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DTA/TG study of CuO and MoO₃ co-reduction by combined Mg/C reducers

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Abstract The mechanism of copper (II) oxide and molybdenum (VI) oxide co-reduction by Mg + C mixture was investigated at non-isothermal conditions by carrying out simultaneous differential thermal (DTA) and thermogravimetric (TG) analyses combined with X-ray diffraction (XRD) analysis of intermediate and final products. The whole process was found to involve several phenomena: interaction between oxides with $CuMoO_4$ salt formation, high-exothermic reactions occurring directly between metal oxides and magnesium, as well as low-exothermic carbothermal reactions. In order to better understand the complex nature of calorimetric and TG curves, the behaviour of each single reagent as well as that of binary, ternary and quaternary mixtures was studied at linear heating. It was revealed that the simultaneous reduction of Cu and Mo oxides proceeds more easily by carbon than by magnesium. Only due to the decisive role of carbon on the reaction pathway, the combined and complete reduction of oxides by Mg/C reducing mixture becomes possible at relatively low temperatures. The sequence of chemical reactions possibly occurring during the heating process on the basis of DTA/TG curves and XRD analyses results of quenched reaction products has been proposed.

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Introduction

During last two decades, an increased interest has been paid to the so-called pseudoalloys based on Cu–refractory metal system (such as Cu–Mo). Their unique properties and multiple functionalities make them ideal for numerous high-tech applications, e.g. instrumentation and portable equipment industries [1, 2]. The development of new preparation methods of Cu–Mo composite materials for thermal management with high physicomechanical properties and bulk density is in the focus of modern research, as their characteristics highly depend on microstructure and phase composition of alloys [3–10].

A number of novel technologies have been developed to enhance Mo–Cu composite densification ability by using finer precursors, such as homogeneously mixed molybdenum and copper oxides/salts. Generally, MoO_3–CuO powder mixtures were ground in a ball mill and reduced at 600–1000 °C up to 10 h in the hydrogen atmosphere [6–8, 11, 12], which is a energy-consuming process and accompanied with undesirable growth of Cu grains, as well as results in drastic decrease in process efficiency.

In our previous work [13], molybdenum and copper oxides joint reduction was performed by energy-saving combustion synthesis approach using Mg + C mixture as combined reducer. The use of such reducing mixture allows to control the reaction temperature in a wide range and to synthesize Mo–Cu composite powders in a controllable combustion mode. It should be underlined that it is highly challenging to monitor and reveal mechanism of the combustion reaction due to its high velocity. Note that

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according to the available literature data, the mechanism of joint reduction of MoO_3 and CuO was not studied at all. To fill the gap, one of the approaches is the modelling of the process at "soft" conditions (e.g. low heating rates and tuning the process within the time) by using the DTA/TG method. This approach provides an enhanced opportunity to reveal the stepwise nature of complex reactions in the multicomponent systems.

In this work, the mechanism and kinetics of molybdenum and copper oxides joint reduction by Mg + C mixture were studied by DTA/TG method combined with XRD analysis of intermediate products quenched from various stages.

Materials and methods

The following powders were used as raw materials: MoO_3 (high grade, Pobedit Company, Russia, particle size less than 15 μm), CuO (high grade, STANCHEM, Poland, particle size less than 40 μm), magnesium powder (MPF-3, Russia, 150- to 300-μm particle size) and carbon black (P-803, Russia, particle size less than 1 μm).

Differential thermal (DTA) and thermogravimetric (TG) analyses were carried out using DTA/TG, Q-1500 instrument ("Derivatograph Q1500" MOM, Hungary) which is connected to 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, and Al_2O_3 powder was used as reference material. Measurements were taken in argon atmosphere at flow rate of 120 mL min^{-1}. Heating rate was programmed to be 2.5, 5, 10 and 20 °C min^{-1}. The thermoanalytical curves were recorded up to a temperature 1000 °C. In order to stop the reaction and quench the intermediate and final products for further examinations, the heater 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 °C (more interesting area) was around 300 °C min^{-1}. The samples obtained in this way were examined by XRD method with monochromatic CuKα radiation (diffractometer DRON-3.0, Burevestnik, Russia) operated at 25 kV and 10 mA. The microstructure of the initial reagents and obtained products was evaluated using scanning electron microscope (BS-300, Tesla, CZ).

Results and discussion

To clarify the interaction laws and mechanism in the complex quaternary (CuO–MoO_3–Mg–C) system, it was expedient firstly to explore the interaction patterns in binary (CuO–MoO_3, CuO–Mg, CuO–C, MoO_3–Mg, MoO_3–C) and ternary (CuO–C–Mg, MoO_3–C–Mg, CuO–MoO_3–C, CuO–MoO_3–Mg) systems at the identical conditions of linear heating.

Binary systems

CuO–MoO₃ system

As it can be seen from DTA/TG curves (Fig. 1), at heating the mixture of CuO and MoO_3 oxides with 1:1 molar ratio (V_h = 20 °C min^{-1}), low-endothermic process takes place in a 470–650 °C temperature range, which corresponds to the formation of copper molybdate, $CuMoO_4$, according to the X-ray analysis results. Note that five different modifications for $CuMoO_4$ have been reported in the literature (α-$CuMoO_4$, β-$CuMoO_4$, γ-$CuMoO_4$, $CuMoO_4$-II, $CuMoO_4$-III). In our investigations, up to 700 °C α-modification is stable and endothermic peak at that temperature (D point) corresponds to the change in copper molybdate modification (α-$CuMoO_4$ to $CuMoO_4$-III) [14–16]. According to the literary data [17, 18], at 820 °C copper molybdate incongruent melting takes place.
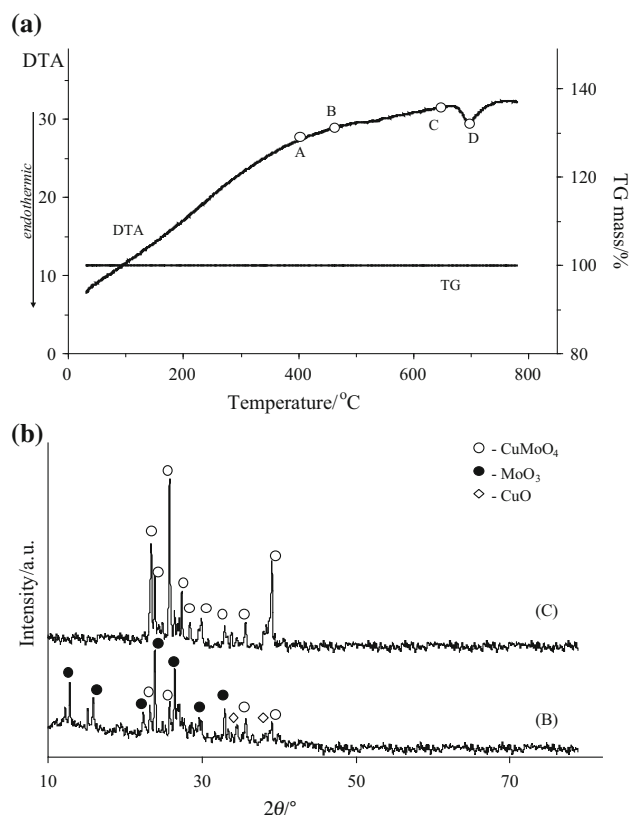
Fig. 1 DTA/TG curves (a) and XRD patterns of intermediate products (b) formed at various stage of linear heating of CuO + MoO_3 oxides mixture, V_h = 20 °C min^{-1}

Thus, in the case of the absence of reducers, copper molybdate, CuMoO$_4$ formation occurs from the MoO$_3$ and CuO oxide equimolar mixture. The quenched sample at 420 °C (A point) contains only initial oxides, but at 470 °C (B) partial formation of CuMoO$_4$ is observed; some amount of initial oxides are also present. At 650 °C (C point), product consists solely of CuMoO$_4$ (Fig. 1; see also Table 1). Experiments also showed that the change in oxides ratios brings the formation of copper molybdates with various compositions (e.g. Cu$_3$Mo$_2$O$_9$).

CuO–Mg, CuO–C, MoO$_3$–Mg, MoO$_3$–C systems

In the CuO–Mg binary system, the exothermic interaction begins before the melting of magnesium (T_s = 570 °C, V_h = 20 °C min^{-1}), the process is single stage, with the maximum temperature of DTA peak T_{max} = 600 °C, and is accompanied by the formation of metallic copper and magnesium oxide (Fig. 2a).

The carbothermal reduction of copper oxide is a low-exothermic process with two sequential stages (Fig. 2b). The first stage is the CuO interaction with carbon by the formation of Cu$_2$O suboxide (440–530 °C), and then, Cu$_2$O is reduced to copper at 530–650 °C temperature interval. The mass change in the TG curve corresponds to the removal of carbon dioxide either during the first or second stage and makes about 11.9 and 14.8 %, respectively (according to reactions' equations: 13.3 and 15.0 %).

According to our previous studies [19], the reduction of molybdenum trioxide by magnesium is a single-step reaction, with high-exothermic effect, which starts at about the same temperature as the reduction of copper oxide by magnesium (T_s = 580 °C, T_{max} = 620 °C, V_h = 20 °C min^{-1}). On the other hand, the carbothermal reduction of
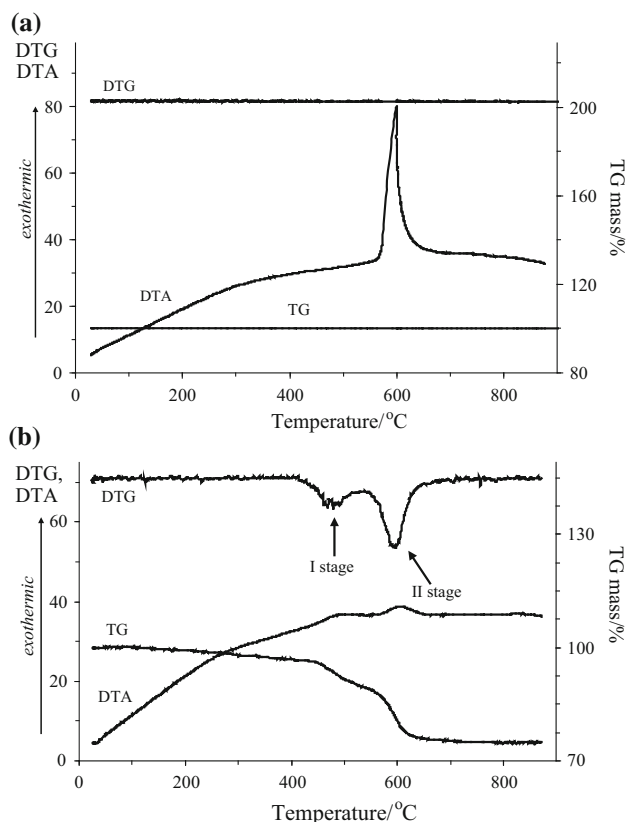
Fig. 2 DTA/TG/DTG curves of the CuO + Mg (**a**) and CuO + 0.5C (**b**) mixtures, V_h = 20 °C min^{-1}

molybdenum trioxide proceeds in two stages: first stage (MoO$_3$ → MoO$_2$) is low exothermic (560–650 °C) and the second stage is endothermic (>850 °C) [19]. The latter is accompanied by the formation of molybdenum and molybdenum carbide.

Table 1 Characteristic parameters of binary, ternary and quaternary systems at linear heating

Mixture composition	DTA peak temperature/°C	Mass loss/%
CuO + MoO$_3$	500	–
CuO + Mg	600	–
CuO + 0.5C	I stage—480, II stage—600	I stage—11.9, II stage—14.8
MoO$_3$ + 3Mg	620	–
MoO$_3$ + 1.5C	I stage—580, II stage—860	I stage—13, II stage—17.5
CuO + 0.5Mg + 0.25C	I stage—500, II stage—730	I stage—8.3, II stage—no mass change
CuO + 0.5Mg + C	I stage—495, III stage—730	I stage—8.5, II stage—3.5, III stage—no mass change
MoO$_3$ + 1.5Mg + 2C	I stage—610, II stage—725	I stage—8.1, II stage—no mass change
CuO + MoO$_3$ + 2C	I stage—490, II and III stages—555	I stage—7, II and III stages—8
CuO + MoO$_3$ + 4Mg	I stage—600, II stage—695	No mass change
CuO + MoO$_3$ + 1.1Mg + 2C	I stage—480, II and III stages—525, 575, IV stage—760	I stage—8.7, II and III stages—10.1, IV stage—no mass change

According to these data obtained, during the reduction of complex mixtures, it should be taken into account the fact that the second stage of carbothermal reduction of CuO ($Cu_2O + C \rightarrow Cu + CO_2$) and the first stage of molybdenum trioxide carbothermal reduction ($MoO_3 + C \rightarrow MoO_2 + CO_2$) take place at the same temperature range, which coincides also with their separate reduction processes by magnesium.

Ternary systems

CuO–C–Mg system

The reduction regularities of copper oxide have been explored for different ratios of Mg/C reducer's mixture. Therefore in the case of carbon-poor mixtures, when carbon amount is less than 0.5 mol, which is insufficient for full reduction of CuO (e.g. $CuO + 0.25C + 0.5Mg$ mixture), it has been shown that as it was expected, in the 430–540 °C temperature range, the carbothermic reduction of copper oxide takes place up to Cu_2O formation (Fig. 3a). Mass loss according to TG curve makes about 8.3 % (according to the

(a)

(b)

Fig. 3 DTA/TG curves of the $CuO + 0.25C + 0.5Mg$ (1, 1′) and $CuO + C + 0.5Mg$ (2, 2′) mixtures (**a**) and XRD patterns of intermediate products of $CuO + C + 0.5Mg$ mixture (**b**); $V_h = 20$ °C min^{-1}

$CuO + 0.25C + 0.5Mg = 1/2Cu_2O + 0.25CO_2 + 0.5Mg$ reaction equation—11.6 %). Then, magnesiothermic reduction occurs at higher temperature. It means that for this type of mixtures, carbothermic and magnesiothermic reduction stages are fully separated. Moreover, in contrast to pure magnesiothermic reduction process (carbon absence case), in this case, the reduction stage by magnesium moves to the higher temperature range and proceeds after magnesium melting (at about 730 °C).

In the carbon-rich mixtures, the first stage of carbothermal reduction of copper (II) oxide to copper (I) oxide takes place at the same temperature range as that for carbon-poor mixtures. At higher carbon content, when it is sufficient for complete reduction of copper oxide (≥ 0.5 mol), it was supposed that magnesiothermic reduction stage will be absent. However, this stage is still displayed (Fig. 3a, DTA curve), indicating that at the presence of magnesium, the carbothermic reduction of Cu_2O is shifted to higher temperatures: it starts at ~ 550 °C and is drawn up to a temperature above the melting point of magnesium (see Fig. 3a, TG curve). As a result, magnesium also participates in the reduction process. In fact, in this case, there is overlapping of carbothermal with magnesiothermal reduction stages of Cu_2O.

Total mass loss is about 12 % (full carbothermic reduction of CuO must be 21 %): during the first stage, copper (II) oxide reduces by carbon up to copper (I) oxide ($\Delta m = 8.5$ %), and the second stage begins with carbothermic reduction of Cu_2O but did not manage to complete ($\Delta m = 3.5$ %). Then, it continues by magnesium after its melting. The foregoing is confirmed by the XRD analysis results of quenched samples (Fig. 3b) from the different characteristic temperatures [590 °C (A), 840 °C (B)].

MoO₃–Mg–C system

According to the results of our previous studies [19] (Fig. 4, curve 2, 2′), in this system, the interaction starts with carbothermal reaction: molybdenum trioxide is reduced by carbon to molybdenum dioxide, MoO_2 at 560–630 °C. Then, the process is continued after the melting of magnesium, and molybdenum dioxide is reduced by magnesium up to metallic molybdenum at 700–800 °C [19]. In fact, in this case also, the first carbothermal stage of reduction ($MoO_3 \rightarrow MoO_2$) occurs approximately at the same temperature range as that in the absence of magnesium. On the other hand, the magnesiothermal stage of reduction, as in the case of copper oxide, moves to higher temperature range and takes place after the melting of magnesium.

In fact, the participation of carbon during the first stage of interaction leads to the significant shift of the magnesiothermic reduction temperature (compare curves 1 and 2).
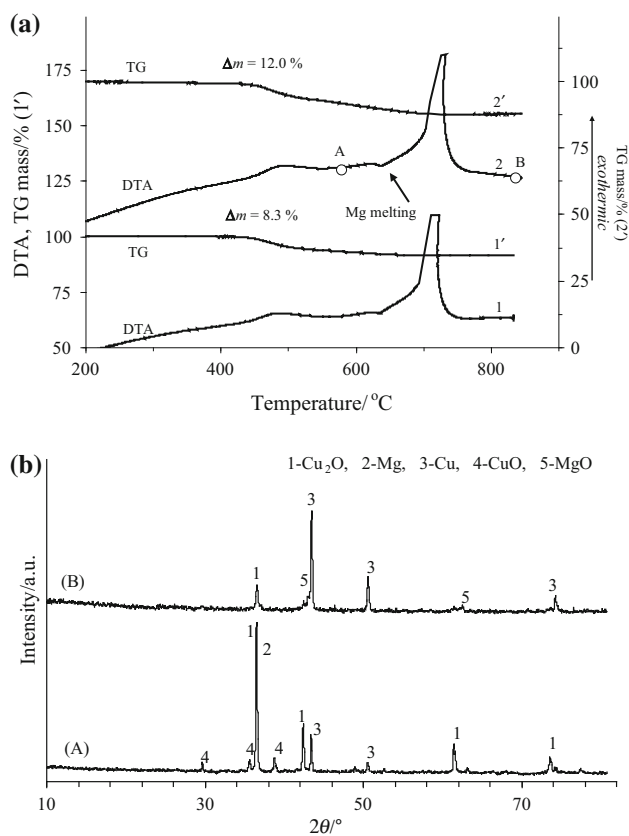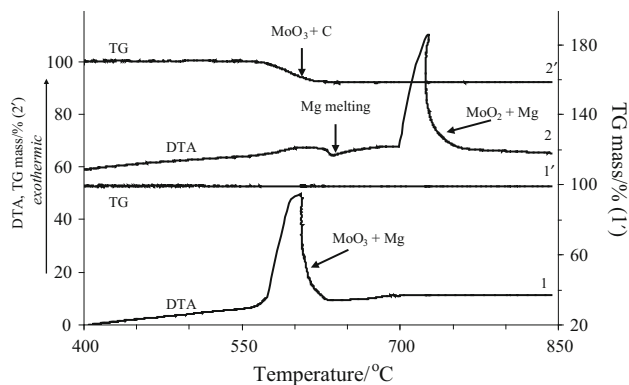
Fig. 4 Comparison of DTA/TG analyses results for $MoO_3 + 3Mg$ (1, 1′), $MoO_3 + 1.5Mg + 2C$ (2, 2′) mixtures, $V_h = 20\ °C\ min^{-1}$

Note that similar phenomenon was observed also in [20] at tungsten (VI) oxide reduction by Mg + C mixture, although in that case, carbon was implicated in low extent.

CuO–MoO₃–C system

DTA/TG analyses performed for the $CuO + MoO_3 + 2C$ mixture showed that at heating of this mixture, sequential reduction of oxides occurs (Fig. 5; Table 1). At the first stage, copper oxide reduces up to Cu_2O; moreover, the first step of the molybdenum trioxide's reduction (MoO_3 to MoO_2) coincides with the second stage of copper oxide reduction (Cu_2O to Cu), as it was mentioned above (see "CuO–Mg, CuO–C, MoO₃–Mg, MoO₃–C systems" section). The foregoing is confirmed by the XRD analyses of the quenched samples obtained from characteristic temperatures (Fig. 5b). Thus, carbon addition into the oxides' mixtures prevents the formation of $CuMoO_4$ (please see "CuO–MoO₃ system" section), because the carbothermal reduction of CuO starts earlier and occurs faster (Fig. 5a) than the salt formation process.

CuO–MoO₃–Mg system

DTA/TG results obtained for the CuO–MoO₃–Mg ternary system (Fig. 6) showed that up to 520 °C, interaction has not occurred (point A), but at $T_{max} = 600\ °C$, low-exothermic reaction was accompanied with the formation of $CuMoO_4$, as well as $MgMoO_4$ according to the XRD analysis of quenched sample at the point B (630 °C). After the melting point of magnesium (650 °C), another low-exothermic reaction occurs. The recent corresponds to the partial reduction of $CuMoO_4$ up to $Cu_2Mo_3O_{10}$ and Mo, and formation of $MgO·MoO_2$ mixed oxide (see Fig. 6b, curve C). Thus, one may state that the salt formation from oxides at low heating conditions prevents the magnesio-thermal reduction processes of oxides. As a result, the
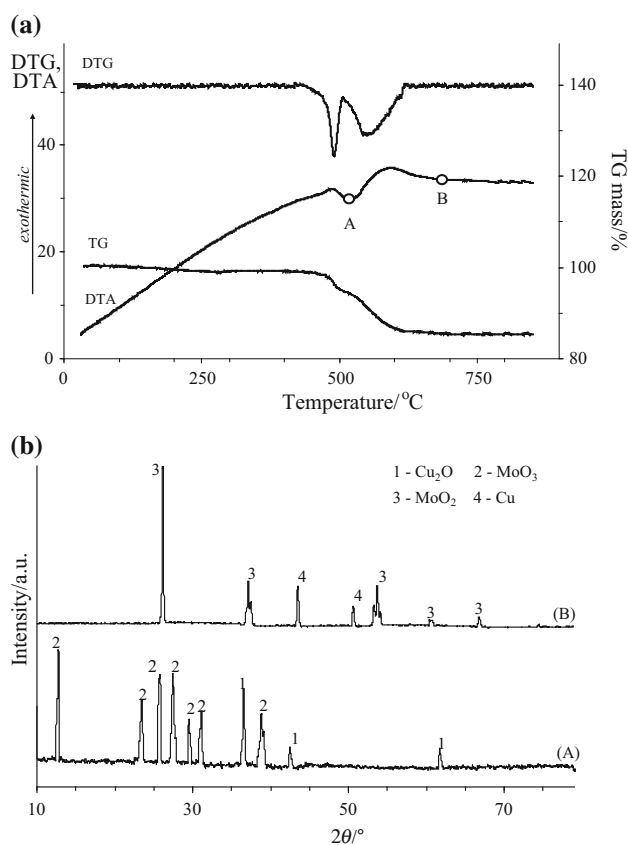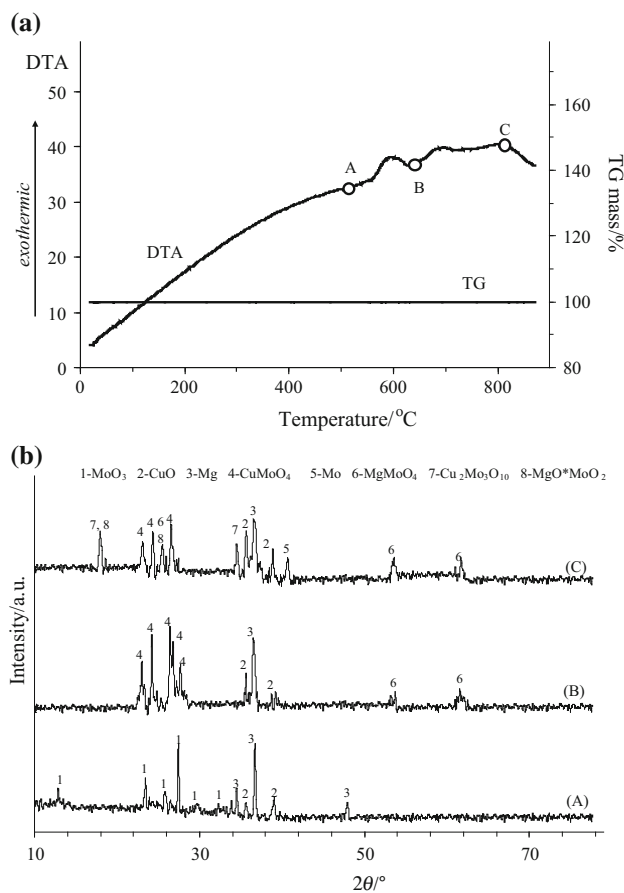

Fig. 5 DTA/TG/DTG curves of the $CuO + MoO_3 + 2C$ ternary reactive mixture (**a**) and XRD patterns of quenched samples from different characteristic temperatures (**b**)

simultaneous reduction of oxides proceeds more easily by carbon than by magnesium.

Quaternary CuO–MoO₃–C–Mg system

As it can be seen in Fig. 7, at 480 °C (A point), interaction has not been started yet (initial mixture is immutable); then, up to 600 °C two-step reduction of copper oxide to copper and the molybdenum trioxide reduction to MoO_2 occur. In the above-listed reactions, only carbon figures as a reducer. This is confirmed both by the mass change in TG curve and by XRD analysis of quenched sample. The mass losses correspond to the $CuO + C \rightarrow Cu + CO_2$ and $MoO_3 + C \rightarrow MoO_2 + CO_2$ interactions. Besides, magnesium oxide has not been found in the samples quenched at 600 °C (B point). The latter proves that magnesium has not been entered into interaction yet. The magnesiothermal reaction starts after magnesium melting at 720 °C and is accompanied by the formation of molybdenum, magnesium oxide and composite oxide of molybdenum and magnesium (C point). Most likely, molybdenum and magnesium mixed oxide ($MoO_2·MgO$) formed at

Fig. 6 DTA/TG curve of the CuO + MoO$_3$ + 4Mg ternary reactive mixture (**a**) and XRD patterns of quenched samples from different characteristic temperatures (**b**)

Fig. 7 DTA/TG/DTG curves (**a**) and XRD patterns of quenched samples from different characteristic temperatures (**b**) for the CuO + MoO$_3$ + 1.1Mg + 2C   quaternary   reactive   mixture. *A T* = 480, *B* 600, *C* 720 °C
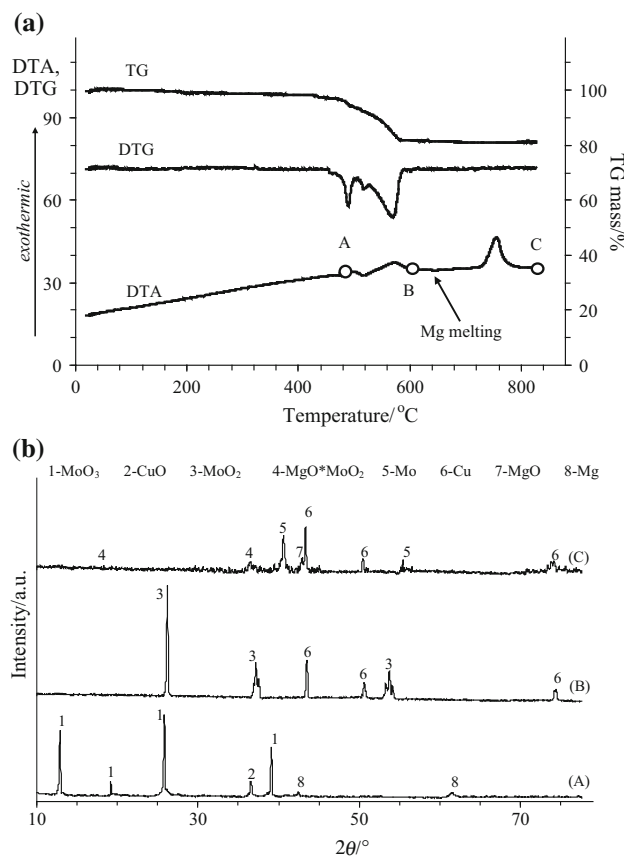
insufficient amounts of reducers by interaction of magnesia and MoO$_2$ [19]. The mass change in TG curve (Fig. 7a) is missing above 600 °C which also proves that only magnesium has participated as a reducer in the second stage.

Based on DTA/TG/DTG and the XRD analyses results of quenched samples (Fig. 7a, b), the following scheme may be presented for the reactions pathway:

1. $CuO + C \rightarrow Cu_2O + CO_2(CO)$
2. $Cu_2O + C \rightarrow Cu + CO_2(CO)$ and $MoO_3 + C \rightarrow MoO_2 + CO_2(CO)$
3. Melting of Mg
4. $MoO_2 + Mg \rightarrow Mo + MgO$;
5. $MoO_2 + MgO \rightarrow MoO_2 \cdot MgO$

Thus, according to DTA/TG and XRD analysis results of the CuO–MoO$_3$–C–Mg system, the reduction of oxides occurs sequentially; therefore, process starts with low-exothermic reaction (carbothermal reduction) and then continued with high-exothermic one (reduction by magnesium) (Fig. 7a).

The proceeding of the reactions by suggested mechanism facilitates the fact that in the presence of carbon,

temperature shift of magnesiothermal reduction takes place, which is conditioned by several factors:

1. The carbothermal reaction precedes both CuMoO$_4$ salt formation process and magnesiothermal interaction. Due to this, it becomes possible to realize reduction process in mild conditions. On the other hand, in this case, instead of initial oxides, the intermediate products (in this case Cu$_2$O and MoO$_2$) participate in magnesiothermal reduction, but at different temperature range, than the initial oxides.
2. The addition of carbon to the MoO$_3$–CuO–Mg initial mixture and subsequent CO/CO$_2$ gas release loosens the sample, leading to the weakening of contact of reactants' particles and, as a result, moves the subsequent reaction stages to a higher temperature range.
3. The addition of carbon strongly affects the direct contact of reagents (regardless of possible gas releasing) and makes spatial difficulties for interacting particles.

Finally, it should be noted that only due to such pathway of reduction reactions, which excludes the possibility of

salt formation process between oxides, the combined reduction of oxides at relatively low temperatures by Mg/C reducing mixture becomes possible.

Conclusions

The interaction pathway in the MoO$_3$–CuO–Mg–C complex system was explored by thermal analysis method combined with XRD analyses of quenched intermediate and final products. It was shown that the whole process involves several phenomena: interaction between oxides with salt formation, high-exothermic reactions occurring directly between oxides and magnesium, as well as low-exothermic carbothermal reactions. It has been demonstrated that in the presence of magnesium as a reducer, salt formation process takes place and prevents the magnesiothermal reduction of oxides. In contrast to magnesium, the addition of carbon into the oxides' mixtures prevents the formation of CuMoO$_4$, because the carbothermal reduction of oxides occurs earlier and faster than the salt formation process. As a conclusion, one may state that the simultaneous reduction of oxides proceeds more easily by carbon than by magnesium. And finally, only due to such pathway of reduction reactions becomes possible the combined and complete reduction of oxides at relatively low temperatures by Mg/C reducing mixture.

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