UDC 546.78:546.562-31:543.57

DTA/TG STUDY OF REDUCTION MECHANISM OF WO₃+CuO MIXTURE BY COMBINED Mg/C REDUCER

O. M. NIAZYAN[1], S. V. AYDINYAN[1,2] and S. L. KHARATYAN[1,2]

[1]A.B. Nalbandyan Institute of Chemical Physics NAS RA
5/2, P. Sevak Str., Yerevan 0014, Armenia
[2]Yerevan State University
1, A. Manukyan Str., Yerevan 0025, Armenia
E-mail: sofiya.aydinyan25@gmail.com

Abstract. The mechanism of copper (II) and tungsten (VI)oxides co-reduction by Mg+C mixture was investigated at non-isothermal conditions by carrying out simultaneous differential thermal (DTA) and thermal-gravimetric (TGA) analyses combined with X-ray diffraction (XRD) analysis of intermediate and final products. The behavior of each single reagent as well as that of binary, ternary and quaternary mixtures was studied at linear heating. The whole process was found to be multistage. It was revealed that at first carbon reduces copper oxides, after that WO₃ is reduced by magnesium. Reaction mechanism in the WO₃-CuO-Mg-C system on the basis of DTA/TG curves and XRD analysis results of the quenched reaction products has been proposed.

Figs. 6, references 17.

During last two decades an increased interest has been paid to pseudoalloys based on Cu - refractory metal system (such as Cu-W, Cu-Mo) due to their high physicomechanical properties and multiple functionalities for numerous high-tech applications, thermal management materials, etc. [1-7]. The development of new preparation methods of Cu-W composite materials with bulk density is in the focus of modern research [6-15]. A number of novel technologies have been developed to enhance Cu-W composite densification ability [5,7,9,13]. In our previous work [15], joint reduction of tungsten and copper oxides by energy saving combustion synthesis approach using Mg+C mixture as combined reducer was performed. The use of such reducing mixture allows to control the reaction temperature in a wide range and to synthesize W-Cu composite powders in a controllable combustion mode. However, considering that combustion processes are characterized by high temperatures and high self-heating rates of reagents in the combustion wave, considerable difficulties

arise at studying the mechanism of combustion process. Note, that according to the available literature data, the mechanism of joint reduction of WO_3 and CuO was not studied at all. To fill the gap one of the approaches is modeling of the process at controllable conditions (e.g. with programmed heating rates and tuning the process within the time) by using thermal analysis method. This approach provides an enhanced opportunity to reveal the stepwise nature of complex reactions in the multicomponent systems, as well as to estimate the optimum conditions for target material preparation in combustion mode.

In this work the mechanism of joint reduction of tungsten and copper oxides by the Mg+C mixture was studied by thermal analysis (DTA/TG) method combined with XRD analysis of final and intermediate products quenched at various stages.

Experimental

The following powders: WO_3 (High grade, Pobedit Company, Russia, particle size less than $15\,\mu m$), CuO (High grade, STANCHEM, Poland, particle size less than $40\,\mu m$), magnesium powder (MPF-3, Russia, 150-300 μm particle size) and carbon black (P-803, Russia, particle size less than $1\,\mu m$) were used as raw materials.

Differential thermal (DTA) and thermogravimetric (TG) analyses with low heating rates were carried out using DTA/TG instrument ("Derivatograph Q1500" MOM, Hungary) which is connected to multichannel acquisition system and output signals are recorded by a computer. DTG and DTA points were registered in every $1\,s$, samples 50-200 mg were placed in Al_2O_3 crucibles with 1 ml volume, Al_2O_3 powder was used as reference material. Measurements were conducted in argon atmosphere at flow rate of 120 $ml \cdot min^{-1}$. Heating rate was programmed to be 2.5, 5, 10, $20^o C$ min^{-1}. The thermoanalytical curves were recorded up to a temperature $1000^o C$. In order to stop the reaction and quench the intermediate and final products for further examinations, the power was switched off automatically at preset temperatures, then the furnace was removed and sample was cooled down by inert gas flow. The cooling rate in the temperature range from 1000 to 600 $^o C$ (more interesting area) was around $300^o C$ min^{-1}.

The samples were examined by XRD method with monochromatic CuKα radiation (diffractometer DRON-3.0, Burevestnik, Russia) operated at 25 kV and 10 mA.

Results and discussion

Under the conditions of continuous temperature growth mass change (TG) of the samples under study, the rate of this change (DTG) and thermal phenomena (DTA) occurring in the system were tracked. Firstly ternary (CuO-WO_3-C, CuO-WO_3-Mg) systems were studied. Separate reduction of WO_3 and CuO by Mg/C reducers were studied earlier [16,17].

WO₃-CuO-C system. The mechanism of joint carbothermic reduction of tungsten and copper oxides was studied. To reveal the sequence of reactions occurring in the WO_3-CuO-C system and carbothermic reduction temperatures, firstly the behavior of the binary mixture of oxides under linear heating regime was studied to elucidate the possibility of interaction between oxides with salt formation.
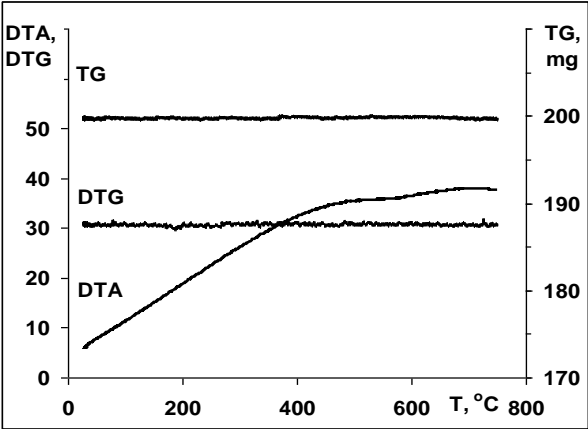

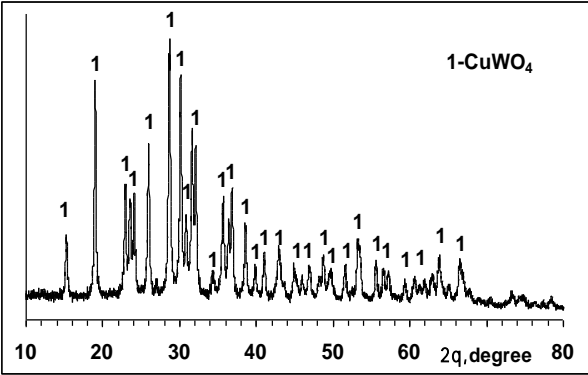Fig. 1a. DTA/DTG/TG curves of the CuO+WO₃ mixture, $V_h=20^o/min$, $m_o=200$ *mg.*

Fig. 1b. XRD pattern of the CuO+WO₃ mixture quenched at 750°C.

As it follows from the Fig. 1a at T=500-650°C low endothermic interaction of oxides takes place. XRD analysis (Fig. 1b) of the sample quenched at 750°C testifies that $CuWO_4$ is formed as a result of interaction between the oxides.

Fig. 2 demonstrates DTA/DTG/TG curves of carbothermic reduction of the CuO+WO₃ mixture. According to the results obtained, coreduction of WO_3-CuO oxides by carbon is a multistage process. At that TG/DTG curves indicate that no chemical conversion occurs in the initial WO_3-CuO-C mixture up to 450-500°C.
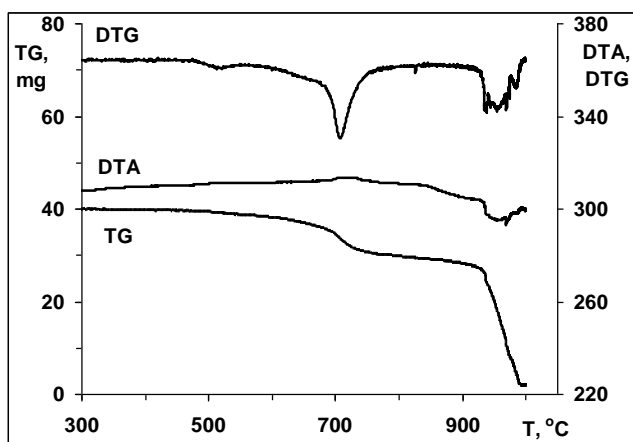
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Fig. 2. DTA/DTG/TG curves of the WO_3-CuO-C mixture, V_h=20 $^oC/min$, m_o=300 mg.

Then, starting with this temperature partial reduction of copper oxide up to suboxide, Cu_2O, takes place (T_{max}=520^oC according to the DTG curve). Then (at 600-800^oC) mainly the reduction of copper suboxide into metallic copper takes place accompanied by corresponding mass loss (7.5% for two stages). At temperatures above 900^oC the reduction of WO_3 occurs via the following consecutive stages: $WO_3 \rightarrow WO_{2..9} \rightarrow WO_2 \rightarrow W$. These facts were confirmed by comparing the data obtained from DTA/TG curves with the results of XRD analysis for samples quenched from different characteristic temperatures (Fig. 3). Under these conditions only partial carbothermic reduction of WO_3 up to the metallic tungsten was observed.

The studies were continued in the direction of magnesiothermic reduction of the oxide mixture, as well as using combined Mg+C reducer aimed at full reduction of both the oxides, CuO & WO_3.
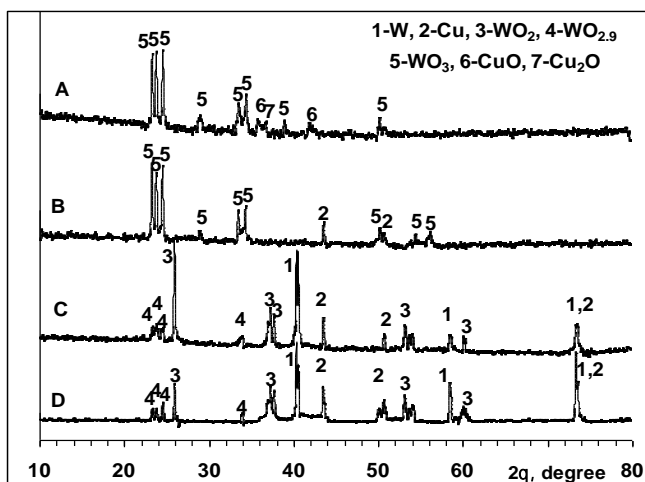

Fig. 3. XRD patterns of the products of carbothermic reduction of the CuO+WO_3 mixture, A – T=575, B – 800, C – 970, D – 1000^oC.

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CuO-WO₃-Mg system. Fig. 4 demonstrates a derivatogram of the magnesiothermic reduction of WO_3+CuO oxides mixture. As can be seen a strong exothermic very rapid magnesiothermic reaction occurs.
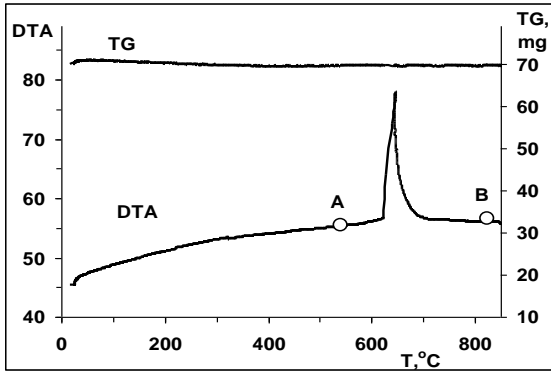

Fig. 4. DTA/TG analysis of the WO_3+CuO+4Mg mixture, m=70 *mg*, V_h=20°/*min*.

During the process a mass change of the initial mixture was not detected as the formed magnesia remains in the final mixture. As may be seen from the derivatogram, the maximum value for the temperature shifting at magnesiothermic reaction of oxides corresponds to T_{max} =647°C, and the reaction begins before magnesium melting, involving temperature interval 620-760°C.

The results of XRD analyses for the samples interrupted and cooled at T=550°C and 820°C are presented in the Fig. 5. According to the XRD analysis data at T=550°C only initial reagents are present – the reaction doesn't start yet (Fig. 5A). At 820°C (Fig. 5B) mainly reduced metals were detected in the quenched product with a small amount of $MgWO_4$.
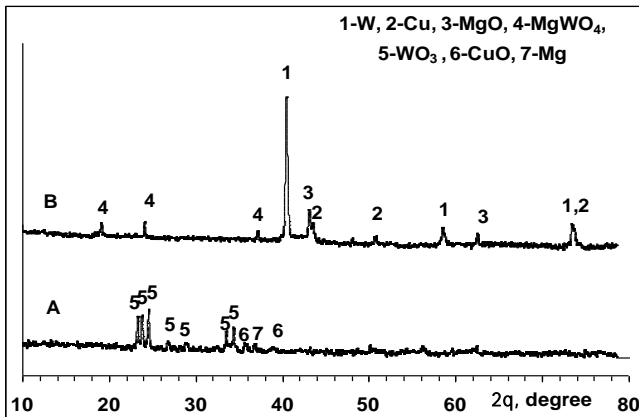

Fig. 5. XRD patterns of the CuO+WO₃+4Mg mixture for the samples quenched at different characteristic temperatures, A – T=550, B – 820°C.

CuO-WO₃-Mg-C system. Similar to the magnesiothermic reduction of oxides, in this case, again the process is described by exothermic behavior (T_{max} =703°C) mainly as a result of magnesiothermy (Fig. 6a).
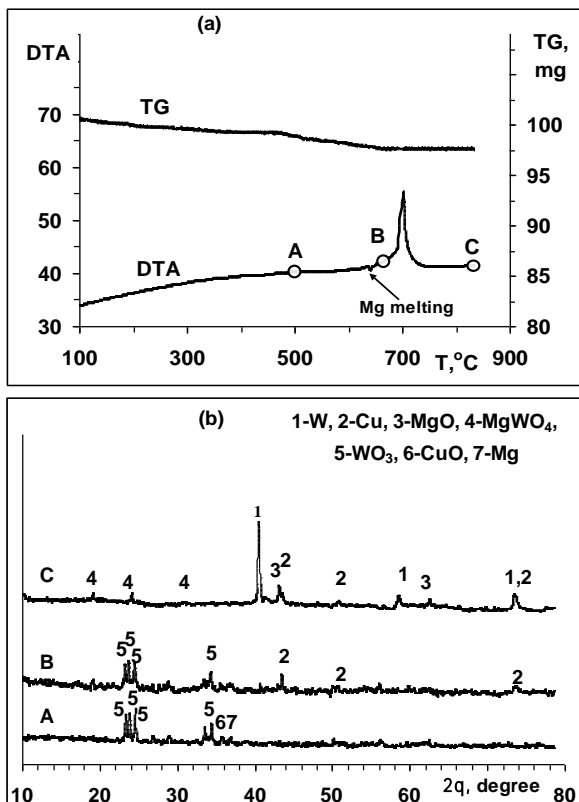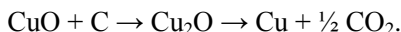
Fig. 6. DTA/TG analysis results (a) and XRD patterns (b) of the $WO_3+CuO+2C+Mg$ mixture, cooled down from various temperatures. $V_h=20°/min$, m=100 mg, A – T=470, B – 660, C – 850°C.

In this case, according to TG data, mass loss at temperature interval 480-650°C is conditioned by stepwise reduction of CuO by carbon:

$$CuO + C \rightarrow Cu_2O \rightarrow Cu + ½ CO_2.$$

Magnesiothermic reduction starts at a temperature higher than melting point of Mg ($T_{melt.}=650°C$). According to the resuts of XRD analysis (Fig. 6b), in fact, up to 650°C the reduction reaction proceeds with relatively weak reducer (carbon), and then the process is continued by the metallic reducer. Thus, the reduction, as well as the conversion of metals drastically increases after exothermic interaction, which is magnesiothermic process. And at point "C" the product represents mainly copper and tungsten with certain amount of magnesium tungstate.

Summarizing and comparing the results for the all systems studied, one may conclude that while the separate magnesiothermic reduction processes of copper and tungsten oxides starts in solid state at about the same temperature ($T_s=560-570°C$) before magnesium melting [16,17], their joint reduction shifts to higher temperature area (670-760°C) and interaction proceeds predominately with molten magnesium. Note, that during the heating of oxide mixture with reducers no formation of copper tungstate takes place. This fact was confirmed by XRD analysis of the quenched product at 550°C. Thus, it can be concluded that the shift of reduction temperature may be exclusively caused by the mutual influence of oxides.

The next important issue that should be epmhasized, is that copper oxide is reduced by carbon at lower temperature (440-530°C), than with magnesium (570°C). In addition, the presence of carbon shifts the CuO-Mg reaction to higher temperature area: from 570 to 730°C [17]. The carbothermic reduction temperature area of oxides taken together is wider, but closer to WO$_3$+C reduction reaction, which is higher by about 60°C as compared to CuO+C one. And finally, in the presence of both the reducers, the joint reduction of oxides starts with the CuO+C reaction at 440°C, similar to the separate CuO+C reaction, and continues with WO$_3$+Mg one, but at a temperature higher by 100°C than in the case of solely WO$_3$+Mg interaction. Thus, carbothermal reduction of copper oxide precedes the magnesiothermal reduction of tungsten oxide.

Based on DTA/TG/DTG and XRD analyses results of quenched samples (Figs.6a, b) the following scheme may be presented for reactions pathway:

1) CuO + C $\rightarrow$ Cu$_2$O + CO$_2$(CO); Cu$_2$O + C $\rightarrow$ Cu + CO$_2$(CO); T=480-650°C

2) Melting of Mg, T = 650°C

3) WO$_3$ + Mg $\rightarrow$ W + MgO; T = 670-760°C

4) WO$_3$ + MgO $\rightarrow$ MgWO$_4$; T >850°C (in case of Mg deficiency)

The interaction pathway in the WO$_3$-CuO-Mg-C complex system was explored by the thermal analysis method combined with XRD analysis of the quenched intermediate and final products. It has been demonstrated that in the case of carbon as a reducer, copper oxide is reduced completely (450-760°C), while carbothermic reduction of tungsten oxide starts at >800°C and continues up to 1000°C. At using magnesium as reducer, it reduces the both oxides almost completely at 800°C. In addition, the joint reduction of oxides by Mg/C mixture starts with sequential carbothermal reduction of copper oxide, followed by high-exothermic reaction occurring directly between tungsten oxide and magnesium.

Acknowledgement

Mg/C ՀԱՄԱԿՑՎԱԾ ՎԵՐԱԿԱՆԳՆԻՉՈՎ WO$_3$+CuO ԽԱՌՆՈՒՐԴԻ ՎԵՐԱԿԱՆԳՆՄԱՆ ՄԵԽԱՆԻՉՄԻ ՈՒՍՈՒՄՆԱՍԻՐՈՒԹՅՈՒՆԸ ԴԵՐԻՎԱՏՈԳՐԱՖԻԱԿԱՆ ԵՂԱՆԱԿՈՎ

Օ. Մ. ՆԻԱԶՅԱՆ, Ս. Վ. ԱՅԴԻՆՅԱՆ և Ս. Լ. ԽԱՌԱՏՅԱՆ

Ուսումնասիրվել է պղնձի(II) և վոլֆրամի(VI) օքսիդների՝ Mg+C համակցված վերականգնիչներով համատեղ վերականգնման մեխանիզմը ոչ իզոթերմ պայմաններում՝ համադրելով դիֆերենցիալ ջերմային, ջերմագանգվածաչափական և ռենտգենաֆազային անալիզի եղանակները: Բացահայտվել է, որ նշված օքսիդների վերականգնումն ընթանում է փուլային մեխանիզմով: Ելնելով դերիվատոգրաֆիական և ռենտգենաֆազային անալիզի արդյունքներից, առաջարկվել է վերականգնման հնարավոր մեխանիզմը, համաձայն որի առաջին փուլում, համեմատաբար ցածր ջերմաստիճաններում, ածխածնով վերականգնում է պղնձի օքսիդը, ապա WO$_3$ը վերականգնվում է հալված մագնեզիումով:

ИССЛЕДОВАНИЕ ВОССТАНОВЛЕНИЯ СМЕСИ WO₃+CuO КОМБИНИРОВАННЫМ Mg/C ВОССТАНОВИТЕЛЕМ ДЕРИВАТОГРАФИЧЕСКИМ МЕТОДОМ

О. М. НИАЗЯН[1,2], С. В. АЙДИНЯН[1,2] и С. Л. ХАРАТЯН[1,2]

[1] Институт химической физики им. А.Б. Налбандяна НАН Республики Армения
Армения, 0014 Ереван, ул. П. Севака, 5/2
[2] Ереванский государственный университет
Армения, 0025, Ереван, ул. А. Манукяна, 1
E-mail: sofiya.aydinyan25@gmail.com

Исследован механизм совместного восстановления оксидов меди(II) и вольфрама(VI) комбинированным восстановителем Mg/C в неизотермических условиях методами дифференциально-термического (ДТА) и термогравиметрического (ТГА) анализов в сочетании с рентгенофазовым анализом промежуточных и конечных продуктов. Установлено, что процесс восстановления оксидов вольфрама и меди протекает стадийно. На основе кривых ДТА/ТГ и результатов рентгенофазового анализа закаленных промежуточных продуктов реакции предложен механизм процесса, в соответствии с которым на первой стадии, при относительно низких температурах углерод восстанавливает оксид меди, далее WO₃ восстанавливается расплавленным магнием.

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