ՀԱՅԱՍՏԱՆԻ ՀԱՆՐԱՊԵՏՈՒԹՅԱՆ ԳԻՏՈՒԹՅՈՒՆՆԵՐԻ ԱՁԳԱՅԻՆ ԱԿԱԴԵՄԻԱ НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ АРМЕНИЯ NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF ARMENIA

Հայшиտանի քիմիական հանդես Химический журнал Армении 74, №3-4, 2021 Chemical Journal of Armenia

UDC 536.46:546.56:546.77

THE REDUCTION MECHANISM OF COPPER MOLYBDATE AT NONISOTHERMAL CONDITIONS

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The mechanism of interaction in the CuMoO₄-xMg-yC system was studied at low and high heating rates by thermal analysis technique to reveal the reduction pathway of the copper molybdate by combined Mg/C reducing agents.

According to the obtained results, the process initiates directly from the salt reduction and proceeds in two successive stages, first is a low and second is a strong exothermic interaction. Moreover, depending on the heating rate, a merging of different stages can be observed. The effective activation energy of the magnesiothermic reduction reaction for the CuMoO₄+1.2Mg+2.2C mixture was calculated to be 199.5 \pm 7.2 *kJ/mol*.

Fig.4, references 15.

Due to the high conductivity of copper and low thermal expansion coefficient of molybdenum, Mo-Cu alloys are widely used in various fields of modern technology, in particular, for the manufacturing of super-powerful electronic contacts and welding electrodes, vacuum technologies, military, aviation and a number of other leading fields [1,2].

Numerous studies have been conducted in the last decade to improve the sinterability of Mo-Cu composite powders, considering growing interest in the variety of applications as well as to meet the requirements for the production of compact sintered parts.

Among them are the mechanical alloyaing, the addition of sintering aids, as well as hydrogen reduction of oxygen-containing compounds of molybdenium and copper [1-6]. One of the most effective methods to obtain fine-grained and high sinterability Mo-Cu nanocomposite materials is the co-reduction of metals from oxides (MoO₃, CuO) and/or salt (copper molybdate) by Mg + C reducing mixture via energy-saving self-propagating high-temperature synthesis method [7,8].

However, considering that combustion processes are characterized by high temperatures and high self-heating rates of substances in the combustion front [9-11], considerable difficulties arise for exploring the interaction mechanism of reactions in combustion wave.

One of the approaches to study the mechanism of fast processes is to extend the process within the time, model it at programmed and moderate heating conditions (in this case slow heating mode) using various methods of thermal analysis, such as derivatographic analysis and high-speed temperature scanner [12,13].

As a result, it becomes possible to reveal the interaction mechanism, identify endothermic and exothermic effects of different stages, determine the kinetic parameters of the individual stages or the total process.

In this work, the mechanism of reduction of copper molybdate under slow and high heating rates by Mg/C combined reducers was investigated, utilizing DTA/TG method of thermal analysis (low heating rates region from 2.5 to 20°C/*min*) and High-Speed Temperature Scanner (HSTS). The latter allows to examine powdered mixtures in a wide range of heating rates (from 10 to 10000°C/*min*) up to 1300°C temperature, which, being closer to the heating rates and combustion temperatures of the material in the combustion wave, provides a greater opportunity to disclose the sequence of reactions in the combustion wave [12,13]. Combining the results derived from the thermograms with XRD examinations of the quenched samples at different characteristic temperatures, it is possible to determine the nature and sequence of reactions in the complex system under study.

Experimental part

The following powders were used as raw materials: copper molybdate, magnesium (MPF-2, pure, 150-300 μ m) and carbon black (P-803TM, granul, particle size less than 1 μ m, S=35 m^2/g). Copper molybdate was prepared from the mixture of MoO₃ and CuO powders with a molar ratio of 1:1, which were homogeneously mixed in a ceramic mortar and calcined in air at 700°C for 3 *hrs*. The obtained copper molybdate was milled for 5 *min* using a Vibratory Mill machine (model 75T-DrM). After the milling process yellow brown flour-like powder was obtained with <300 *nm* average size (Fig. 1).



Fig. 1. XRD pattern (a) and SEM micrograph (b) of copper molybdate.

The mechanism of interaction in the CuMoO₄-xMg-yC system by thermal analysis at low (DTA/TG) and high (HSTS) heating rates was investigated for the determination of the reduction mechanism of copper molybdate by Mg/C combined reducing agent. Derivatographic studies were performed using "Derivatograph Q1500" MOM instrument in argon atmosphere (120 *ml/min* flow rate) by linear heating of 200 *mg* powder mixture at a heating rate of 2.5-20°C/*min* until the required temperature was reached.

The principle of operation of the HSTS system is based on the direct electric heating of a cell made of thin metal foil. The reactive powder mixture (50 *mg*) was placed into the metallic envelope made from thin nickel foil with 0.1 *mm* thickness, and a K-type thermocouple (chromel-alumel) spot-welded directly to the foil in the central area of powder location. All measurements were conducted at 0.1 *MPa* argon (>99.98 %, $O_2 - \langle 0.01 \rangle$) pressure.

At the both low and high heating rates, the process was interrupted at different characteristic stages and the quenched samples were analyzed by XRD analysis (XRD, DRON-3.0, Burevestnik, Russia)

Results and discussion

Interaction mechanism in the CuMoO₄-xMg-yC system at low heating rates

The mixture of CuMoO₄+1.2Mg+2.2C composition was experimentally selected to be optimum for the reduction of copper molybdate in the combustion mode [8]. The results of the DTA/TG studies of the CuMoO₄+1.2Mg+2.2C mixture are presented in Figure 2. The process was interrupted at characteristic temperatures (490, 625, 920°C), taking into consideration the completion of the stages proceeding by carbon and magnesium, and XRD analysis of the quenched products from those temperatures was performed.



Fig. 2. DTA/DTG/TG curves of the CuMoO₄+1.2Mg+2.2C mixture, m=200 mg, V=20°C/min.

Based on the results derived from the DTA/TG curves, it can be seen that there is no interaction detected in the CuMoO₄+1.2Mg+2.2C mixture up to 420 °C, and starting from 420°C (up to 490°C) the first carbothermal reduction of copper molybdate takes place, which is accompanied by a decrease in the sample wieght (5.08%, vs to the calculated value of 3.81%). According to XRD analysis (fig. 3), copper molybdate is reduced up to non-stoichiometric salts (some copper oxide is also present).

The second carbothermic stage of copper molybdate reduction continues from 490°C and ends at about 600°C. According to the XRD examinations of the quenched sample at 625°C, the partially reduced salts were converted to Cu and MoO₂. The third stage is a strongly expressed exothermic interaction (690-810°C), where, according to the TG and DTG curves, there is no mass change. This stage occurs after the melting of magnesium and based on the aforementioned observations refers to the magnesiothermic reduction of MoO₂ to molybdenum. Note that according to the XRD patterns of the sample quenched at 920°C, MoO₂ is not completely reduced to molybdenum, and some amount of the no reducted dioxide remains in the product.



Fig. 3. XRD patterns of the intermediates and products quenched from different characteristic temperatures: CuMoO₄+1.2Mg+2.2C reactive mixture. A - T=490, B - 625, C - 920°C.

Interaction mechanism in the CuMoO₄-xMg-yC system at high heating rates

In order to clarify the role of the heating rate on the interaction mechanism in the CuMoO₄-xMg-yC system and to model the processes under similar conditions to the combustion wave, experiments were performed in the range of high heating rates (V_h =100-1200°C/*min*, T_{max} = 1300°C). In the region of high heating rates, in contrast to slow heating, the reduction process initiates after the melting of magnesium. As can be seen from the thermograms presented (fig. 4), the carbothermic reduction is not expressed at 100°C/*min* heating rate, but the magnesiothermic reduction is strongly expressed in the form of highly exothermic interaction. The increase in the heating rate leads to approaching of the mentioned stages up to their merging. In the case of heating rates up to 600°C/*min*, there are low and high exothermic stages due to the carbothermic and magnesiothermic reduction processes, respectively observed in the thermograms. At higher rates (>600°C/*min*), these two stages combine and the process is expressed only by one exothermic peak.



Fig. 4. Heating thermograms of the CuMoO₄+1.2Mg+2.2C mixture at various heating rates. A - V_h =100, B - 150, C - 300, D - 600, E - 1200°C·*mir*¹.

Given that the high heating conditions are quite close to the interaction conditions (heating rate and temperature) in the combustion mode, the corresponding data was processed and used to calculate the effective values of the activation energy of the magnesiothermic reduction process using Kissinger equation [14]. The calculated value is $199.5\pm7.2 \ kJ/mol$, which exceeds the activation energy ($155\pm10.7 \ kJ/mol$) of the combined reduction of oxides by 1.3 times [15]. The observed difference in activation energy values is probably connected to the fact that the reduction process of oxides begins before the melting of magnesium, with the carbothermic reduction of copper oxide (560° C), while the reduction process of the salt begins after the melting of magnesium.

Experimental studies have shown that in contrast to low heating conditions, individual stages of salt reduction are shifted to a higher temperature range under high heating conditions. Particularly, at 100°C/*min* heating rate, the temperature of magnesiothermic reduction is shifted to a higher temperature zone by 170°C as compared to that at 20°C/*min*.

It should also be noted that in the case of high heating, the carbothermic interaction begins after the melting of magnesium, as opposed to low heating rates. Moreover, a relatively higher degree of salt reduction occurs at high heating conditions as compared to low heating mode.

Based on the results, the mechanism of interaction in the CuMoO₄-Mg-C system can be represented according to the following scheme.

1. $CuMoO_4 + C \rightarrow Cu_2O + Cu_{4-x}Mo_3O_{12} + CO/CO_2$ 2. $Cu_{4-x}Mo_3O_{12} + Cu_2O + C \rightarrow Cu + MoO_2 + CO/CO_2$ 3. $MoO_2 + Mg \rightarrow Mo + MgO$

	T, °C	
	DTA	HSTS
1	420-480	550-610
2	500-590	670-810
3	>680	>940

Thus, the reduction of copper molybdate begins with the formation of copper-poor molybdates without pre-decomposition to oxides. Moreover, in contrast to low heating rates, at high heating rates, a relatively higher degree of salt reduction takes place. Besides, at high heating rates the reduction process takes place immediately after the melting of magnesium. The reduction begins with a weaker (C) and ends with a stronger (Mg) reducers. Increasing the heating rate results in the approaching of carbothermic and magnesiuothermic stages (up to $V_h=600^{\circ}C/min$) and merging (starting from $V_h=1200^{\circ}C/min$). In the studied system, the process of copper reduction takes place at lower temperatures, exclusively with carbon. And the reduction of molybdenum initiates with carbon up to the formation of MoO₂, which is then reduced to molybdenum by magnesium at higher temperatures.

ՊՂՆՁԻ ՄՈԼԻԲԴԱՏԻ ՎԵՐԱԿԱՆԳՆՄԱՆ ՄԵԽԱՆԻԶՄԸ ՈՉ ԻԶՈԹԵՐՄ ՊԱՅՄԱՆՆԵՐՈՒՄ

۲. Վ. ԿԻՐԱԿՈՍՅԱՆ

Ուսումնասիրվել է պղնձի մոլիբդատի վերականդնման մեխանիզմը CuMoO4-xMg-yC Համակարդում ջերմային անալիգի եղանակով տաքացան արադությունների լայն տիրույթում: Ըստ ստացված արդյունքների մոլիբդատի վերականդնումը տեղի է ունենում անմիջապես աղից, իրար Հաջորդող երկու փուլերով. առաջինը՝ թույլ, իսկ երկրորդը ուժեղ էկղոթերմ փոխազդեցությամբ: Տաքացման արադության մեծացմանը զուդընթաց դիտվում է նչված փուլերի միաձուլում: Որոչվել է CuMoO4+1.2Mg+2.2C խառնուրդում մադնեդիումաթերմ վերականդնան փուլի ակտիվացման էներդիան. $E=199.5^{\circ}7.2$ կՋ/մոլ:

МЕХАНИЗМ ВОССТАНОВЛЕНИЯ МОЛИБДАТА МЕДИ В НЕИЗОТЕРМИЧЕСКИХ УСЛОВИЯХ

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В работе изучен механизм взаимодействия в системе CuMoO₄-xMg-уC в широком диапазоне скоростей нагрева методом термического анализа с целью выявления последовательности превращений при восстановления молибдата меди с помощью комбинированных восстановителей Mg/C.

Согласно полученным результатам установлено, что восстановление молибдата меди начинается с образования различных молибдатов с низким содержанием меди без предварительного разложения на оксиды в две последовательные стадии: первая – слабое, а вторая – сильное экзотермическое взаимодействие. При этом с повышением скорости нагрева имеет место перекрывание упомянутых стадий. Рассчитана энергия активации стадии магнезиотермического восстановления для смеси CuMoO₄+1.2Mg+2.2C: E=199,5 ± 7,2 кДж/моль.

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