A study on mechanochemical behavior of MoO$_3$–Mg–C to synthesize molybdenum carbide

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ABSTRACT

The influence of Mg value in the MoO$_3$–Mg–C mixture on the molybdenum carbide formation and the mechanism of reactions during mechanochemical process were investigated. In keeping with this aim, magnesium and carbon contents of the mixture were changed according to the following reaction: $2MoO_3 + (6 − x) Mg + (1 + x) C = (6 − x) MgO + Mo_2C + x CO$. The value of x varied from 0 to 6. Differential thermal analysis (DTA) results for sample with stoichiometric ratio ($x = 0$) revealed that in the early stage, carbon reduced the MoO$_3$ to MoO$_2$ and subsequently highly exothermic magnesiothermic MoO$_2$ reduction occurred after magnesium melting. Also, it was indicated that the exothermic reaction temperature shifted to before magnesium melting in the 11 h-milled sample ($x = 0$) and all the exothermic reactions happened, simultaneously. According to the experimental findings, molybdenum carbide (Mo$_2$C) was synthesized in the mixture powder with stoichiometric ratio ($x = 0$) after 12 h milling process and the type of reactions was mechanically induced self-sustaining reaction (MSR). However, at lower Mg content in the MoO$_3$–Mg–C mixture ($0 < x ≤ 2$), the magnesiothermic reduction occurred in MSR mode and activated the carbothermal reaction. Further decrease in Mg value ($2 < x ≤ 3$) resulted in MSR mode magnesiothermic reaction and gradual carbothermal reduction. In samples with lower magnesium contents, partial molybdenum oxide reduction proceeded through a gradual mode magnesiothermic reaction.

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Introduction

In recent years, transition metal carbides are widely used in industry because of some outstanding properties in mechanical hardness, thermal stability, and especially catalytic performance, which has been extensively studied over the past three decades [1,2]. Among these transition metal carbides, molybdenum carbide (Mo$_2$C) is receiving considerable attention because of catalytic behavior. Some interesting examples of the type of reactions carried out using it are: the removal of sulfur (hydrodesulfurization) and the removal of nitrogen (hydrodenitrogenation), hydrogenation, dehydrogenation, and the Fischer–Tropsch reaction [1–3].

Currently, many processes are available for the synthesis of molybdenum carbide and each process varies in the characteristics of the powder produced and the processing cost. Mo$_2$C can be conventionally prepared by temperature-programmed reaction (TPR) method via carbonization of molybdenum trioxide with gas hydrocarbon, such as C$_2$H$_2$, CH$_4$ and their gas mixtures [1–4]. In addition, many other chemical methods were reported for synthesis of molybdenum carbide including chemical vapor deposition (CVD) [5], high temperature during dc discharge [6], solution reactions [7], and Microwave Induced Alloying (MIA) [8]. Solid state carbothermal reaction has been investigated earlier in several papers with various carbon resources and performed at different temperatures [1,2,4]. Moreover, metallothermic reduction of molybdenum oxide has been studied, with aluminum, calcium, magnesium or Al–Si alloy as a reducing agent [9,10]. These active metals generate a great amount of heat, which can be used for activation of carbothermal reaction. In this regard, K. Manukyan et al. in two papers [11,12] reported self-sustaining reduction and reaction pathway in the MoO$_3$ + Mg + C mixtures may yield molybdenum or molybdenum carbide, depending on the process conditions.

Mechanochemical activation is a solid state powder processing method which involves inducing chemical reactions in a mixture of reaction powders at room temperature or at least much lower temperatures. An increase in the kinetic of reaction during high energy milling can be a result of microstructural refinement, repeated cold deformation and fracture of particles [13,14]. A. Ataie et al. [3] synthesized nanocrystalline molybdenum by mechanical activation of MoO$_3$ powder and its subsequent hydrogen reduction. In several attempts [3,15–17], nanocrystalline molybdenum carbide was prepared through the reduction of molybdenum oxide by carbon using high energy ball milling. Also, Mo$_2$C was mechanosynthesized by ball milling mixtures (MoO$_3$ + 2Al + C) with different molar graphite contents at room temperature by Z.Q. Li et al. [10]. Our researches indicated that the synthesis of molybdenum carbide in the MoO$_3$–Mg–C mixtures was done by thermal processes and heretofore the mechanochemical behavior of this system has not been reported elsewhere.

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In our previous works [18,19], the mechanical activation process was used to synthesize Al$_2$O$_3$/B$_4$C and MgO/B$_4$C nanocomposite by using commercial pure materials, such as Al/Mg, B$_2$O$_3$ and C (graphite). As reported by authors in previous papers, Al/Mg content plays a key role in the mechanochemical behavior of the ternary system Al/Mg–B$_2$O$_3$–C.

The aim of this work is to explore the possibility of in-situ synthesis of molybdenum carbide powder via mechanochemical method by using the MoO$_3$–Mg–C mixture as precursor materials at room temperature. The influence of Mg content in this system on the carbide formation phenomena and the mechanism of reactions during the ball milling process were studied. Thermodynamic calculations and thermal analysis were performed to get an insight about the probable reactions.

Experimental work

Combination of carbothermic and magnesiothermic reduction of MoO$_3$ to Mo followed by solid-state reaction of Mo and C to form MoC$_2$ could be expressed as reaction Eq. (1).

$$2MoO_3 + (6 - x)Mg + (1 + x)C = (6 - x)MgO + Mo_2C + x \ CO \quad (1)$$
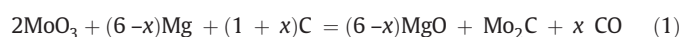
In the above reaction, x is a variable which gradually influences the primary carbon and magnesium amount (mole). Value of x varied from 0 to 6 (samples S1–S7) to investigate the influence of Mg content on the mechanochemical behavior of the mentioned system.

The precursor materials were magnesium (Merck, 99.7% purity, particle size $= 40 \pm 5$ μm), molybdenum oxide (Sigma Aldrich, 99.95% purity, mean particle size $= 30 \pm 5$ μm) and graphite (Merck, 99.5% purity, mean particle size $= 50$ μm).

The precursor materials were milled in a planetary ball mill for various times at room temperature. Details of ball mill machine and milling conditions are given in Table 1. To prevent the oxidation process, the container vessel of milling was filled with high purity argon gas before ball milling.

In this study, the amounts of the remaining C (free carbon) were calculated to understand carbothermic reduction progress. For removing probable Mg and MgO, the obtained powder was leached with 18% hydrochloric acid for 1 h at 60 °C. The solution was filtered after leaching and the purified products were washed by distilled water for several times to eliminate extra HCl acid until the pH value is about 7. Afterward, the residue on the filter was dried at the 90 °C for 2 h and weighed as W$_1$. At the end, the obtained powder was oxidized at 700 °C for 30 min in the air and was then weighed as W$_2$. Therefore, the different W$_1$ − W$_2$ = W$_3$ yields the amount of free carbon. Finally, to report changes in data as percentage change, the following formula was used: [(obtained value / initial value) × 100]. In an attempt to reduce errors, the reported data are average of three experimental values.

XRD analysis was carried out using Cu-Kα radiation to identify different phases of the starting powders and mechanically alloyed powders. The diffractometer (Philips X-ray diffractometer) was operated at 40 kV and 30 mA. Scans were performed between 10 < 2θ < 90. "PANalytical X'Pert HighScore" software was also used for the analysis of different peaks. The diffraction patterns of products were compared to proposed standards by the Joint Committee on Powder Diffraction and Standards (JCPDS). The reaction process and features were also

Table 1
Details of ball mill machine and milling conditions.

Rotation speed of vial (rpm)	500
Diameter of vial (mm)	100
Vial material	Hardened chromium steel
Ball material	Hardened carbon steel
Diameter of balls (mm)	20
Number of balls	5
Balls to powder weight ratio	20:1
Total powder mass (g)	7

investigated by thermal analyses (STA; model BÄHR 503). A small amount of the reactants weighing about 50 ± 5 mg were held in an alumina crucible and heated under argon flow (flow rate: 50 ml/min) at a heating rate of 10 °C/min up to 1100 °C.
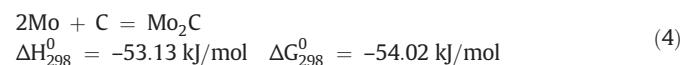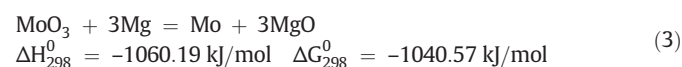
Results and discussions

To investigate the effect of Mg amount in the Mg–MoO$_3$–C mixture on the carbide formation phenomena, the various values of Mg and graphite were prepared (S1–S7). The concept behind the proposed route has been the investigation of the heat of magnesiothermic reaction on the probability of activation carbothermic reduction. For better discussion and understanding, the samples are categorized into four groups (A to D), as follows.

(A): Mg = 6 mol and x = 0 (stoichiometric ratio)

The first aim was to ensure that the molybdenum oxide could be reduced during the mechanochemical process; in this regard, sample S1 was ball-milled for different times. The general form of the reaction taking place in the Mg–MoO$_3$–C system (stoichiometric ratio) is represented in reaction (2).

$$2MoO_3 + 6Mg + C = 6MgO + Mo_2C \quad (2)$$

This reaction includes two stages: first, reduction of MoO$_3$ with Mg which is a highly exothermic reaction (3) (thermite reaction), and second, the reaction of elemental Mo with C which leads to Mo$_2$C formation (4) (synthesis reaction).

$$MoO_3 + 3Mg = Mo + 3MgO$$
$$\Delta H^0_{298} = -1060.19 \text{ kJ/mol} \quad \Delta G^0_{298} = -1040.57 \text{ kJ/mol} \quad (3)$$

$$2Mo + C = Mo_2C$$
$$\Delta H^0_{298} = -53.13 \text{ kJ/mol} \quad \Delta G^0_{298} = -54.02 \text{ kJ/mol} \quad (4)$$

ΔH and ΔG of samples containing different amounts of Mg ($0 \leq x \leq 6$) were calculated, and the results are listed in Table 2. According to the thermodynamic data [20], all above reactions can thermodynamically be possible to occur and extremely exothermic. Depending on the milling conditions and enthalpy of reaction, the mechanochemical process was classified into two categories: progressive (gradual) reaction and mechanically induced self-sustaining reaction (MSR) [13,14]. In the first type, the synthesis of final products yields to a very small volume slowly during each collision between the milled material and the grinding medium that contributes to the comminution, mixing, and defect formation. In the second type, a self-propagating combustion reaction is begun after a critical amount of milling process. During the milling, intimate contact between the reactant phases is an essential requirement for the self-propagating synthesis. Therefore, occurrence of the combustion reaction causes a rapid rise in temperature at the wall of the mill container vessel, and provides the conditions for quick transformation [13,14]. Usually, the adiabatic temperature (T_{ad}) is calculated to characterize the degree of self-heating. For MSR mode reaction to take place it is necessary that these quantities be at least $T_{ad} > 1800$ K [13]. In this group, the calculated T_{ad} value (Table 2) of reaction (2) is 4651 K which meets the critical value of MSR mode.

Fig. 1 exhibits the XRD patterns of the initial powder Mg–MoO$_3$–C mixture together with those of the samples mechanically alloyed for 6, 11 and 12 h. The XRD trace of as-received mixture included only the peaks of Mg, MoO$_3$, and graphite. In the case of the sample milled for 6 h, all the sharp peaks correspond to Mg and MoO$_3$ and that corresponding to C have low intensity. Fig. 1 indicates that ball milling up to 11 h had no effect on as-received powder mixture except broadening of Bragg peaks which is caused by the significant refinement of