The Mechanism of Joint Reduction of MoO$_3$ and CuO by Combined Mg/C Reducer at High Heating Rates

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Abstract

Understanding of the decisive role of the interaction mechanism and kinetics in the combustion processes is highly relevant for the elaboration of optimal conditions for obtaining Mo-Cu composite powders. From this perspective, the efficient delivery of the reduction mechanism of copper and molybdenum oxides with combined Mg + C reducing agents at high heating rates is crucial to develop a valuable approach for the combustion synthesis of Mo-Cu composite powders.

Herein, we shed light on the mechanism of the reactions in all the studied binary, ternary and quaternary systems contemporaneously demonstrating the effect of the heating rate on the conversion degree. The combination of two highly exothermic and speedy reactions (MoO$_3$+3Mg and CuO+Mg vs MoO$_3$+CuO+4Mg) led to a slow interaction with weak self-heating (dysynergistic effect) due to a change in the reaction mechanism. On the other hand, it has been shown that during the simultaneous utilization of the Mg and C reducing agents, the process begins exclusively with carbothermic reduction, and at relatively high temperatures it continues with magnesiothermic one. The effective activation energy values of the magnesiothermic stages of the studied reactions were determined by Kissinger isoconversional method.

Keywords: Joint reduction of oxides; high heating rate; Mg/C combined reducer; dysynergistic effect; activation energy

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1. Introduction

Plasma facing materials (PFMs) build the key structural components for the controlled nuclear fusion engineering pretending to be the basic source of energy for mankind in the 21st century [1,2]. Few refractory metals are nominated as potential candidates for PFMs armors simultaneously possessing high melting temperature, high thermal conductivity, thermal fatigue, low vapor pressure and low sputtering erosion yield (W, Mo and their multicomponent alloys) [1-3]. Copper is a heat-sink component for nuclear fusion devices due to its good thermal conductivity [3]. The conventional welding of Mo and Cu is an extremely difficult task caused by their miscibility gap in both solid and liquid states [4]. However, the so called reactive bonding by the utilization of Mo-Cu composite alloy between Mo and Cu may guarantee the connection of Mo/Cu and promote high-tech development of thermonuclear fusion energy applications. The successful bonding is of primary dependance on the materials used. Self-propagating exothermic reaction (SHS) for synthesizing composite materials and intermetallic compounds has shown its effectiveness in providing predisposition for reactive bonding of various metals due to the released energy capable of melting adjacent particles followed by subsequent solidification and creating favorable conditions for solid joints [5-7]. Moreover, the in-situ preparation of Mo-Cu composite powder by coreduction of metal oxide precursors in SHS process via reaction's coupling approach was demonstrated recently [8,9]. The mechanism and kinetics of reactions in the MoO$_3$-CuO-Mg-C system has been investigated at non-isothermal conditions by DTA/TG method at low heating rates [10]. However, the intensive nature of localised exothermic reactions, with the heating rate of over 10$^2$ K s$^{-1}$, followed by slow cooling of less than 10$^2$ K min$^{-1}$ make it difficult the exploration of the interaction mechanism of condensed constituents (solid, liquid) in the combustion wave.

Without underestimating other transformations, one may note that among nature’s phase transformations the solid-solid and solid-liquid intercollisions are unquestionably the most abundant [11, 12]. They perceive transformations and transitions in alloys and minerals, synthesis of ceramic and composite materials of wide variety. However, despite their considerable technological and scientific importance, the macroscopic kinetics of these transformations remain poorly understood. The mechanisms that underly on these phenomena present substantial challenges for theory, simulation, experiment and application. A central question concerning to their kinetic pathways was studied so far by means of X-ray diffraction, electron microscopy, thermal analysis techniques and didn’t consider the influence of high heating rates on the interaction dynamics being characteristic feature at synthesis in combustion wave. Our recent findings [13] suggest that the investigation of interaction dynamics in condensed phase at heating rates from 100 to 2500 K s$^{-1}$ region grabs valuable knowledge about intermediate states of solid and liquid phases, their nucleation processes, phase and structure formation pathways. Stimulated by the open questions and technical difficulties of kinetics exploration, our experiments sought to follow interaction pathways by a novel thermal analysis technique, so called high speed temperature scanner (HSTS) [14,15]. Here we report on the investigation of the reaction mechanism in CuO-MoO$_3$-Mg-C powder mixtures under high heating conditions (from 100 up to 1200 K min$^{-1}$) up to 1300 °C through revealing the phase- and microstructure formation sequence by HSTS technique. The technique of local high heating enable us to study the sequence of concurrent reduction processes of different oxides, reveal the not obvious reduction mechanism with a Mg/C reductant pair, the effect of heating rate on the conversion degree. The multi-step transformations in the CuO-MoO$_3$-Mg-C powder mixtures was demonstrated to be significantly influenced by the formation of intermediate molybdates, even up to the drastic change in reaction pathway.
Furthermore, the comparative overview of Arrhenius kinetic parameters enabled to directly identify beneficial precursors, to study the main facets of phases involved per stage, indicate which direction should be preferred when designing the reduction process.

2. Materials and methods

MoO$_3$ (High grade, Pobedit Company, Russia, particle size < 15 μm), CuO (High grade, STANCHEM, Poland, particle size < 40 μm), magnesium powder (MPF-3, Russia, particle size 150-300 μm) and carbon black (P-803, Russia, particle size < 1 μm) powders were utilized as precursors.

The mechanism of reduction of copper and molybdenum oxides mixture by Mg/C combined reducers under conditions of high heating rates was investigated by HSTS technique. It allows to carry out experiments in a wide range of heating rates (from 10 to 10000 K min$^{-1}$) up to 1300 °C. The HSTS operation is based on the direct electric heating of thin metallic foil (e.g. Ni foil with 0.05-0.1 mm thickness). The small amount of powder (about 50 mg) is placed inside the middle part of thin metallic heater and then was heated by direct electrical current in the HSTS reaction chamber (Figure 1). Before heating, the chamber is sealed, evacuated and filled with argon of 0.1 MPa pressure (Ar, 99.98% purity, oxygen <0.1%). The heating of the sample was carried out in a pre-programmed heating mode, and the temperature change (up to 1300 °C) was recorded using K type chromel-alumel thermocouples fixed in the central area of the foil and with a photocell fixed to the reactor wall. The inert experiment is characterized by linear temperature-time history defined by the heating rate and coinciding with the reactive temperature profile where interactions are absent. The reaction onset temperature ($T_o$), the maximum peak temperature observed during self-heating ($T_{max}$) and the temperature prescribed by linear heating, where the maximum exothermic effect is observed ($T^*$) were determined from the heating thermograms [13].

During the heating, the process was interrupted at characteristic temperatures and the quenched samples were subjected to XRD analysis (diffractometer DRON-3.0, Burevestnik, Russia, CuKα radiation, 25 kV, 10 mA).

Figure 1. The experimental steps for the kinetic studies using high-speed temperature scanner.

(a) envelope-heater with reactive mixture under study; (b) reaction chamber and controller: 1 - reactive mixture, 2 - boat made from nickel foil, 3 - powder mixture in Ni boat, 4 - envelope with mixture and thermocouple, 5 - heated sample, 6 -reaction chamber, 7 - electronic unit and PC for control and registration.
Besides, for the characterization of the samples cooled at characteristic temperatures, the IR spectral analysis (PerkinElmer Spectrum Two FT-IR, TL8000) was utilized as well. Based on the results of HSTS investigations in a heating rate region of 100-1200 K min\(^{-1}\), the effective activation energy values of magnesiothermic reduction stage for all studied mixtures were determined by Kissinger method.

### 3. Results and discussion

In our previous works [8, 16-17], energy-saving combustion synthesis was applied for the joint reduction of MoO\(_3\) and CuO utilizing Mg+C combined reducer. The privilege of such reducing mixture is to govern the reaction thermal regime in a wide range of temperature and to prepare Mo-Cu composite powders in a controllable combustion conditions. As extreme conditions in the combustion wave make it difficult to disclose the interaction mechanism, the process was preliminary modelled at “soft” conditions (e.g., low heating rates and adjusting the process within the time) using the DTA/TG technique [10] under programmed heating rates from 5 to 20 K min\(^{-1}\) up to 1000 °C. Furthermore, to monitor and reveal mechanism of the combustion reaction due to its high velocity is still the challenge. Here we report the results of study of the reaction mechanism in CuO-MoO\(_3\)-Mg-C powder mixtures under conditions of high heating rates (from 100 to 1200 K min\(^{-1}\)) up to temperature 1300 °C through revealing the phase- and microstructure formation sequence by HSTS-1 setup. Firstly, the reduction pathways were studied in binary (CuO-MoO\(_3\), MoO\(_3\)-Mg, MoO\(_3\)-CuO, CuO-C) and ternary (MoO\(_3\)-Mg-C, MoO\(_3\)-CuO-Mg, and MoO\(_3\)-CuO-C) systems, then the quaternary CuO-MoO\(_3\)-Mg-C system under the same heating conditions was examined. The mechanism of copper oxide reduction under fast heating conditions both with Mg and (Mg+C) reducers is detailed in [13]. The interaction patterns in the CuO-Mg \(\alpha\) CuO-Mg-C systems here are presented for the purpose of comparative discussion.

#### 3.1. CuO-MoO\(_3\), CuO-C, MoO\(_3\)-C, MoO\(_3\)-Mg Binary Systems

##### 3.1.1. CuO-MoO\(_3\) system

It is well documented that the interaction of copper and molybdenum oxides is accompanied by the formation of molybdates of different composition, depending on the processing/synthesis conditions [10, 18]. In particular, when an equimolar mixture of copper and molybdenum oxides is heated at 20°C/min heating rate, a weak endothermic reaction in a quite wide temperature range (470-650 °C) results in the formation of the salt of CuMoO\(_4\) composition. When the same mixture is heated at 300°C/min heating rate (Figure 2) a weak endothermic interaction is observed in the temperature range of 550-630 °C, which corresponds to the formation of copper molybdates of different ratios (\(\alpha\)-CuMoO\(_4\), Cu\(_3\)Mo\(_2\)O\(_9\)) resolved by X-ray analysis. In the sample quenched at the mentioned temperature there is also unreacted MoO\(_3\). Later, at temperatures above 700 °C, a wide endothermic range is observed, which is expected to be the sum of several transformations, in particular, corresponding to the continuation of the salt formation process (the amount of molybdenum oxide decreases in the product) and to the change in modification of the produced salt (\(\alpha\)-CuMoO\(_4\) to CuMoO\(_4\) III conversion) [19-21]. Note that, the complete formation of only CuMoO\(_4\) III was possible to achieve only by holding reactive mixture at 800 °C by 10 min. Meanwhile, under slow heating rate by DTA/TG method (5-20 K min\(^{-1}\)) the salt formation ends relatively earlier, at 650 °C. To complement the aforementioned observations, the FTIR (Figure 3) bands of the CuMoO\(_4\) were detected at 460, 865 and 965 cm\(^{-1}\). The peak at 865 cm\(^{-1}\) is assigned to vibrations of the Mo=O–Mo. The featured peak at
965 cm\(^{-1}\) is attributed to Mo=O bond frequency. Furthermore, the absorption peak at 460 cm\(^{-1}\) is assigned to superposition of bending mode of MoO\(_3\) lattice and stretching vibration of square planar CuO\(_4\). IR peaks of Cu\(_3\)Mo\(_2\)O\(_9\) and MoO\(_3\) were appeared at 717 cm\(^{-1}\) and 560 cm\(^{-1}\), respectively, in their fingerprint region matching well with the literature reports [22, 23]. IR peaks appeared at 810 cm\(^{-1}\) and 1380 cm\(^{-1}\) correspond to in-plane B-N stretching and out-plane B-N-B bending vibrations, respectively, of boron nitride which the thermocouple was covered by during HSTS experiments. Some of the bands of Cu\(_3\)Mo\(_2\)O\(_9\) were overlapped (818 cm\(^{-1}\), 902 cm\(^{-1}\), 942 cm\(^{-1}\) and 969 cm\(^{-1}\)) with the CuMoO\(_4\) bands in the 800-1000 cm\(^{-1}\) region and didn’t observed due to their lower intensity compared to CuMoO\(_4\) peaks.

**Figure 2.** The heating thermogram of the CuO+MoO\(_3\) mixture with the XRD analysis results of the quenched samples at different characteristic temperatures, A - T=500, B - 650, C - 750, D - 800, E - 800 (t=10 min) °C, V\(_h\)=300 K min\(^{-1}\).

**Figure 3.** The IR spectrum of the product obtained from CuO+MoO\(_3\) mixture cooled from 750 °C, V\(_h\)=300 K min\(^{-1}\).
3.1.2. CuO-C system

Carbothermic reduction of copper oxide (CuO + C) is a successive two-stage weak exothermic process (Figure 4). The first stage takes place in the temperature range 550-700 °C and is accompanied by partial reduction of CuO with the formation of Cu2O (Figure 4 B,C). The second stage begins at temperatures above 700 °C and corresponds to the formation of copper from copper suboxide (Figure 4 C-D). The further increase in temperature leads to an increase in the conversion degree and pure copper formation (Figure 4 D).

![Figure 4](image)

**Figure 4.** The heating thermogram of the CuO+C mixture with the XRD analysis results of the quenched samples at different characteristic temperatures, A - T=500, B - 600, C - 700, D - 880 °C, \( V_h=300 \text{ K min}^{-1} \).

It is worthy of remark that in the range of low heating rates (5-20 K min\(^{-1}\)) a stepwise reduction was also observed, but the interaction was started at a temperature lower by about 100 °C [10].

3.1.3. MoO\(_3\)-C system

Two weak exothermic and one endothermic peaks occur during the carbothermic reduction of molybdenum oxide (MoO\(_3\)+2C) (Figure 5). The process begins with a weak exothermic interaction (660-790 °C) corresponding to the formation of molybdenum dioxide (B) according to the following reaction scheme:

\[
\text{MoO}_3 + C \rightarrow \text{MoO}_2 + \text{CO}_2 \text{ (+trace amount of CO)} \quad (660-790 \degree C).
\]

Under further heating conditions, the reduction process continues with the residual carbon. In particular, a weak endothermic interaction occurs in the temperature range 1000-1100 °C, and in the XRD pattern of the quenched sample MoO\(_2\) and Mo\(_2\)C (C) are identified as a result of the following interaction:

\[
\text{MoO}_2 + C \rightarrow \text{Mo}_2\text{C} + \text{CO}/\text{CO}_2 \quad (1000-1100 \degree C).
\]

Further increase in temperature lead to the formation of metallic molybdenum (D) according to the following scheme:

\[
\text{MoO}_2 + \text{Mo}_2\text{C} \rightarrow \text{Mo} + \text{CO}/\text{CO}_2 \quad (1210-1300 \degree C).
\]

As compared to low heating rates (\( V_h=20 \text{ K min}^{-1} \)) [24], the carbothermic reduction of molybdenum trioxide is also a two-step process. And again, the first stage (MoO\(_3\)→MoO\(_2\)) is a weak exothermic reaction (but at lower temperature - 560-680 °C), and the second is an endothermic one (>850 °C) accompanied by the formation of...
metallic molybdenum and/or molybdenum carbide. Thus, in contrast to the low heating rate, at high heating rates these stages are shifted to a higher temperature range, which makes it possible to achieve complete reduction of metallic molybdenum at high temperature.

![Graph showing heating thermogram of MoO₃+2C mixture with XRD analysis results of quenched samples at different characteristic temperatures, A - T=620, B - 790, C - 1100, D - 1300 °C, Vₜ=300 K min⁻¹.](image)

**Figure 5.** The heating thermogram of the MoO₃+2C mixture with the XRD analysis results of the quenched samples at different characteristic temperatures, A - T=620, B - 790, C - 1100, D - 1300 °C, Vₜ=300 K min⁻¹.

### 3.1.4. MoO₃-Mg system

By the next, the magnesiothermic reduction mechanism of MoO₃+3Mg mixture was examined in a wide range of heating rates, 100-1200 K min⁻¹. Magnesiothermic reduction of molybdenum oxide over the entire heating rate region occurs with molten magnesium. With an increase in the heating rate from 100 up to 1200 K min⁻¹ an increase in characteristic temperatures (T, T*, T max) was observed. In addition, at heating rates of 100-300 K min⁻¹ (Figure 6), the process begins immediately after the melting of magnesium. In particular, at a heating rate of 300 °C/min, the reduction begins at 670 °C along with a severe exothermic peak (670-785 °C) on the heating thermogram with a maximum temperature of 1150 °C (T*=740 °C). As compared to the reduction of copper oxide with magnesium, that began approximately at the same temperature range at 300 K min⁻¹ heating rate (680-800 °C, T*=720 °C, T max=1285 °C) [13]. At higher heating rates (600 and 1200 K min⁻¹) the reduction process of MoO₃ begins quite late after the melting of magnesium at temperatures of 790 and 810 °C, respectively.
The XRD pattern of the sample quenched at a temperature of 650 °C (A) contains only characteristic diffraction lines of MoO$_3$ and Mg ($V_h = 300$ K min$^{-1}$). Immediately after the exothermic interaction, a partial reduction of molybdenum oxide with the formation of MoO$_2$ (B) was observed. Further increase in temperature leads to the formation of molybdenum, but in parallel to the reduction process the formation of MgMoO$_4$ salt also occur (C, D). However, MgMoO$_4$ is absent at the end of the process, but some unreduced molybdenum dioxide is registered. Incomplete reduction of molybdenum oxide can be explained by the vigorous manner of the interaction and evaporation of magnesium.

3.2. MoO$_3$–Mg–C, MoO$_3$–CuO–Mg and MoO$_3$–CuO–C ternary systems
3.2.1. MoO$_3$–Mg-C system
In the ternary MoO$_3$-Mg-C system, at low heating rate of 20 K min$^{-1}$, the interaction began before the melting of magnesium at 560-630 °C according to the results of work [10]. And the weak exothermic carbothermic reduction was attributed to the reduction of MoO$_2$ from MoO$_3$. The process was further continued with magnesiothermic reduction after the melting of the magnesium up to the formation of metallic molybdenum at 700-800 °C. In the contrary, at high heating rates, the process begins with the melting of magnesium at 660 °C, which is immediately followed by the carbothermic reduction of molybdenum (VI) oxide and lead to the formation of molybdenum dioxide at a temperature of 680-800 °C (Figure 7).
Figure 7. The heating thermogram of the MoO$_3$+1.5Mg:C mixture with the XRD analysis results of the quenched samples at different characteristic temperatures, A - T=650, B - 800, C - 880, D - 1000, E - 1150, F - 1300 °C, $V_h=300$ K min$^{-1}$

In contrast to the pure carbothermic reduction of molybdenum (VI) oxide (see Section 3.1.3), in the case of utilizing Mg/C combined reducers, the formation of molybdenum carbide was not observed and the formation of molybdenum occurs as a result of a strong exothermic interaction of MoO$_2$ and magnesium (300 K min$^{-1}$, 850-890 °C, T*=860 °C). The maximum exothermic temperature of the magnesio-carbothermic interaction is registered to be 1350°C, which is by ~200°C higher than the temperature recorded during the pure magnesiothermic reduction reaction of molybdenum oxide.

For the comparative overview, one may note, that in the CuO-0.5Mg-0.5C system the interaction began immediately after the melting of magnesium with carbothermic reduction of CuO up to the formation of copper suboxide. Then magnesium continues the reduction of Cu$_2$O up to the metallic copper formation [13].

3.2.2. CuO-MoO$_3$-Mg system

According to the heating thermogram of CuO+MoO$_3$+4Mg mixture, the process of joint magnesiothermic reduction of copper and molybdenum oxides (Figure 8) is preceded by the melting of magnesium. The weak endothermic effect observed after magnesium melting is accompanied with the formation of copper molybdate (Cu$_3$Mo$_2$O$_9$) at 800 °C, which is immediately followed by the salt reduction process and the formation of metallic copper (870-1000 °C). Metallic molybdenum is formed at a higher temperature range (1000-1100°C).

The aforementioned considerations were confirmed by X-ray analysis of the samples quenched at characteristic temperatures, according to which the XRD pattern of the sample interrupted at point C contains Cu$_6$Mo$_5$O$_{18}$, Mg$_2$MoO$_4$, Cu$_2$O, Cu, Mg. At higher temperatures, between 1100 °C and 1200 °C, there are characteristic peaks of molybdenum and MgO-MoO$_2$ mixed oxide as well. The latter occurs as a result of the interaction between MgO and MoO$_2$. 
The data derived from the analysis of the heating thermograms revealed, that in contrast to the magnesiothermic reduction of individual oxides, which are highly exothermic interactions (CuO+Mg with $T^*=720 \, ^\circ C$, $T_{\text{max}}=1210 \, ^\circ C$ [13] and MoO$_3$+3Mg with $T^*=740 \, ^\circ C$; $T_{\text{max}}=1155 \, ^\circ C$), the combined magnesiothermic reduction of oxides proceeds with weak exothermic stages. As a matter of fact, when two highly exothermic reactions, MoO$_3$+3Mg and CuO+Mg, are carried out together, a slow interaction is observed, which exhibits a typical dysynergistic effect and may be explained by a total change in the interaction pathway. In particular, as follows from the XRD analysis results of the samples quenched at different stages of the interaction, the reduction process of metal oxides by magnesium is preceded by the formation of Cu$_3$Mo$_2$O$_9$ salt. In addition, the magnesiothermic reduction of Cu$_3$Mo$_2$O$_9$ is significantly slower as compared to the reduction of individual oxides. Indeed, according to the XRD data obtained, after the melting of magnesium before the initiation of the reduction process of oxides, a copper molybdate Cu$_3$Mo$_2$O$_9$ (at 800 $^\circ C$) is identified (Figure 8B) along with copper oxide. This is further followed by the gradual/stepwise reduction of the salt and accompanied firstly by the formation of Cu, Cu$_2$O, MgMoO$_4$, Cu$_6$Mo$_5$O$_{18}$.

To explain the difference between the combined and separate reduction processes of molybdenum and copper oxides, the magnesiothermic reduction of CuMoO$_4$ salt was studied at the same heating rate, 300 K min$^{-1}$ (Figure 9). From the heating curve of the reduction of CuMoO$_4$ by magnesium, two successive and weak exothermic stages were revealed. Similar to the combined magnesiothermic reduction of oxides (after the salt formation process), the melting of magnesium at 650 $^\circ C$ is immediately followed by the weak exothermic reduction of copper (670-880 $^\circ C$), and later the weak exothermic reduction of molybdenum in the temperature range of 1060-1070 $^\circ C$ (Figure 9).

**Figure 8.** Heating thermogram of the CuO+MoO$_3$+4Mg mixture with the XRD analysis results of the quenched samples at different characteristic temperatures, A - $T=650$, B - 870, C - 1000, D - 1100, E - 1200 $^\circ C$, $V_h=300 \, K \, \text{min}^{-1}$.
3.2.3. CuO-MoO$_3$-C system

In the ternary CuO+MoO$_3$+3C system (Figure 10) the reduction process begins with the weak endothermic reaction of copper molybdate formation (B), followed by a weak exothermic interaction. According to XRD analysis results, the complete reduction of copper and partial reduction of molybdenum (C) occur during the weak exothermic reaction. Further increase in temperature leads to the formation of molybdenum carbide (D, 1000 °C). And at higher temperatures (T≥1150 °C), by the interaction of molybdenum carbide and dioxide metallic molybdenum is formed. The sequence of processes in CuO+MoO$_3$+3C system can be represented by the following scheme:

MoO$_3$+CuO $\rightarrow$ Cu$_6$Mo$_5$O$_{18}$+Cu+MoO$_2$, \( T=550-640 \) °C

Cu$_6$Mo$_5$O$_{18}$+C$\rightarrow$Cu+MoO$_2$+CO/CO$_2$, \( T=650-750 \) °C

MoO$_2$+C$\rightarrow$Mo$_2$C+CO/CO$_2$, \( T=750-1120 \) °C

MoO$_2$+Mo$_2$C$\rightarrow$Mo+CO/CO$_2$, \( T=1120-1300 \) °C

Thus, it can be inferred from the experimental evidences detailed above, that the joint reduction of CuO and MoO$_3$ oxides with separate reducers, such as magnesium or carbon, does not lead to the complete reduction of metals (Mo and Cu).

Figure 9. The heating thermogram of the CuMoO$_4$+4Mg mixture with the XRD analysis results of the quenched samples at different characteristic temperatures, A - T=650°C, B - 850, C - 1050, D - 1140, E - 1300 °C. \( \nu_v=300 \) K min$^{-1}$. 

3.2.3. CuO-MoO$_3$-C system

In the ternary CuO+MoO$_3$+3C system (Figure 10) the reduction process begins with the weak endothermic reaction of copper molybdate formation (B), followed by a weak exothermic interaction. According to XRD analysis results, the complete reduction of copper and partial reduction of molybdenum (C) occur during the weak exothermic reaction. Further increase in temperature leads to the formation of molybdenum carbide (D, 1000 °C). And at higher temperatures (T≥1150 °C), by the interaction of molybdenum carbide and dioxide metallic molybdenum is formed. The sequence of processes in CuO+MoO$_3$+3C system can be represented by the following scheme:

MoO$_3$+CuO $\rightarrow$ Cu$_6$Mo$_5$O$_{18}$+Cu+MoO$_2$, \( T=550-640 \) °C

Cu$_6$Mo$_5$O$_{18}$+C$\rightarrow$Cu+MoO$_2$+CO/CO$_2$, \( T=650-750 \) °C

MoO$_2$+C$\rightarrow$Mo$_2$C+CO/CO$_2$, \( T=750-1120 \) °C

MoO$_2$+Mo$_2$C$\rightarrow$Mo+CO/CO$_2$, \( T=1120-1300 \) °C

Thus, it can be inferred from the experimental evidences detailed above, that the joint reduction of CuO and MoO$_3$ oxides with separate reducers, such as magnesium or carbon, does not lead to the complete reduction of metals (Mo and Cu).
3.3. CuO-MoO$_3$-Mg-C quaternary system

After detailed consideration of the behavior of the binary and ternary systems, a quaternary system with a composition of CuO+MoO$_3$+1.2Mg+2.15C was selected according to the optimum area of thermodynamic calculations for the joint and complete reduction of Mo and Cu metals [8]. In the selection of the mentioned composition, the combustion synthesis behavior of individual oxides with combined reducer was also considered.

In the CuO+MoO$_3$+1.2Mg+2.15C mixture, the process begins before the magnesium melting, with the carbothermic reduction of copper oxide at temperatures up to 600 °C (Figure 11). This is evidenced by the presence of Cu$_2$O and the absence of MgO in the sample quenched at 600 °C (Figure 11B). During further heating, magnesium melts, and molybdenum oxide is reduced by carbon (MgO is still absent in the product) up to molybdenum dioxide. At a temperature range of 940-990 °C, the magnesiothermic reduction of MoO$_2$ occurs with the formation of metallic molybdenum with maximum temperature of 1250 °C. The further increase in temperature contributes to the increase in conversion degree (F). The formation of molybdenum carbide by an interaction of the obtained molybdenum and/or molybdenum dioxide with carbon is not excluded.

According to a DTA/TG studies conducted at [10] at a heating rate of 20 K min$^{-1}$ in the CuO-MoO$_3$-Mg-C system, the interaction also begins before the magnesium melting. At 600 °C, a parallel reduction of the oxides takes place: copper oxide is reduced to copper via two-step mechanism, and molybdenum oxide - to MoO$_2$. In addition, at low heating rates, the magnesiothermic reduction process of molybdenum dioxide occurs at a lower temperature range: it begins immediately after the melting of magnesium (650 °C) and molybdenum formation is observed at 720 °C. At the end of the process, the product contains also complex oxide of MoO$_2$ and magnesia.
It was established that regardless the heating rate, the complete reduction of copper oxide and the first stage of reduction of molybdenum trioxide proceed with carbon followed by magnesiothermic or Mg+C combined reduction of MoO₂. In the case of slow heating the process was completed at 880 °C and carbidization was not observed [10], but MoO₂ was present in the quenched product along with target compounds. At high heating rates the process was completed at 1300 °C and may be accompanied by the formation of molybdenum carbide. This difference in the phase composition of the products is conditioned by the difference in heating rates (Table 1), as well as by the difference in maximum temperatures (880 °C vs 1300 °C). In particular, at low heating rates (V_h=20 K min⁻¹), the product contains molybdenum dioxide together with the main product. At relatively high heating rates (100-1200 K min⁻¹) molybdenum dioxide and molybdenum carbide were observed, and at heating rates region from 2600-5200 K min⁻¹ molybdenum carbide is present in addition to the target materials. In the combustion synthesis, where the heating rate reaches up to 60,000 K min⁻¹ [8], complete reduction was observed with the formation of target substances - Mo, Cu, MgO due to utilization of combined reducers in the corresponding mixture with composition CuO+MoO₃+1.2Mg+2.15C. Considering, that combustion synthesis of molybdenum carbide proceeds in the solid phase by the reaction diffusion mechanism, diffusion of carbon through the Mo carbide phase was believed to be the limiting stage of the carbidization process, thus it was possible to avoid carbidization reaction during extremely high heating conditions of the combustion wave. Thus, in the CuO+MoO₃+1.2Mg+2.15C mixture at the heating rate of 300 K min⁻¹ the following sequential processes take place:

\[
\begin{align*}
\text{CuO} + \text{C} & \rightarrow \text{Cu}_2\text{O} + \text{CO/CO}_2, \ T=560-670 \ ^\circ\text{C} \\
\text{Cu}_2\text{O} + \text{C} & \rightarrow \text{Cu} + \text{CO/CO}_2, \ T=670-750 \ ^\circ\text{C} \\
\text{MoO}_3 + \text{C} & \rightarrow \text{MoO}_2 + \text{CO/CO}_2, \ T=650-750 \ ^\circ\text{C} \\
\text{MoO}_2 + \text{Mg} & \rightarrow \text{Mo} + \text{MgO}, \ T=940-990 \ ^\circ\text{C} \\
\text{MoO}_2 + \text{C} & \rightarrow \text{Mo}_2\text{C} + \text{CO/CO}_2, \ T>900 \ ^\circ\text{C}
\end{align*}
\]
Mo+C $\rightarrow$ Mo$_2$C, T>900 °C

**Table 1.** The influence of heating rate on the characteristic temperatures and phase composition of the products of the quaternary CuO-MoO$_3$-Mg-C system

| $V_h$, K min$^{-1}$ | The system under study | T, °C | XRD | T, °C | XRD | T, °C | XRD |
|---------------------|------------------------|-------|-----|-------|-----|-------|-----|
| 20                  | CuO+MoO$_3$+1.1Mg+2C    | 480-520 | Cu$_2$O, MoO$_3$, Mg | 520-600 | MoO$_2$, Cu, Mg | 740-770 | T$_{max}$=760 | Mo, Cu, MgO, MgO-MoO$_2$ |
| 100                 | CuO+MoO$_3$+1.2Mg+2.15C | 500-550 | Cu$_2$O, MoO$_3$, Mg | 650-730 | MoO$_2$, Cu, Mg | 870-890 | T$_{max}$=940 | Mo, Cu, MoO$_2$ (main product), Mo$_2$C, MgO |
| 300                 | CuO+MoO$_3$+1.2Mg+2.15C | 560-600 | Cu$_2$O, MoO$_3$, Mg | 660-740 | MoO$_2$, Cu, Mg | 940-990 | T$_{max}$=1250 | Mo, Cu, MgO, MoO$_2$(trace), Mo$_2$C |
| 2600                | CuO+MoO$_3$+1.2Mg+2.15C | 570-610 | Cu$_2$O, MoO$_3$, Mg | 760-960 | MoO$_2$, Cu, Mg | 1120-1310 | T$_{max}$=1290 | Mo, Cu, MgO, Mo$_2$C |
| 5200                | CuO+MoO$_3$+1.2Mg+2.15C | 580-620 | Cu$_2$O, MoO$_3$, Mg | 780-990 | MoO$_2$, Cu, Mg | 1130-1360 | T$_{max}$=1310 | Mo, Cu, MgO, Mo$_2$C(trace) |

The experimental studies demonstrated that using a combined Mg/C reducer under fast heating conditions confer the possibility to carbon to interact at a lower temperature than magnesium, prevent the salt formation process, which outstrip the reduction process when only the magnesium is used as a reducer. The temperature shift of the reduction process facilitates the joint and complete reduction of the both metals without the noticeable presence of secondary products.

3.4. The effective activation energy of magnesiothermic reactions

Based on the results of experiments performed in a wide range of high heating rates (100-1200 K min$^{-1}$), the effective values of the activation energy for the magnesiothermic reduction processes in the studied systems were calculated by isoconversional method of Kissinger [25].

The derived expression for determination of activation energy by Kissinger has the following form:

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

(1)

where, $V_h$ is the heating rate (K min$^{-1}$), $T_{max}^{DTA}$ is the temperature corresponding to the maximum advance in the DTA curve (K), A is the pre-exponential factor, E is the effective activation energy of the process, (kJ mol$^{-1}$), R is universal gas constant (8.31 J K$^{-1}$ mol$^{-1}$).

In particular, the activation energy of the magnesiothermic reduction reaction of MoO$_3$ (Figure 12 (1)) was calculated to be 110 kJ mol$^{-1}$, which is about 4 times less than the $E_a$ value of magnesiothermic reduction of copper oxide ($E_{a(CuO+Mg)}$=324 kJ mol$^{-1}$) [13]. The both values of the activation energy for the MoO$_3$+3Mg and
CuO+Mg reactions refer to the reduction process with molten Mg, where $T^* > T_{Mg_{melt}}$ in the whole range of surveyed heating rates.

![Figure 12. Linear fitting of the $-\ln(V_h/(1/T^*)) - 1/T^*10^3$ plot to extract effective activation energy of the magnesiothermic reactions in the MoO$_3$+3Mg (1), MoO$_3$+1.5Mg+C (2), CuO+MoO$_3$+1.2Mg+2.15C (3) mixtures. $V_h$=100-1200 K min$^{-1}$](image)

The effective activation energy value of the magnesiothermic reduction stage in the MoO$_3$+1.5Mg+C mixture is 102 kJ mol$^{-1}$ (Figure 12 (2)), which is commensurable with the activation energy value of magnesiothermic reaction in the MoO$_3$+3Mg mixture stated above (110 kJ mol$^{-1}$).

As it was previously delivered in [13], in the CuO+0.5Mg+0.5C mixture, the interaction began with carbothermic reduction immediately after melting of magnesium and led to the formation of copper suboxide. The reduction of Cu$_2$O is then continued with magnesium. The activation energy value of Cu$_2$O+Mg reaction is 320 kJ mol$^{-1}$, which is approximately 3 times higher than the activation energy value of the magnesiothermic reduction reaction in the MoO$_3$+1.5Mg+C mixture.

In the CuO+MoO$_3$+1.2Mg+2.15C mixture the activation energy of the magnesiothermic reduction stage (MoO$_2$+Mg) is calculated to be 155 kJ mol$^{-1}$ (Figure 12 (3)). It is comparatively higher than $E_a$ value for the MoO$_3$+1.5Mg+C mixture, but about 2 times lower than $E_a$ value of the CuO+0.5Mg+0.5C mixture (102 kJ mol$^{-1}$ and 320 kJ mol$^{-1}$, respectively) [13], indicating about the change in mechanism of interaction due to use of combined reducers.

The values of the effective activation energies calculated for the investigated reactions at high heating rates are presented in Table 2 and collated with the results obtained by DTA/TG method at low heating rates.

| Table 2. Effective activation energy values for the magnesiothermic reduction reactions |
|---------------------------------------------|------------------|------------------|------------------|
| Reaction mixture under study | Exothermic reaction | $E_{act}$, kJ mol$^{-1}$ | $E_{act}$, kJ mol$^{-1}$ |
| CuO+Mg | CuO+Mg | 424 [13] | 424 [26] |
| MoO$_3$+3Mg | MoO$_3$+3Mg | 110 [this work] | 123 [27] |
| CuO+0.5Mg+0.5C | Cu$_2$O+0.5Mg | 320 [13] | - |
| MoO$_3$+1.5Mg+C | MoO$_2$+1.5Mg | 102 [this work] | 197 [27] |
| CuO+MoO$_3$+1.2Mg+2.15C | MoO$_2$+2.5Mg | 155 [this work] | - |
According to the data obtained, the magnesiothermic reduction of copper oxide is characterized by the highest value of the activation energy, which decreases when carbon is introduced into the system demonstrating the expediency of utilization of combined reducers.

In MoO$_3$+3Mg and MoO$_3$+1.5Mg+C mixtures, the magnesiothermic reduction is characterized by a lower activation energy value. And the energy of activation of joint reduction of oxides with combined reducers is 155 kJ mol$^{-1}$, which can be attributed to the magnesiothermic reduction of molybdenum dioxide in the presence of already reduced copper.

**Conclusions**

The study on a separate and joint reduction mechanism of copper and molybdenum oxides with combined reducers (Mg + C) under the fast heating conditions revealed that in all the studied systems (CuO-Mg-C, MoO$_3$-Mg-C, CuO-MoO$_3$-Mg-C), the reduction process of copper oxide starts at a lower temperature compared to molybdenum oxide. The reduction of copper oxide and copper suboxide proceed exclusively with carbon, while the reduction of molybdenum oxide occur with both the carbon and magnesium. Moreover, the carbothermic reduction of molybdenum trioxide begins with the formation of MoO$_2$, which is then reduced to molybdenum by magnesium at higher temperatures. Solely carbothermic reduction of molybdenum trioxide under fast heating conditions allowed pure molybdenum to be obtained at temperatures above 1200 °C. In addition, it was revealed that when strongly exothermic and violent 2 reactions MoO$_3$+3Mg and CuO+Mg are carried out together, there is a slow interaction with weak self-heating (dysynergistic effect), which is caused by a change in the reaction mechanism: the process of Mg-thermic reduction of metals is preceded by the formation of the comparatively stable copper molybdate salt, CuMoO$_4$, the reduction of which proceeds slowly. In the quaternary system, the activation energy value of the magnesiothermic reduction stage is significantly lower than the activation energy values of the magnesiothermic reduction of copper oxide, but somewhat higher than $E_a$ value of the magnesiothermic reduction of molybdenium oxide, indicating the expediency of using Mg/C combined reducers. The synergistic influence and reciprocity of combined reducers allows to perform the joint reduction of the both metals (Mo, Cu) with trace amount of by-product at higher (>2600°C/min) heating rates.

**Author Contributions**

Conceptualization, H.K, Kh.N., S.V. and S.K.; Data curation, S.K.; Funding acquisition, S.V., S.K.; Investigation, H.K. and K.N.; Methodology, H.K, Kh.N., S.V.; Resources, S.A., S.K.; Supervision, S.A., S.K.; Visualization, H.K.; Writing - original draft, H.K.; Writing - review & editing, H.K, S.V. and S.K. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest
The authors declare no conflict of interest.

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