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Copper oxide reduction by combined reducers under the combustion mode

M.H. Yamukyan [a], Kh.V. Manukyan [a,*], S.L. Kharatyan [a,b]

[a] *Department of Chemical Physics, Yerevan State University, A. Manukyan str. 1, Yerevan 0025, Armenia*

[b] *Laboratory of Kinetics of SHS Processes, A.B. Nalbandyan Institute of Chemical Physics NAS of Armenia, P. Sevak str. 5/2, Yerevan 0014, Armenia*

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Abstract

The process of copper oxide (CuO) reduction under the combustion mode was studied. A new class of so-called combined reducers (CR) was used which represent solid organic compounds of the C—H—N type. Thermodynamic calculations of combustion in the CuO–CR system were performed. On their basis proper experiments were carried out, revealing that reducing conditions (combustion temperature and velocity) and conversion degree for copper oxide may be controlled by changing the type and amount of the reducer, inert gas pressure, etc. The main factors determining phase composition and microstructure of formed combustion products were established. A possible mechanism of the reduction process during propagation of a combustion wave in the CuO–CR system was suggested based on the researches carried out and their comparison with literature data.

Keywords: Copper powder; Reduction; Combined reducer; Combustion reaction

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1. Introduction

Powdered copper is widely used in the pure state as well as in the composition of various alloys in the power, electrical and engineering industries [1,2] because of its high electrical and thermal conductivity and corrosion resistance. It is a promising material in electronics, in manufacturing dense spray formed molds, electrical circuits, termination pastes, conductive inks, inner electrodes, catalysts, etc.

Various conventional methods for preparing copper powders have been proposed, such as mechanical pulverization, atomization, electrolysis, evaporation and chemical wet reduction of copper salts [3–5].

Powders of several metals have been already obtained by the self-propagation high temperature synthesis (SHS, or combustion synthesis) method [6–8]. In all cases the process was carried out using appropriate oxides and different reducers. Advantages of the combustion synthesis approach in comparison with conventional methods are low energy consumption for achieving high temperatures, high rates of conversion, the simplicity of equipment used and high quality of final products. Taking into account these results it is assumed that powdered copper can be also obtained by reduction of copper oxides under the self-sustaining combustion mode.

It is common knowledge that hydrogen [9,10], carbon monoxide [11,12] or carbon [13–15] are often used as reducers in metal oxide reduction. It is assumed that some C_xH_y-type organic polymers (polystyrene, polyethylene, and polypropylene) or $C_xH_yN_z$-type nitrogen-containing organic substances (melamine, urotropin) can be used as reducing agents. These organic compounds contain different reducing elements (C, H) and can also be considered as so called “combined reducers” (CR). The thermodynamic analyses have shown that copper oxide reduction by CRs is characterized with high enough exothermic effect, which allows to obtain copper from copper oxide under the combustion reaction. At the same time, as follows from calculated date, in all cases adiabatic combustion temperature of reduction process is lower than melting point of copper (1083 °C). This fact points to the possibility

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* Corresponding author at: P. Sevak 5/2, 0014, Yerevan, Armenia. Tel.: +374 10 28 16 10; fax: +374 10 28 16 41.

E-mail address: khachat@ichph.sci.am (Kh.V. Manukyan).

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Table 1
The list of reagents used

Initial powder		Trademark	Purity (%)	Particle size (μm)
Cupric oxide	CuO	Tech. conditions of manufacturing 6-09-4680-78	99.7	Less than 60
Polystyrene (PS)	$(-C_8H_8-)_n$	PES-1	99.5	Less than 10
Polyethylene (PE)	$(-C_2H_4-)_n$	PND 277276-273	99.9	Less than 10
Polypropylene (PP)	$(-C_3H_6-)_n$	Tech. conditions of manufacturing 21030-16	99.5	Less than 10
Urotropin (UR)	$(CH_2)_6N_4$	Tech. conditions of manufacturing 6-09-09-353-74	99.9	Less than 10
Melamine (MA)	$C_3H_6N_6$	Tech. conditions of manufacturing 756729-423	99	Less than 10

of obtaining powdered copper under the self-sustaining mode.

In this work the results of copper reduction from the CuO oxide by solid CRs using advanced combustion synthesis method are presented. Combustion laws for CuO–CR systems depending on the type and amounts of applied reducer, inert gas pressure, particle size of copper oxide and other parameters were studied. The factors influencing on the microstructure of reduction product, as well as the reduction mechanism were revealed.

2. Experimental procedure

The combustion process was performed in a constant pressure reactor in argon atmosphere (with a purity of 99.7%, 0.2% oxygen). In Table 1 the list of used initial reagents is shown. A green mixture of the reactants was homogenized in a ceramic mortar. Then cylindrical pellets 20 mm diameter and 40 mm height were made in a stainless steel mold.

During a typical experiment the pellet was placed into the reactor and the combustion was initiated by means of a nickel–chromium wire connected to the power supply, which was programmed to produce an energy pulse by setting 12–18 V for about 1.0–2.0 s. The maximum combustion temperature (T_c) and the temperature distribution on the combustion wave were measured by chromel–alumel thermocouples 100 μm in diameter, previously covered with a thin layer of boron nitride and embedded in the center of the sample at predefined distances from each other. The output signals of thermocouples were transformed by a data logger at the rate of 2 kHz, and were recorded by computer. The average values of combustion velocity (U_c) were calculated as follows: $U_c = l/t$, where l is the distance between thermocouples; t is temporary distance between the signals of thermocouples. The standard error of measurement for T_c and U_c were $\pm 10\,°C$ and 5%, respectively. The combustion products were exposed to XRD analysis with CuKα radiation (DRON-3.0 diffractometer) and SEM observations were performed via *BS-300* scanning electron microscope. Gas-chromatography technique (LQM-72) was used for analyzing combustion gaseous products.

3. Results and discussion

3.1. Thermodynamic analyses for CuO–CR systems

One of the primary tasks to design the combustion synthesis system successfully is to carefully consider the thermodynamics.

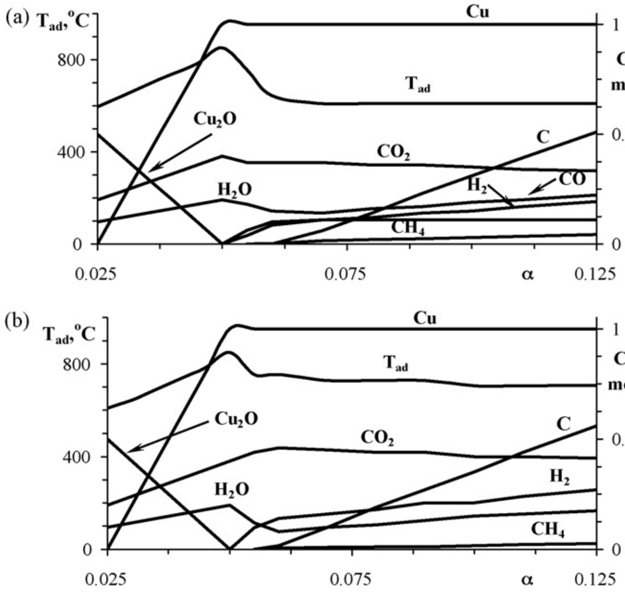

Fig. 1. Thermodynamic analysis for the CuO–αPS system with CO formation (a) and without it (b).

For estimating the value of adiabatic combustion temperature (T_{ad}) and equilibrium composition of the final products, preliminary thermodynamic analyses of the CuO–CR systems were performed using the program "ISMAN–THERMO" [16], developed for multicomponent heterophase systems. Calculation of equilibrium characteristics is based on the minimization of the thermodynamic potential of the system, the expression of which accounts for the contributions of thermodynamic potentials for all the components present in the system taking into account their concentrations.

The results of calculations for the CuO–αPS system (where α is PS/CuO ratio and changes from 0.025 to 0.125) are given in Fig. 1. It should be noted that analyses were performed taking into account the formation of carbon monoxide (Fig. 1a), and its absence (Fig. 1b) in the combustion products[1].

It can be seen that within the interval $0.025 < \alpha < 0.05$ the adiabatic combustion temperature increases from 610 up to 850 °C. It is natural to suppose that the change of T_{ad} resulted from the heat generated at copper oxide reduction. The concentration of polystyrene gradually effects also the equilibrium composition of the products: for $\alpha < 0.05$ the reduc-

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[1] Note, that in the case of only CO_2 formation the stoichiometric ratio: $\alpha = PS/CuO = 0.05$.

Table 2
Combustion parameters, average heating rates of the CuO–CR system in combustion wave, phase compositions and Δm of final products

System	T_c (°C)	U_c (cm/s)	V (°C/s)	Phase composition of combustion products	Δm (%)
CuO–0.05PS	820	0.09	300	Cu; small amounts of Cu_2O	24.1
CuO–0.167PE	720	0.04	120	Cu; Cu_2O	23.7
CuO–0.111PP	700	0.09	100	Cu, Cu_2O and CuO	19.6

tion of CuO occurs incompletely. The interval $0.05 \leq \alpha \leq 0.055$ seems to be optimal, as the thermodynamically expected reaction products are as follows: Cu, H_2O, and CO_2. Within the $0.055 \leq \alpha \leq 0.125$ interval, with taking into account of CO formation in combustion products, the adiabatic combustion temperature is lower by about 100 °C as compared with the absence of carbon monoxide. The lower interaction temperatures can be explained by occurring the $CO_2 + C \Leftrightarrow 2CO$ endothermic reaction. Besides, in the $0.055 \leq \alpha \leq 0.125$ interval for both cases the adiabatic combustion temperature does not depend on α value, which can be related with exothermic decomposition of polystyrene.

Equilibrium concentrations of gaseous compounds (e.g. hydrogen, methane, CO_2(CO), water) were also calculated. It can be seen (Fig. 1) that undesirable carbon (graphite) by-product is also thermodynamically expected at $\alpha > 0.055$ with the basic condensed product (copper).

Similar thermodynamic calculus for CuO–PE(PP) systems were also carried out. The adiabatic combustion temperature diagram and equilibrium compositions of products were found to be analogous with the CuO–PS system. It has been shown that for both systems the maximum adiabatic combustion temperature corresponded to $\alpha = 0.167$ (730 °C) and 0.111 (770 °C), respectively.

Thermodynamic calculations for the reduction of cupric oxide using urotropin and melamine as reducers were also performed. The adiabatic combustion temperatures and equilibrium compositions of products calculated for CuO–UR(MA) systems dependence on CR/CuO ratio had the similar character to the CuO–C_xH_y ones. The maximum combustion temperature (950 °C) for CuO-αUR system is obtained at $\alpha = 0.055$. In the case of melamine maximum interaction temperature was lower enough and made about 650 °C (at $\alpha = 0.111$). In these α values copper is the only solid product of reduction reactions. The results of calculations have also shown that for CuO–UR(MA) mixtures gaseous combustion products basically contain carbon oxides, water, methane, hydrogen, as well as nitrogen.

Summarizing one can see that from thermodynamic viewpoint powdered copper can be prepared by reducing cupric oxide using C_xH_y-type polymers and nitrogen containing substances, such as urotropin or melamine.

3.2. Combustion in the CuO–CR systems

Experiments, performed in accordance with thermodynamic analysis have confirmed that PS, PE, PP and UR reduce copper oxide under the combustion mode, while melamine does not display this ability, probably because of relatively low exothermic effect.

3.2.1. Comparative study of combustion process for CuO-polymer systems

At first comparative study of copper oxide reduction by C_xH_y type polymers was carried out. Particularly, combustion parameters of CuO-polymer systems (mixtures calculated for obtaining pure copper) in inert gas atmosphere ($P = 0.25$ MPa), the temperature distribution within the combustion wave, heating rates and some characteristics of formed products were compared. The studies have shown that the highest combustion temperature (820 °C) was registered when using PS as a reducer (Table 2). On the other hand, in CuO–PE(PP) systems the maximum combustion temperatures were lower by about 100 °C. In all cases combustion velocity did not exceed 0.1 cm/s. Analyses of combustion profiles for CuO-polymer systems (Fig. 2) have shown that in the interaction zone the maximum heating rate ($V = 300$ °C/s) was observed in the case of PS, and for other systems the values of heating rates were three times lower. XRD analyses have shown that in the case of CuO–PS system product obtained contain copper and traces of Cu_2O, while the amount of the last compound tends to grow when passing to the CuO–PE and CuO–PP systems.

Note, that combustion products of the CuO–PP system apart from Cu and Cu_2O contain also significant amounts of non-reacted CuO. These data were compared by measuring the weight gain (Δm, %) of combustion products oxidized in air at 700 °C (see in Table 2). As may be seen, the maximum value of weight gain (24.1%) was observed in the case of oxidation for product obtained at CuO–PS system. Note that the theoretical maximum value of Δm, fitting the case of pure (oxide-free) copper formation is 25.2%). Based on these results it is safe to suggest that polystyrene is the most convenient reducer for copper oxide reduction under the combustion mode.

3.2.2. Combustion of the CuO–PS system

Experiments on combustion of CuO–αPS system have pointed to good correlation with thermodynamic calculations by

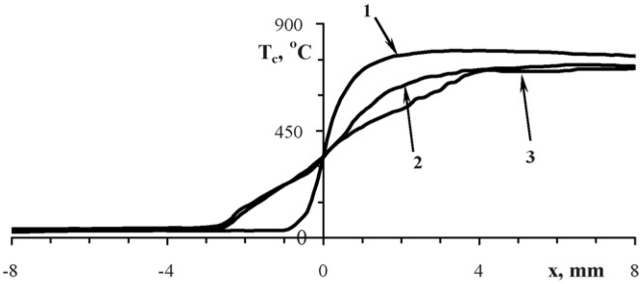

Fig. 2. Combustion profiles for CuO–C_xH_y systems: (1) CuO–PS; (2) CuO–PE; (3) CuO–PP.

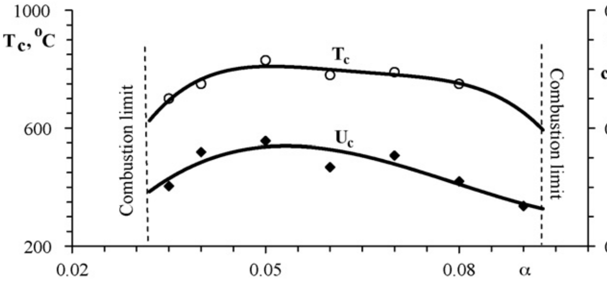

Fig. 3. Combustion parameters vs. ratio of initial compounds for the CuO–αPS system at $P = 0.25$ MPa.

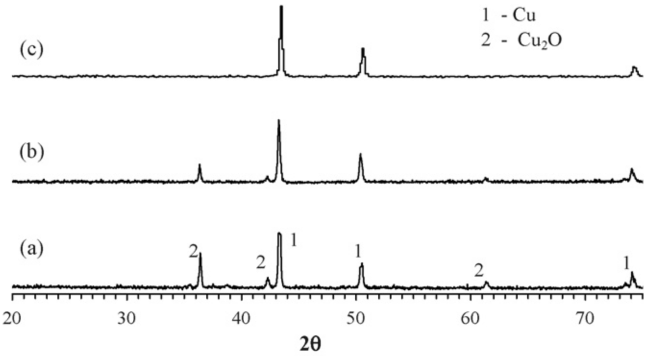

Fig. 5. XRD patterns for the CuO–0.05PS system at inert gas pressures 0.05 MPa (a); 0.2 MPa (b); and 0.5 MPa (c).

the dependency of combustion temperature on α (Fig. 3). Special attention must be given to three features of the interaction in this system: (i) the presence of combustion limits on polystyrene concentration (lower and upper limits were registered for α values 0.035 and 0.09, respectively); (ii) the observed maximum combustion temperature (820 °C at $\alpha = 0.05$) was found to be significantly lower than the melting point of copper (1083 °C); and (iii) the combustion velocity also displays a maximum corresponding to 0.09 cm/s at $\alpha = 0.05$.

It should be noted that for $\alpha > 0.055$ the values of combustion temperatures were higher than adiabatic temperatures when CO was taken into account (Fig. 1a) and were similar to the adiabatic temperatures when CO was excepted in final products (Fig. 1b). Besides, the results of gas-chromatography analysis have shown that at $\alpha = 0.05$ carbon monoxide is absent in gaseous products, and for $\alpha > 0.055$ the amount of CO is very small (20 times smaller than amount of CO_2).

The XRD analyses have indicated that for $0.035 < \alpha < 0.05$ the combustion products contain Cu and significant amounts of Cu_2O. The maximum intensities of copper peaks were registered at $0.05 < \alpha < 0.06$, where only trace amounts of Cu_2O were detected. Visual observations of combustion products have testified that at greater values of α (0.06–0.09) they contain black segments, which were identified as graphite.

For revealing the influence of gas pressure on combustion parameters and phase composition of products interaction in the CuO–0.05PS system was also studied in inert gas atmosphere (Fig. 4). As may be seen an increase in inert gas pressure (from 0.013 to 0.5 MPa) leads to a rise in combustion temperature (from 680 to 820 °C) and velocity (from 0.03 to 0.11 cm/s). XRD data have testified (Fig. 5) that combustion products obtained for pressures up to 0.5 MPa contained copper and cuprous oxide, while at elevated pressures complete reduction of copper oxide was observed (resulting in pure copper). Such character of the reduction process can be explained by the fact that at lower inert gas pressures certain amount of decomposed polystyrene (gaseous intermediates) may move off from the reaction zone prior to reducing the cupric oxide.

Thus, it is obvious that the reduction process in the CuO–0.05PS mixture aimed at obtaining powdered copper may be performed under inert gas pressures higher than 0.5 MPa. It should be noted that in the case of two other polymers at certain pressures of inert gas atmosphere (higher than for reduction by polystyrene) the copper oxide may be completely reduced to pure copper as well.

3.2.3. Combustion laws of the CuO–UR system

Investigations have shown that combustion parameters depending on UR/CuO ratio display similar character as in the CuO–PS system. The maximum combustion temperature (790 °C) and velocity (0.04 cm/s) were registered for $\alpha = 0.055$ at an inert gas pressure of 0.25 MPa. For this system the lower and upper concentration limits of combustion were observed at α values 0.035 and 0.093, respectively.

Influence of inert gas pressure on combustion parameters was studied for the CuO–0.055UR system (Fig. 6). Results obtained have indicated that an increase in gas pressure leads to higher combustion parameters. Particularly, it was established that within the interval of 0.1–0.8 MPa a small increase in the combustion temperature (from 740 up to 830 °C) took

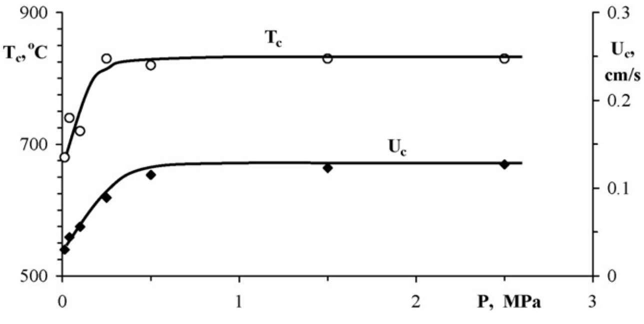

Fig. 4. Combustion temperature (T_c) and velocity (U_c) vs. inert gas pressure for the CuO–0.05PS system.

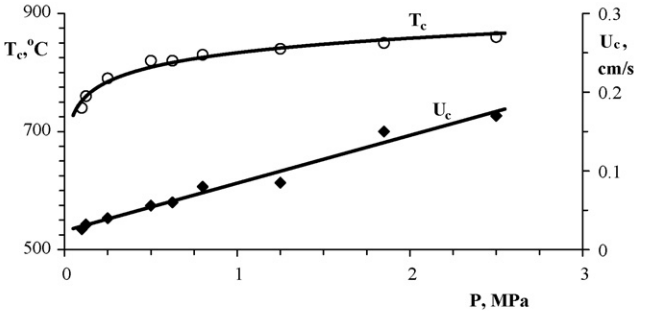

Fig. 6. Combustion temperature (T_c) and velocity (U_c) vs. inert gas pressure for the CuO–0.055UR system.

place. For pressures of 0.8–2.5 MPa the combustion temperature practically does not depend on pressure and changes from 830 up to 860 °C. Simultaneously, at pressures of 0.1–2.5 MPa the combustion velocity increases from 0.026 up to 0.17 cm/s.

XRD analyses for CuO–0.055UR system have shown that at low inert gas pressures (up to 0.5 MPa) combustion products contain copper and significant amounts of unreduced cuprous and cupric oxides. At elevated pressures (from 0.5 to 2.5 MPa) the peaks of cupric oxide in the XRD patterns disappeared (only copper and cuprous oxide were registered), and at higher pressures (more than 2.5 MPa) the combustion product contained copper and traces of cuprous oxide. It is assumed that such incomplete reduction of copper oxide even at relatively higher pressures is conditioned by low decomposition temperature of urotropin (160 °C). Using DTA analysis method (with linear heating rates from 0.04 to 0.33 °C/s) it has been shown [17] that in the CuO–UR system urotropin completely moved off from the initial mixture without reducing any copper oxide. Thus, one can conclude that the possibility of copper oxide reduction by such an easy to decompose reagent as urotropin is conditioned by rather high heating rates (of the order of 100°/s) of the reaction system, which may be realized readily if the reaction proceeds in the combustion mode. On the other hand, the complete reduction is associated with high pressures (more than 2.5 MPa) of the inert atmosphere that is responsible for effective interaction between copper oxide and intermediates of urotropin decomposition before they leave the system.

In Fig. 7 the combustion thermograms for CuO–0.055UR system at various inert gas pressures are presented, and main results for combustion of this system are summarized in Table 3. As may be seen, in the case of 0.1 MPa gas pressure the measured value of average heating rate (minimum) was about 25 °C/s, which is too low for the SHS processes, but is much higher that the heating rates used in DTA.

3.3. Microstrucural features of combustion product

Based on SEM observations the characteristic size of combustion product particles depending on reaction conditions was estimated. It has been revealed that the size of product particle basically depends on combustion temperature and the size of initial copper oxide particles.

An indirect influence of the inert gas pressure on the product particle size and morphology was observed too (Fig. 8). As the combustion temperature for the CuO–0.055UR system was found to be depending on inert gas pressure (see Table 3) and grows from 700 up to 860 °C, this causes enlargement of the product particle size.

Table 3
Combustion parameters of the CuO–0.055UR system and phase compositions of final products at different inert gas pressures

P (MPa)	T_c (°C)	U_c (cm/s)	V (°C/s)	Phase composition of final products
0.1	700	0.025	25	Cu, Cu_2O and CuO
0.5	820	0.055	110	Cu, Cu_2O
0.8	830	0.08	140	Cu, Cu_2O
1.85	850	0.15	160	Cu, Cu_2O
2.5	860	0.17	210	Cu and traces of Cu_2O

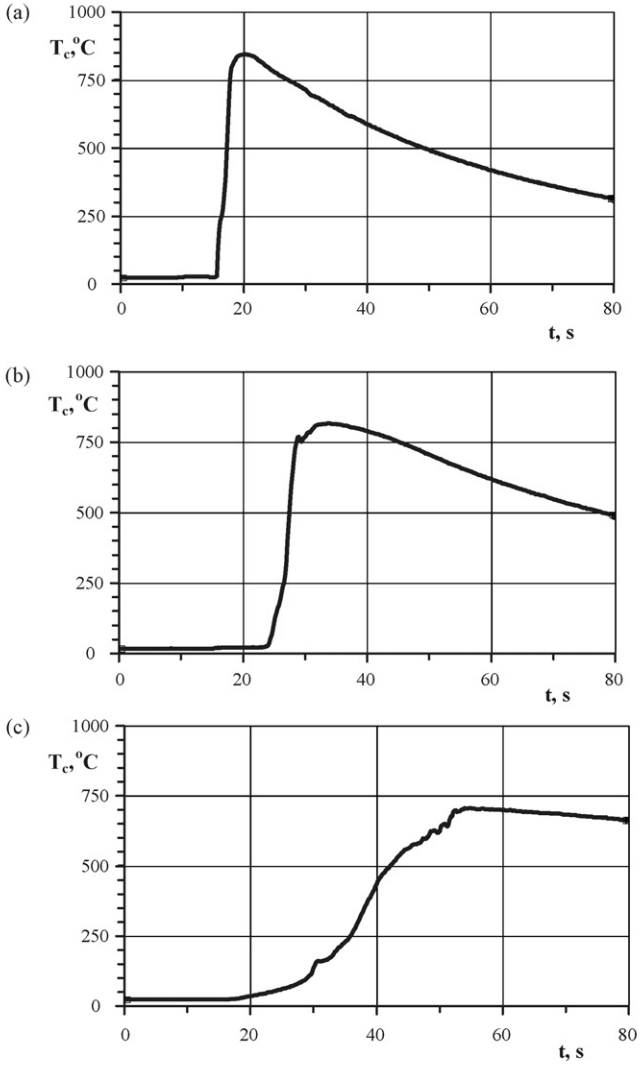

Fig. 7. Combustion profiles of the CuO–0.055UR system at different pressures: (a) −2.5 MPa; (b) −0.8 MPa; (c) −0.1 MPa.

It was revealed that samples burned at lower pressures (Fig. 8b) have morphology similar to the initial oxide powder (non-uniform particles with an average size range 10–30 μm), while at higher pressures (Fig. 8 c and d) enlargement of copper particles was observed. Samples burned at 2.5 MPa pressure consist of particle agglomerates with an average size range of 20–60 μm.

3.4. Reduction mechanism of copper oxide

Based on experimental results obtained and analysis of literature data an approximate scheme of reduction process was suggested. It is assumed that the reduction of copper oxide by combined reducers under the combustion mode begins with decomposition of the reducer. Thus, very initial stages of decomposition are accompanied with allocation of light fragments,

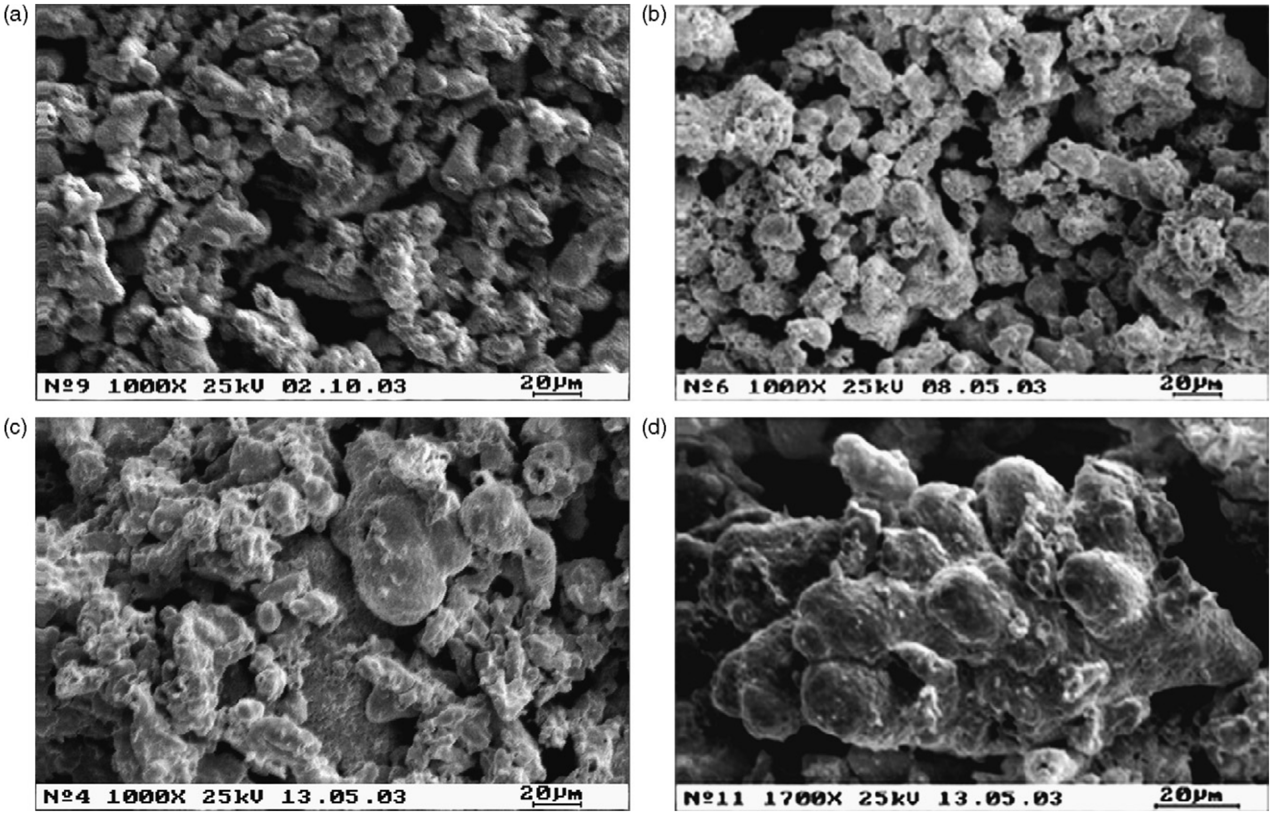

Fig. 8. SEM images of the initial copper oxide (a), and combustion products of the CuO–0.055UR system at inert gas pressures: 0.5 MPa (b); 1.5 MPa (c); (d) 2.5 MPa.

which are capable to reduce copper oxide. Starting from the fact that under certain conditions residual Cu_2O was detected in the combustion products, a two-stage reduction process was supposed to be realized: at the initial stage CuO being reduced to Cu_2O, followed by further reduction to copper. These assumptions are confirmed also by previous investigations on CuO reduction by carbon [18–20]. The sequence of conversions may be described as follows:

$$C_xH_y(UR) \rightarrow P(P_1),$$

$$CuO + P(P_1) \rightarrow Cu_2O + CO_2 + H_2O + (N_2),$$

$$Cu_2O + P(P_1) \rightarrow Cu + CO_2 + H_2O + (N_2),$$

where P and P_1 are gaseous fragments of the polymer and urotropin decomposition.

Completeness of reduction depends on decomposition temperature of the reducer. It was established that incomplete reduction by urotropin is conditioned by its low decomposition temperature, as a result of which significant amounts of gaseous intermediates leave the reaction zone without reacting with copper oxide (at relatively low pressures). On the other hand, as mentioned above, the reduction of CuO by the C_xH_y class polymers proceeded at a high degree in the case of polystyrene. Most likely this fact is associated with the higher reactivity of fragments formed at polystyrene decomposition as compared to those of formed at polyethylene or polypropylene decomposition. This assumption is somewhat supported by the DTA data [17,21] showing that the activation energy for reduction of copper oxide by polystyrene and polyethylene were determined to be 30 and 39 kcal/mol, respectively.

4. Conclusions

It was demonstrated that using combined reducers (polystyrene, polyethylene, polypropylene and urotropin) it is possible to reduce copper oxide to metallic copper under the combustion mode. Experimental investigations based on thermodynamic calculations have allowed to reveal the dependence of combustion parameters for CuO–CR systems on the ratio of reagents in the initial mixture and external pressure. Also the combustion limits depending on the parameters mentioned were determined. The effect of the main process parameters on the phase composition and microstructure of combustion products were found. Optimum conditions for obtaining powdered copper with certain microstructure were determined. Comparing our results with literature data it was concluded that during the reduction process in the CuO–CR system decomposition of organic compound takes place yielding lighter fragments, which react with copper oxide reducing to free copper.

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