{Ag}_2\operatorname{WO}_4 \downarrow + 2\operatorname{Na}\operatorname{NO}_3 + 2\operatorname{H}_2\operatorname{O}$$

The composition of the product, ascertained by the XRD analysis, has shown that it is single phase α -Ag₂WO₄ (Fig. 3).



Fig. 3. XRD pattern of the product obtained by chemical precipitation method.



Fig. 4. SEM images of the product obtained by chemical precipitation method.

Microstructural examinations testify that the final product obtained by chemical precipitation represents fine-grained rod-like particles with average size 10-20 nm (Fig. 4).

Thermodynamic analysis results

Prior to the experimental investigations thermodynamical analysis has been performed in a wide range of reducers' amounts in order to reveal the possibility of silver and tungsten reduction from Ag_2WO_4 under the combustion mode, as well as to find the optimal conditions for formation of Ag-W alloy by using "ISMAN-THERMO" software package [16]. The latter enables to calculate adiabatic combustion temperature (T_{ad}) and equilibrium composition of combustion products. The main calculations were carried out for the pressure 0.5 *MPa*. As a result, corresponding phase diagram was constructed depending on magnesium and carbon amounts (Fig. 5). As can be seen, there are different areas of products formation depending on the amount of magnesium and carbon. Formation of the target product is achieveable in a definite area of magnesium (from 1.55 to 2.1 *moles*) and carbon (from 1.5 to 1.9 *moles*) amounts (marked on

Fig. 5). Within this area the calculated values of the adiabatic temperature changed from 1500 to 1900°C.



Fig. 5. Thermodynamic analysis results for the Ag₂WO₄-yMg-xC system, P = 0.5 MPa.

According to the thermodynamic calculations, within the whole interval of reducers' amount the main gaseous products are CO and CO_2 . At that, the ratio of carbon oxides (CO/CO₂) depends on the temperature and with its increasing this ratio increases too.

For preparing tungsten-silver composite powders with homogenous microstructure characteristics and enhanced properties the SHS co-reduction of the prepared salt was performed. For selecting optimal composition of the Ag₂WO₄-yMg-xC initial charge and to reveal the influence of reducers' amount on the combustion parameters to yield the target W-Ag alloy a series of experiments was carried out at a constant magnesium content (1.6 *moles*) and a varying carbon amount within certain intervals, at nitrogen pressure of 0.5 *MPa* (Fig. 6). The mentioned amount of magnesium was selected on the basis of thermodynamically calculated optimal area.



Fig. 6. Combustion temperature and velocity vs carbon amount for the Ag₂WO₄-yMg-xC system, P = 0.5 *Mpa*.

According to the results obtained, with the increase of carbon amount in a green mixture, both combustion parameters (T_c , U_c) decrease, thus creating moderate thermal conditions for implementing the reduction reaction, which is very important for preparing nanomaterials. This phenomenon is conditoned by the growth in the portion of low-caloric carbothermal reactions in the system. As may be seen from Figure 6, increase of carbon amount (from 0 up to 6 *moles*) causes a drop in the combustion velocity by 25 times (from 3.50 to 0.14 *cm/s*), and combustion temperature - about 2 times (from 2100 to 1000°C). According to the results, at x = 6.25 *mole* combustion limit is observed.

Table

Carbon amount	Phase composition
x = (0-2) mole	Ag, W, MgO, MgWO ₄
x = (2-3) mole	Ag, W, MgO
x = (4-6) mole	Ag, W, MgO, W ₂ C

Phase composition of combustion products for the Ag₂WO₄+1.6Mg+xC mixtures

To determine phase composition of the combustion products, XRD analysis was performed indicating that the reduction degree increases with the increase of carbon amount. According to the results obtained, magnesium tungstate was formed at small amounts of carbon (x < 2). The amount of magnesium tungstate decreases in parallel with the increase of carbon amount and fully disappears in the combustion products beginning at x = 2 moles. At higher amounts of carbon (x > 3), along with the metals formation of tungsten carbide was observed (Table).



Fig. 7. XRD pattern of the combustion product for the Ag_2WO_4 +1.6Mg+2.5C mixture after acid traetment.

For removing magnesia byproduct from the target metals, the reaction products after cooling, were crushed into a powder, subjected to acid treatment by hydrochloric acid ($\omega = 10\%$) at room temperature, washed with deionized water and dried in vacuum oven (at 90°C for 2 *hours*).

According to XRD analysis results, after acid leaching the product contained only target metals (Fig. 7).

Thus, it was established that the reduction of silver tungstate under combustion mode using a Mg+C combined reducer (in the ratio of 1.6:2.5 *moles*) enabled at moderate thermal conditions to obtain the target W-Ag composite powders with necessary purity.

ԱՐԾԱԹԻ ՎՈԼՖՐԱՄԱՏԻ ՄԱԳՆԵԶԻՈԻՄԱ-ԿԱՐՔՈԹԵՐՄ ՎԵՐԱԿԱՆԳՆՈԻՄՆ ԱՅՐՄԱՆ ՌԵԺԻՄՈԻՄ ԵՎ W-Ag ԿԵՂԾ ՀԱՄԱՉՈԻԼՎԱԾՔԻ ՍԻՆԹԵԶԸ

Մ. Կ. ԶԱՔԱՐՅԱՆ

Ուսումնասիրվել է այրման ռեժիմում W-Ag կեղծ Համաձուլվածքի ստացման Հնարավորությունն արծաթի վոլֆրամատից, Mg+C Համակցված վերականդնիչով, կիրառելով ռեակցիաների ջերմակինետիկական զուգորդման մոտեցումը։ Ցույց է տրվել, որ C/Mg Հարաբերության մեծացմանը զուգընթաց նվազում է ինչպես այրման ջերմաստիճանը, այնպես էլ այրման ալիքի տարածման արադությունը` պայմանավորված ցածրկալորիական կարբոթերմ վերականդնման ռեակցիայի մասնաբաժնի ավելացմամբ։ Վերջինս թույլ է տալիս կառավարել այրման պրոցեսի ջերմային ռեժիմը, ինչը կարևոր է նանոչափսի փոչիների ստացման Համար։ Գտնվել են օպտիմալ պայմաններ W-Ag կոմպոզիտային փոչու ստացման Համար։

МАГНИЙ-КАРБОТЕРМИЧЕСКОЕ ВОССТАНОВЛЕНИЕ ВОЛЬФРАМАТА СЕРЕБРА В РЕЖИМЕ ГОРЕНИЯ И СИНТЕЗ ПСЕВДОСПЛАВА W-Ag

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В работе исследована возможность получения псевдосплава W-Ag путем восстановления вольфрамата серебра в режиме горения комбинированным восстановителем Mg+C с применением метода термо-кинетического сопряжения реакций. Выявлено, что с ростом отношения C/Mg имеет место уменьшение как температуры, так и скорости горения, обусловленное ростом доли низкокалорийной реакции карботермического восстановления. Последнее позволяет контролировать тепловой режим протекания реакции, что важно для получения наноразмерных материалов. Найдены оптимальные условия получения композитного порошка W-Ag.

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