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Reaction pathway in the WO_3-CuO-Mg-C system at nonisothermal conditions

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Abstract. The mechanism of tungsten (VI) and copper (II) oxides co-reduction by Mg+C mixture was investigated at non-isothermal conditions in a wide range of heating rates: i. carrying out combustion process in the copper wedge, ii. using high-speed temperature scanner (HSTS-1), iii. performing differential thermal (DTA) and thermal-gravimetric (TG) analyses combined with X-ray diffraction (XRD) analysis of intermediate and final products. The sequence of chemical reactions occurring during the heating process on the basis of copper wedge results, HSTS analysis, DTA/TG curves and XRD analyses results of quenched reaction products have been proposed. It was revealed that the carbothermic reduction preceded the magnesiothermic reduction process. Due to the suggested reaction pathway, the combined and complete reduction of oxides by Mg/C reducing mixture becomes possible at relatively low temperatures.

Keywords: copper-tungsten composite, combustion synthesis, reaction mechanism, thermal analysis, combined reducer

Introduction

Tungsten–Copper composites exhibit low thermal expansion coefficient, high thermal and electrical conductivity, high strength, density, ductility, good machinability and corrosion resistance. In view of the mentioned unique combination, W–Cu composites are mainly used for heavy-duty electrical contacts, resistance welding electrodes, electro-discharge machining electrodes, heat sinks, arcing tips and microwave materials [1-4]. W–Cu alloy parts are generally fabricated by Cu infiltration in tungsten skeleton or liquid phase sintering of W–Cu powder mixture [5, 6]. However, because of the W–Cu system exhibits mutual insolubility, W–Cu powder compacts show very poor sinterability [7], while in most of the applications, high-dense W–Cu materials with homogeneous microstructure are required for high performance, which has led in turn to attempts to prepare ultra-fine and well-dispersed W–Cu powders. Therefore, various methods have been tested to prepare ultrafine or nanosized W–Cu powders. There are a number of processes, such as chemical co-precipitation [8-10] and co-reduction [11], mechanical alloying [12], as well as combinations of chemical and mechanical methods, such as mechanochemical process [13]. All these methods produce well dispersed mixtures of tungsten and copper. However, these techniques, especially the last two ones, include long time ball milling and the powders have the problem of contamination, which decreases electrical conductivity after sintering of powdered compacts [14, 15]. The development of new preparation methods of Cu-W composite materials is in the focus of modern research, as their characteristics highly depend on microstructure and phase composition of powder mixture. In our previous work [16], tungsten and copper oxides joint reduction was performed by energy saving combustion synthesis approach using Mg+C mixture as combined reducer. The using 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.

It was shown that at sufficient amount of reducers and slow propagation of combustion wave, it becomes possible the joint and complete reduction of both oxides. After the acid treatment (10%wt. HCl) of the product obtained at optimal conditions, it represents a desired W-Cu composite with submicron size particles. EDS analysis certify the homogeneity of obtained W-Cu composite material with similar distribution of both metals.

Current research is aimed to investigate the interaction mechanism in the CuO-WO_3-Mg-C system that may contribute to the estimation of optimum conditions of complete reduction of both oxides and preparation of W-Cu alloys.

It should be underlined that it is highly challenging to monitor and reveal mechanism of the combustion reaction due to its high velocity. To explore the interaction mechanism in the combustion wave, three different approaches were used.

i. The method of stopped combustion front (SCF) by quenching the process in a copper wedge (the vertex angle 10°) followed by XRD of the characteristic SCF areas was used (Fig. 1).

ii. The second approach was the modeling of the process at “soft” conditions (e.g. low heating rates and tuning the process within the time) by using the DTA/TG method combined with XRD analysis of intermediate products quenched from various stages. This approach provides an enhanced opportunity to reveal the stepwise nature of complex reactions in the multicomponent systems at low heating rates (up to 20^o/min).

iii. in the third case, high speed temperature scanner (HSTS-1 instrument) with high heating rates (up to 10000^o/min and T_{max}=1300^{o}C) was used, which is being more closed to the reagents heating rates and temperatures in the combustion wave, gives more opportunities to reveal the reactions mechanism taking place in combustion wave.

Materials and methods

The following powders were used as raw materials: WO_3 (Krasniy khimik, Russia, particle size less than 15 *μm*), CuO (High grade, STANCHEM, Poland, particle size less than 40 *μm*), magnesium powder (MPF-3, Russia, 150-300 *μm* particle size) and carbon black (P-803, Russia, particle size less than 1 *μm*). In a typical reduction experiment, the green mixture of the reactants was homogenized in a ceramic mortar for 0.5 h. Wedge shaped samples were prepared from the green mixtures of reagents by uniaxial pressing using copper wedge with definite parameters (=10^o, H=45 *mm*). Thermocouple technique was used to register temperature profiles in different parts (a and e) of the wedge. The output signals of thermocouples were transformed by a multichannel acquisition system and recorded by a computer with up to 2 *KHz* frequency. The average value of combustion velocity (U_c) was calculated by the $U_c=L/\Delta t$ formula, where L is the distance between thermocouples, Δt is the time distance between the signals of thermocouples. The standard errors of measurements for T_c and U_c were ±20 ˚*C* and 5*%*, respectively.

The reacted samples were studied by X-ray diffraction (XRD) 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.

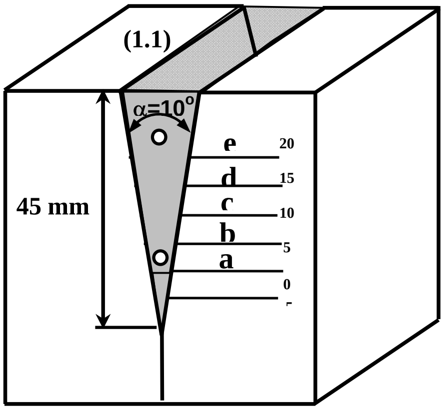
Differential thermal (DTA) and thermogravimetric (TG) analyses were carried out using DTA/TGA, Q-1500 instrument (“Derivatograph Q1500” MOM, Hungary) which is connected to the multichannel acquisition system and output signals are recorded by a computer. Differential thermogravimetric (DTG) and DTA points 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 (purity 99.97 *%*) atmosphere at flow rate of 120 *ml/min*. Heating rate was programmed to be 2.5, 5, 10, 20 *°C/min*. The thermoanalytical curves were recorded up to a temperature of 1000 *^oC*. In order to stop the reaction and quench the intermediate and final products for further investigations, the heater power was switched off automatically at preset temperatures, and the 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 $^{o}C/min$.

High-speed temperature scanner (HSTS-1) was also used for reveal the interaction mechanism in the powdered mixture at non-studied earlier interval of heating rates. Samples 50 – 100 *mg* were placed into nickel foil and preheated by passing electric current through the foil with desired temperature - time schedule provided by PC-assisted controller. Temperature-time histories were registered with frequency 50 *Hz*, Heating rate was programmed to be 300 – 2500°*C/min*. The thermoanalytical curves were recorded up to a temperature 1300^{o}C. Cooled down samples were studied by XRD analysis method.

Results and discussion

SCF technique

To explore the mechanism of processes occurring in the combustion wave, a mild combustible $CuO+WO_3+Mg+3C$ mixture was selected and combustion process was realized in the section of bulk copper wedge (Fig. 1.1). Temperature profiles of the combustion wave were registered by thermocouples located in two defferent zones of the wedge (Fig. 1.2). Phase composition of samples taken from various sections of the wedge after the combustion was examined by XRD analysis (Fig. 1.3). According to results obtained, non-reacted precursors (CuO, WO_3, Mg) are detected in the quenched zone and below (Fig. 1.1a, 1.3a), and in the preceding upper zone (Fig. 1.1b, 1.3b) complete reduction of copper oxide into copper (Fig. 1.1c, 1.3c) and then partial reduction of tungsten were registered (phases Cu, WO_3, WO_2 and W are present). Note that in the opposite direction of combustion wave propagation (Fig. 1.1d,e, 1.3d,e), an increase in the reduction degree of tungsten was observed. Based on these results, general understanding about the reduction mechanism of copper and tungsten oxides during the combustion process was outlined. According to the obtained preliminary data, firstly the copper oxide reduction into copper and then reduction of the tungsten oxide into tungsten take place.



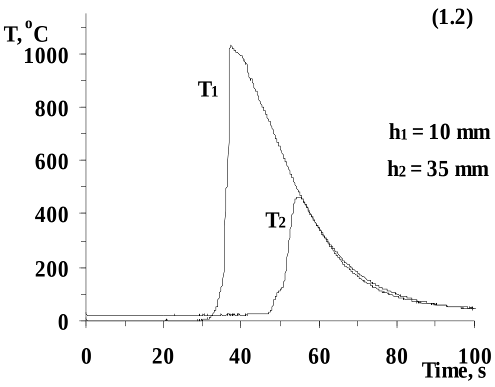


Fig. 1.1. Combustion in the copper wedge

Fig. 1.2. Combustion thermograms of the $CuO+WO_3+Mg$-3C mixture

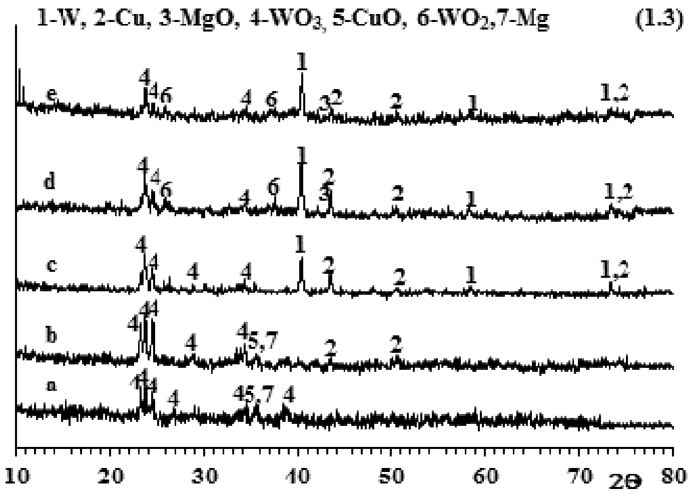


Fig 1.3. XRD patterns of samples taken from different parts of the copper wedge

DTA/TG analysis of the CuO-WO_3-Mg-C system

By DTA/TG method, in the CuO-WO_3-Mg-C system, the process is described by exothermic behavior (T_{max}=703°*C*), which is mainly the result of magnesiothermic reduction (Fig. 2a). In this case, according to TG data, mass loss at temperature intervals 440-550°**C** and 570-690°*C* is conditioned by the reduction steps of the CuO oxide by carbon:

$$CuO + C \rightarrow Cu_2O \rightarrow Cu + \frac{1}{2} CO_2$$

Magnesiothermic reduction takes place at temperatures higher than melting point of Mg ($T_{melt.}$=650°*C*). According to the resuts of XRD analysis (Fig. 2b), in fact, up to 680°*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" product represent mainly copper and tungsten, and only small amount of magnesium tungstate was observed.

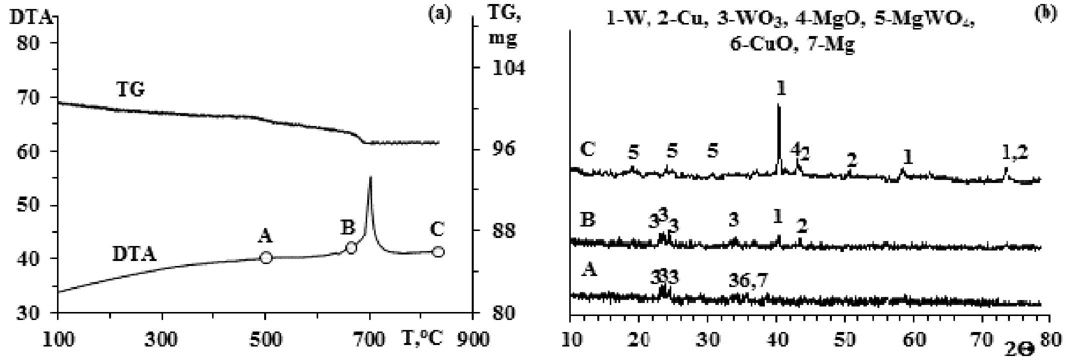


Fig. 2. DTA/TG analysis results (a) and XRD patterns (b) of the WO_3+CuO +3C+Mg mixture, cooled down from various temperatures. V_h=20°*C/min*, m=100 *mg*

Study of interaction mechanism in the CuO-WO_3-Mg-C system at high heating rates

To reveal the influence of heating rate and temperature on the intraction mechanism, the studies were continued at high heating rate, mainly at V_h=300°*C/min* and T_{max}=1300°*C* using the high-performance HSTS-1 setup. As it was mentioned above, this method is also expedient to use for disclosing mechanism of reactions occurring in the combustion wave, wherein it allows to interrupt the process at different characteristic stages and subject the cooled samples to XRD analysis. Note that when heating has been interrupted, the cooling took place with high rate (up to 12000 $^{o}C/min$), which practically excluded further interaction during the cooling stage. Experiments were performed with the quaternary $CuO+WO_3+2.5Mg+1.5C$ system. As the results obtained have shown, a multistage reduction process takes place and in contrast to the slow heating rate it begins after magnesium melting (fig. 3). At that, firstly a weak exothermic interaction takes place corresponding to the reduction of copper by carbon, which was confirmed by XRD analysis data for the sample cooled at $770^{o}C$ (Fig.4A). A weakly exothermic carbotherm reduction is followed by a sharp exothermic magnesiothermic one, which goes to end at $820^{o}C$, and appropriate diffraction pattern (Fig.4B) indicates to Cu, W, WO_3, WO_2, MgO. Note that at higher temperatures (point C) complete reduction of tungsten was observed (Fig.4C). Thus, reduction of the oxide mixture under consideration firstly begins with carbothermic reduction of copper oxide, followed by magnesiothermic reaction of tungsten oxide.

Thus, it was shown that in general, the similar mechanism was observed at various heating rates and occasionally various stages are merged because of proceeding at the same temperature interval. In the quaternary mixtures at low and high heating rates as well, the reduction starts with carbon, then magnesium participates to the reduction after the its melting. Therefore, by increasing the heating rate the interaction temperatures of separate stages are shifted by about 100-200^{o}C, in some cases by 200-300^{o}C, toward to high temperature region.

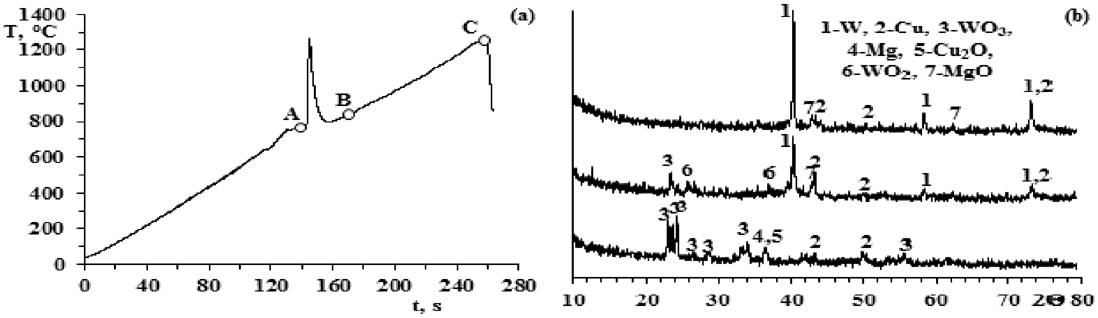


Fig. 3. Heating thermogram of the $CuO+WO_3+2,5Mg+1,5C$ mixture (a) and XRD patterns (b) after interruption process at different temperatures: A - T= 770^{o}C, B - 830^{o}C, C - 1230 ^{o}C, V_h=300$^{o}C/min$

To conclude, the reduction of oxides proceeds by stepwise mechanism and by varying heating rates of reagents it is possible to separate the main stages and to examine intermediate compounds, making useful tool for the exploration of interaction mechanism in the complex systems.

Finally, the detailed investigation of combustion thermograms and phase composition of quenched products from different areas of combustion wave, as well as at high (HSTS-1) and low (DTA/TG) heating rates asserted that the whole process was found to involve the sequential reduction of oxides according to the following stages:

- low-exothermic double-stage carbothermal reduction of copper oxide;
- high-exothermic reactions occurring directly between metal oxides (mainly tungsten) and magnesium.

Additionally note that by increasing the heating rate the interaction temperatures of separate stages are shifted by about 100-200^{o}C, in some cases by 200-300^{o}C, toward to high temperature region. Thus, the carbothermic reduction preceded the magnesiothermic reduction process, and due to such pathway of reactions, the combined and complete reduction of oxides at relatively low temperatures by Mg/C reducing mixture becomes possible.

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References

[1] J. R. Davis, Copper and Copper Alloys, ASM International, (2001).
[2] M. Amirjan, N. Parvin, K. Zangeneh-Madar, Mat. Sci. & Eng. A, **527** (2010) 6922.
[3] Young Do Kim, Nang Lyeom Oh, Sung-Tag Oh, In-Hyung Moon, Mat. Let., **51** (2001) 420.
[4] Yutaka Hiraoka, Hideaki Hanado, Takeshi Inoue, Int. J. Ref. Met. & Hard Mater., **22** (2004) 87.
[5] A. Ghaderi Hamidi, H. Arabi, S. Rastegari, Int. J. Ref. Met. & Hard Mater., **29** (2011) 538.
[6] V.I. Nizhenko, V.Yu. Petrishchev, V.V. Skorokhod, Powder Metal. & Met. Cer., **47** (2008) 163.
[7] M. Nastasi, F.W. Saris, L.S. Hung, and J.W. Mayer, J. Appl. Phys., **58** (1985) 3052.
[8] Y. Zhou, Q.X. Sun, R. Liu, X.P. Wang, C.S. Liu, Q.F. Fang, J. Alloys & Compd., **547** (2013) 18.
[9] L. Wan, J. Cheng, P. Song, Y. Wang, T. Zhu, Int. J. Ref. Met. & Hard Mater, **29** (2011) 429.
[10] J. Cheng, Ch. Lei, E. Xiong, Y. Jiang, Y. Xia, J. Alloys & Compd., **421** (2006)146.
[11] E. Ahmadi, M. Malekzadeh, S.K. Sadrnezhaad, Int. J. Ref. Met. & Hard Mater, **28** (2010) 441.
[12] S.N. Alam, Mat. Sci. & Eng. A **433** (2006) 161.
[13] J. Cheng, P. Song, Y. Gong, Y. Cai, Y. Xia, Mat. Sci. & Eng. A **488** (2008) 453.
[14] P. Chen, G. Luo, Q. Shen, M. Li, L. Zhang, Mat. & Des., **46** (2013) 101.
[15] T. Aboud, B.-Z. Weiss, R. Chaim, Nanostruct. Mater, **6** (1995) 405.
[16] H. Kirakosyan, T. Minasyan, S. Aydinyan, S. Kharatyan, ECERS 2015 14th Europian Ceramics Society Conference, 21-25 June, (2015) 2261.