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MAGNESIO-CARBOTHERMIC REDUCTION OF Ag_2WO_4. DTA/TG STUDY

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In the paper the mechanism of reduction of silver tungstate with combined (Mg+C) reducer under the conditions of linear heating with the rates of 5-30°C *min*$^{-1}$ was studied. It was shown that for both the cases of using separate reducing agents and a combined reducer, the interaction begins before reaching the melting point of magnesium, and increase in the heating rate shifts the value of T_{max} towards the high-temperature region. It was revealed that the magnesio-carbothermic reduction of silver tungstate is started by carbon at 410°C, followed by simultaneous action of magnesium and carbon at 640°C (V_h=10°C *min*$^{-1}$); wherein the reaction starts with the solid+solid and continues with the solid+liquid mechanism. The effective values of activation energy (E_a) for the magnesiothermic reduction stages for the binary (Ag_2WO_4-Mg) and ternary (Ag_2WO_4-Mg-C) systems were determined.

Figs. 8, table 1, references 27.

1. Introduction

W-Ag composite materials are widely using for manufacturing of super-powerful electrical contacts since they offer the advantages of both refractory tungsten (welding and erosion resistance) and silver (high thermal and electrical conductivities) [1-3]. Low coefficient of thermal expansion makes it possible to obtain such substructures that can later be used in semiconductor devices. These alloys could also be used in microwave ovens, micro-electrical devices as heat dissipating materials and in electrical contacts of powerful switches [4-8].

It should be mentioned that the properties of W-Ag pseudo-alloys depend not only on the composition, but also on the method of production. This means that the size, shape, heat-resistant phase distribution, homogeneity of particle and degree of porosity have a huge impact on the mechanical, electrical and thermophysical features of the composite [9-11].

For the preparation of W-Ag pseudo-alloys several methods are used: powder metallurgy [12], reduction of silver tungstate by hydrogen [13], explosive pressing [14], reduction of silver tungstate (prepared by chemical precipitation) and Ag+WO_3 mixture (prepared by solution combustion method) by Mg+C combined reducer in combustion mode [15-16].

In the work [15] α-silver tungstate, Ag_2WO_4, is suggested to use as an initial precursor due to the fact, that both the metals are in the same crystalline structure, thus the formation of more homogeneous composite is expected. For reduction of silver tungstate, a combined reducer (Mg+C) was used that allows to control the reaction temperature in a wide range. This approach is known as reactions' thermo-kinetic coupling [17] when a low exothermic or endothermic reaction is coupled with a high caloric one with possible change of reaction pathway [18-20].

Because of the high rates of processes ongoing in the combustion wave it is often difficult to control them and to reveal the reaction mechanism. One of the approaches for clarifying the interaction mechanism in the combustion wave is thermal analysis method or process modeling in temperature-programmed heating conditions. In the Ag_2WO_4-Mg-C ternary system at low heating rates (V_h=2.5-30^{o}C min^{-1}) the experiments were carried out by DTA/TG method. This gives an opportunity to reveal the sequential character of interaction mechanism of the process, to explore intermediate states and calculate kinetic parameters for each stage.

Note that according to the available literature data, the reduction mechanism of Ag_2WO_4 by magnesium, carbon and the combined Mg+C reducer was not studied yet. In our previous studies in the NiO-Mg-C [21-22], NiO-WO_3-Mg-C [23], WO_3-Mg-C [24], $CuMoO_4$-Mg-C [25] systems at low and high heating rates the use of Mg+C reducing mixture was found attractive, especially due to the crucial influence of carbon addition on a reaction pathway. This study is motivated by the need to reveal the interaction mechanism and kinetic features of the Ag_2WO_4-Mg and Ag_2WO_4-C binary and Ag_2WO_4-Mg-C ternary systems at non-isothermal conditions using the DTA/TG technique. The data obtained will serve as a basis for optimizing the synthesis conditions of the Ag-W composite powder in the combustion mode.

2. Materials and methods

Sodium tungstate ($Na_2WO_4\cdot 2H_2O$, chemically pure grade), silver nitrate ($AgNO_3$, 7761-88-8, Czechia), magnesium powder (MPF-3, Russia, pure grade, particle size $0.15<\mu<0.3$ *mm*), carbon (P-803, Russia, $\mu<0.1$ *μm*) were used in experiments as raw materials.

Chemical precipitation route was utilized for the preparation of Ag_2WO_4 nanopowders by reacting aqueous solutions of silver nitrate and sodium tungstate:

$$2Ag(NO_3)+Na_2WO_4\cdot 2H_2O=Ag_2WO_4\downarrow+2NaNO_3+2H_2O$$

These solutions were mixed slowly in 2:1 molar ratio with contineous stirring at room temperature for 20 *min*, keeping the pH value at the constant magnitude 7. The precipitate formed was centrifuged, filtered and washed by ethanol and distilled water several times. Then it was dried at 70°C for 4 *hrs*. A light yellow final product was obtained. The formation of single phase α-Ag_2WO_4 was confirmed by XRD examination. Microstructural examinations testify that the final product obtained by chemical precipitation represents fine-grained rod-like particles with average size of 10-20 *nm* [16].

The reactive powder mixture in amounts of 50-100 *mgs* was used in the differential thermal analysis (DTA) and thermogravimetric (TG) experiments on the Q-1500 instrument (Derivatograph Q1500 MOM, Hungary). As a reference material Al_2O_3 powder was used. All measurements were conducted in N_2 flow (120 $ml\cdot min^{-1}$). Heating rate was programmed to be 2.5, 5, 10, 15, 20, 30°C$\cdot min^{-1}$.

Intermediate and final products were examined by the X-ray diffraction (XRD) method with monochromatic CuKα radiation (diffractometer DRON-3.0, Burevestnik, Russia) operated at 25 *kV* and 10 *mA*. To identify the products from the XRD spectra, the data were processed using the JCPDS database.

The isoconversion method suggested by Kissinger [26] was used to calculate the effective activation energy values for the systems under study. This method is based on the shift of temperature corresponding to the maximum advance in the DTA curves depending on the heating rate kept constant. The derived expression for determination of activation energy by Kissinger has the following form:

$$\ln\left(\frac{V_h}{\left(T_{\max}^{DTA}\right)^2}\right)=\ln A-\frac{E}{R}\left(\frac{1}{T_{\max}^{DTA}}\right) \qquad (1)$$

where A is a constant, E is the effective activation energy of the process, ($kJ\cdot mol^{-1}$), V_h is the heating rate ($K\cdot min^{-1}$), T_{max} is the reduction temperature

(K) corresponding to the maximum advance in the DTA/DTG curve, R is the universal gas constant.

3. Results and discussion

To clarify the interaction mechanism in Ag_2WO_4-Mg-C ternary system, first, the stability of silver tungstate synthesized by the chemical precipitation method up to T_{max}=1000°C was investigated. Then the behavior of Ag_2WO_4-Mg and Ag_2WO_4-C binary systems in identical heating conditions was studied.

Ag_2WO_4 was heated at a rate of 20°C min^{-1} under conditions of continuous N_2 flow. According to the results (Fig. 1), there is an endothermic area on the DTA curve (T_{min}=630°C) within temperature interval 620-650°C, which corresponds to the melting point of Ag_2WO_4 [27]. It should be mentioned, that in the investigated temperature interval the sample's weight (TG curve) remains constant.

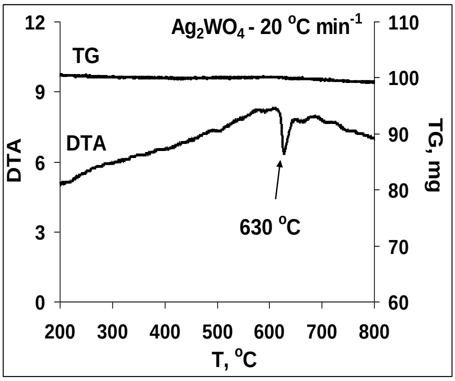

Fig. 1. DTA/TG curves of Ag_2WO_4, V_h=20°C min^{-1}.

3.1. Ag_2WO_4-Mg binary system

Figure 2 depicts DTA/TG curves of Ag_2WO_4+4Mg binary mixture under heating conditions at the rate of 20°C min^{-1}. As seen, there is no mass change, because all the reactants and products are in condensed phase. An exothermic interaction registered on the DTA curve in the wide temperature interval 560-800°C (T_{max}=674°C), which corresponds to the magnesiothermic reduction of the silver tungstate (Fig. 2). Endothermic effect at the beginning of exothermic interaction corresponds to the melting of Ag_2WO_4. It follows from the provided data that the magnesiothermic reduction starts with a solid+solid mechanism and continues with a solid+liquid one. It should be mentioned that the reduction reaction comes to end with a liquid+liquid mechanism, because exothermic reduction range includes also the melting point of the reducer, Mg (650°C).

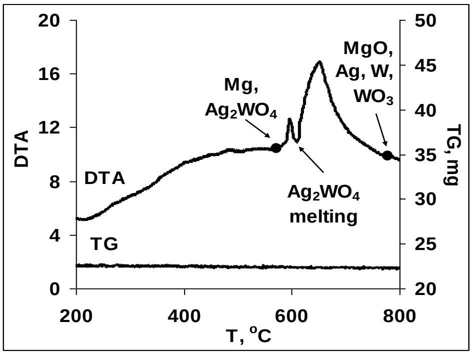

Fig. 2. DTA/TG curves of the Ag_2WO_4+4Mg mixture,V_h=20 °C *min*$^{-1}$.

As seen in the Fig. 3, with increasing of the heating rate, magnesiothermic reduction of silver tungstate shifts to higher temperature area (see also Table).

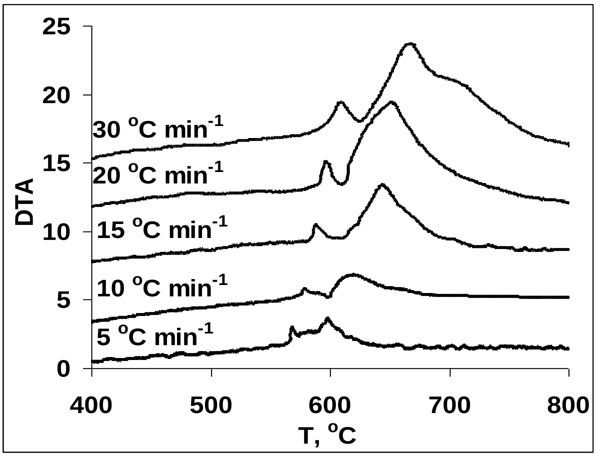

Fig. 3. DTA curves of the Ag_2WO_4+4Mg mixture at various heating rates, V_h=5, 10, 15, 20, 30°C *min*$^{-1}$.

Therefore, in cases of all investigated heating rates (5, 10, 15, 20, 30°C *min*$^{-1}$) the interation starts with a solid+solid and continues with a liquid+liquid mechanism (melting of Ag_2WO_4 is expressed on the reduction exothermic peaks for all the samples). Except the heating rate value of 5°C *min*$^{-1}$, in all other cases the process comes to end with a liquid+liquid mechanism because the reduction temperature interval includes also melting point of magnesium.

Table

$T_{\max}^{DTA}$ values of magnesiothermic and magnesio-carbothermic reduction of Ag_2WO_4 at various heating rates

V_h, °C *min*$^{-1}$	$T_{\max}^{DTA}$, °C		
	Ag_2WO_4+4Mg		Ag_2WO_4+2Mg+2C
	I stage	II stage	
30	612	671	689
20	600	655	666
15	591	648	660
10	583	622	641
5	569	600	617

3.2. Ag_2WO_4-C binary system

As can be seen from the Fig. 4, the carbothermic reduction of silver tungstate proceed in two stages, which are distinctly expressed on TG, DTG and DTA curves. According to the data obtained from TG and DTG curves, the carbothermic reduction starts at 460°C. At that the first stage includes temperature area up to 535°C followed by the second stage including mainly temperature interval of 540-610°C.

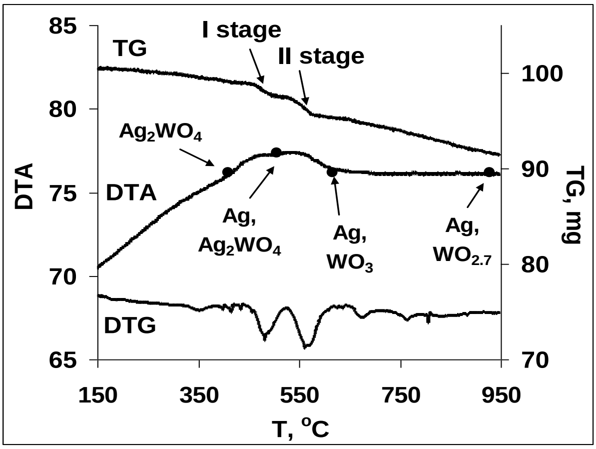

Fig. 4. DTA/TG curves of the Ag_2WO_4+3C mixture, V_h=20°C *min*$^{-1}$.

In any case the decrease in the mass of the mixture continues up to the studied maximum temperature (950°C). Change (loss) of the mass is 9 *mg* (from 100 *mg* mixture), which corresponds to complete reduction of silver and partial reduction of tungsten (Fig. 4). This fact was approved by the results of XRD analyses.

The absence of endothermic peak of Ag_2WO_4 melting on the DTA curve indicates that there is no silver tungstate in the mixture at that temperature, because its carbothermic reduction starts earlier – at about 460°C.

3.3. Ag_2WO_4-Mg-C ternary system

Fig. 5 demonstrates DTA/DTG curves of the Ag_2WO_4+2Mg+2C mixture at the heating rate of 10°C *min*$^{-1}$. As may be seen from the figure, in this case the endothermic peak of silver tungstate melting is also absent on the DTA curve. This is explained by the fact that carbothermic reduction of silver tungstate (410°C) starts before the melting point of the letter. For this system magnesiothermic reduction at the heating rate of 10°C *min*$^{-1}$ starts at 640 and ends at 720°C: the melting point of the reducer Mg (650°C) is also highlighted on the curve.

Thus, magnesio-carbothermic reduction of silver tungstate starts with carbon at 410°C, which is lower by 50°C as compared with carbothermic reduction, then it continues with Mg at 640°C: the reaction starts with solid+solid and continues with solid+liquid mechanism.

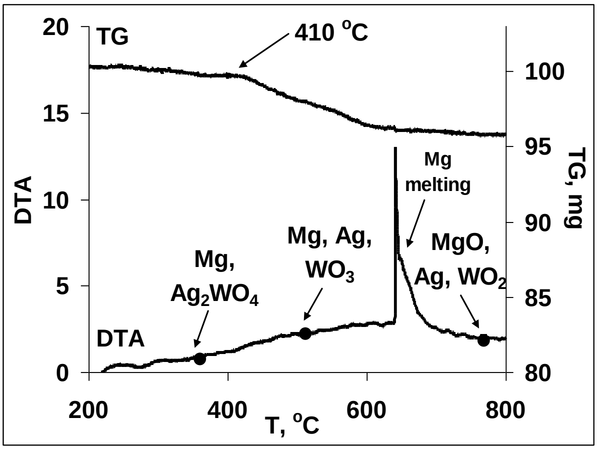

Fig. 5. DTA/TG curves of the Ag_2WO_4+2Mg+2C mixture, V_h=10°C *min*$^{-1}$.

Based on the results of XRD analyses the reaction's sequence during magnesio-carbothermic reduction of silver tungstate may be presented as follows:

$$Ag_2WO_4+C \rightarrow Ag+WO_3+CO/CO_2\uparrow,$$
$$WO_3+Mg \rightarrow W+WO_2+MgO.$$

Therefore, it can be concluded that the investigated temperature area (T_{max}=950-1000°C and heating rate up to 30°C *min*$^{-1}$) are not enough for complete reduction of silver tungstate.

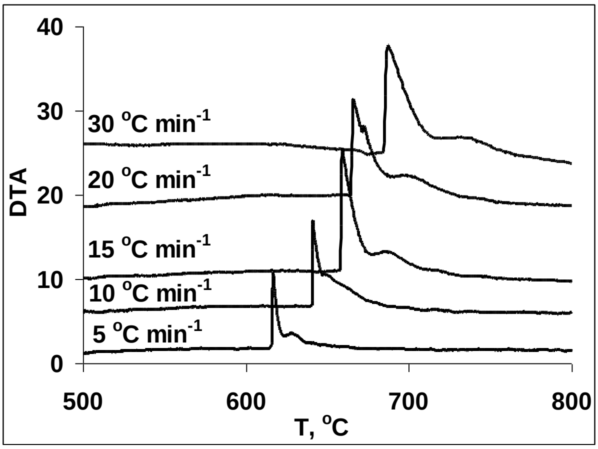

Fig. 6. DTA curves of the Ag_2WO_4+2Mg+2C mixture at various heating rates. V_h=5, 10, 15, 20, 30°C·*min*$^{-1}$.

Thus, in studied conditions: (a) magnesiothermic reduction of Ag_2WO_4 proceeds by the formation of Ag, W and WO_3, (b) carbothermic reduction – by the formation of Ag, W and $WO_{2.7}$, and (c) magnesio-carbothermic reduction – by the formation of Ag, W and WO_2.

As in the case of the above discussed system, at magnesio-carbothermic reduction of silver tungstate with the increasing of heating rate the exothermic peak corresponding to the magnesiothermic reduction stage, shifts to higher temperature area (Fig. 6, Table 1).

Using the data for the temperatures of exothermic peak's maximum deviation at different heating rates, the values of the effective activation energies for the magnesiothermic reduction stages were calculated by Kissinger's method (Figs. 7 and 8), using equation (1).

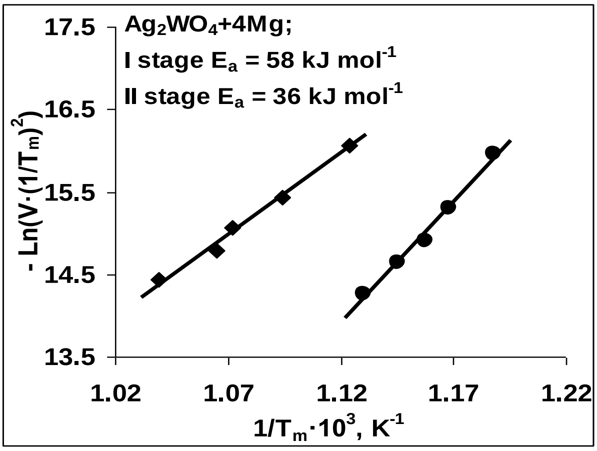

Fig. 7. Linear fitting of the -ln($V_h(1/T_m)^2$) - $1/T_m.10^3$ plots to extract effective activation energy of the reaction Ag_2WO_4+4Mg.

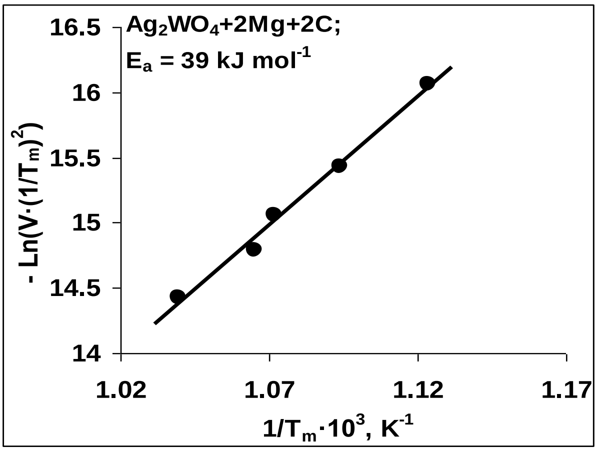

Fig. 8. Linear fitting of the $-\ln(V_h(1/T_m)^2)$ - $1/T_m.10^3$ plots to extract effective activation energy of the reaction $Ag_2WO_4+2Mg+2C$.

According to the results obtained, activation energy for the first stage of Ag_2WO_4+Mg magnesiothermic reduction is 58 $kJ{\cdot}mol^{-1}$, and for the second stage is 36 $kJ{\cdot}mol^{-1}$. Activation energy for the $Ag_2WO_4+2Mg+2C$ magnesio-carbothermic reduction is 39 $kJ{\cdot}mol^{-1}$. When using the combined Mg+C reducer, the E_a value of the Ag_2WO_4 reduction reaction is almost identical to the E_a value of the second stage of magnesiothermic reduction (after the melting of Ag_2WO_4) and almost 1.5 times smaller than the E_a value of the first stage of magnesiothermic reduction reaction.

Ag_2WO_4-Ի ՄԱԳՆԵԶԻՈՒՄԱ-ԿԱՐԲՈԹԵՐՄ ՎԵՐԱԿԱՆԳՆՄԱՆ ՀԵՏԱԶՈՏՈՒԹՅՈՒՆԸ ԳԾԱՅԻՆ ՏԱՔԱՑՄԱՆ ՊԱՅՄԱՆՆԵՐՈՒՄ

Մ. Կ. ԶԱՔԱՐՅԱՆ, Ա. Ս. ԱՐԶՈՒՄԱՆՅԱՆ և Ս. Լ. ԽԱՌԱՏՅԱՆ

DTA/TG մեթոդով ուսումնասիրվել է ոչ-իզոթերմ պայմաններում Mg+C համակցված վերականգնիչի կիրառմամբ արծաթի վոլֆրամատի վերականգնման մեխանիզմը տաքացման արագության 5-30°C րոպե$^{-1}$ *միջակայքում: Ցույց է տրվել, որ ինչպես առանձին վերականագնիչների, այնպես էլ Mg+C համակցված վերականգնիչի կիրառման դեպքում փոխազդեցությունը սկսվում է նախքան մագնեզիումի հալվելը: Ընդ որում, տաքացման արագության բարձրացմանը զուգընթաց DTA կորի շեղմանը համապատասխանող առավելագույն ջերմաստիճանի արժեքը շեղվում է դեպի ավելի բարձր ջերմաստիճանային տիրույթ: Բացահայտվել է, որ արծաթի վոլֆրամատի մագնեզիումա-կարբոթերմ վերականգնումը սկսվում է ածխածնով 410°C-ում, 640°C-ից սկսած շարունակվում է մագնեզիումով (*$V_{տ}=10°C\ min^{-1}$*) և ածխածնով միաժամանակ: Հաստատվել է, որ բոլոր դեպքերում մագնեզիումաթերմ վերականգնման փուլը սկսվում է պինդ+պինդ, և շարունակվում պինդ+հեղուկ մեխանիզմով: Բինար (*Ag_2WO_4*-Mg) և եռյակ (*Ag_2WO_4*-Mg-C) համակարգերի համար որոշվել են մագնեզիումով վերականգնման փուլի էֆեկտիվ ակտիվացման էներգիայի (Ea) արժեքները:*

МАГНЕЗИО-КАРБОТЕРМИЧЕСКОЕ ВОССТАНОВЛЕНИЕ Ag_2WO_4. ДТА/ТГ ИССЛЕДОВАНИЕ

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В работе исследован механизм восстановления вольфрамата серебра комбинированным восстановителем Mg+C в неизотермических условиях методом ДТА/ТГ в диапазоне скоростей линейного нагрева 5-30°C *мин*$^{-1}$. Показано, что как для случаев использования отдельных восстановителей, так и комбинированного восстановителя взаимодействие начинается до достижения точки плавления магния, а увеличение скорости нагрева сдвигает значение максимальной температуры, соответствующей смещению кривой DTA в сторону высокотемпературной области. Выявлено, что магнезио-карботермическое восстановление вольфрамата серебра начинается углеродом при 410°C с последующим одновременным участием магния и углерода при 640°C ($V_н$=10^{o}C *min*$^{-1}$). Установлено, что во всех случаях магниетермическая стадия восстановления начинается по механизму твердое+твердое, и продолжается по механизму твердое+жидкое. Определены эффективные значения энергии активации (E_a) для стадий магниетермического восстановления для бинарной (Ag_2WO_4-Mg) и тройной (Ag_2WO_4-Mg-C) систем.

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