SOLID STATE REDUCTION OF MoO_3 WITH CARBON VIA MECHANICAL ALLOYING TO SYNTHESIZE NANO-CRYSTALLINE MoO_2

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In this research, effect of milling time on solid state reduction of MoO_3 with carbon has been investigated. It was found that mechanical activation of a mixture of MoO_3 and carbon at ambient temperature by high energy ball milling was not able to reduce MoO_3 to metallic molybdenum. MoO_3 was converted to MoO_2 at the first stage of reduction and peaks of the latter phase in X-ray diffraction patterns were detected when the milling time exceeded from 50 hours. The main effect of increased milling time at this stage was decreasing of MoO_3 peak intensities and significant peak broadening due to decrease in size of crystallites. After prolonged milling, MoO_3 was fully reduced to nano-crystalline MoO_2 and its mean crystallite size was calculated using Williamson–Hall technique and found to be 17.5 nm.

Thermodynamic investigations also confirm the possibility of reduction of MoO_3 to MoO_2 during the milling operation at room temperature. But, further reduction to metallic molybdenum requires thermal activation at higher temperature near 1100 K.

XRD and SEM techniques were employed to evaluate the powder particles characteristics.

Keywords: Nano-crystalline; Mechanical milling; Solid state reduction.

1. Introduction

In recent years, mechanical alloying and mechano-chemical processing have been shown to be effective processes for producing a variety of nano-crystalline and ultra fine metallic powders. The principle of mechano-chemical processing is based on

mechanically activated solid-state chemical reactions.¹ Chemical reduction of metal oxides could occur when milled with a suitable reductant.² Solid state reduction of MoO_3 by various metals has been investigated earlier.³ It was also reported that reduction of MoO_3 by Al during high energy ball milling taken place through a rapid combustion reaction.^{4, 5}

Most solid-state mechano-chemical reactions studied to date have been displacement reactions involving the formation of two or more solid product phases. The separation of these product phases can be difficult due to the nano-crystalline grain sizes and inter-mixing of the phases induced by the milling process.⁶

When metal oxides react with carbon, one of the reaction products is CO or CO_2 , which is gaseous and readily separated from the solid reaction products. This means that the use of carbon as a reducing agent may eliminate the need for an additional process for separation of the reaction products.¹

Previous study has shown that after high energy ball-milling of Ag_2O , CuO and Fe_2O_3 , respectively, with carbon powder at room temperature, metallic silver and copper could be obtained but Fe_2O_3 was only reduced to Fe_3O_4 .⁷

In this research, solid state reduction of MoO_3 with graphite via mechano-chemical process in a high energy ball mill has been investigated.

2. Experimental procedure

Starting materials were commercially pure MoO_3 (99.5%, 1-15 μm) and graphite (99.2%, 0.05-5 μm). They were accurately weighed according to the reaction (1) and then mixed together and milled in a high-energy planetary ball mill with a rotation speed of 290 rpm at room temperature in argon atmosphere for various times. The ball to powder weight ratio was selected to be 35:1. The vial and balls were both made of hardened steel.

A 30 %mol. excess carbon was added to compensate the probably losses during handling and milling.

The morphology and phase identification of the products were examined by SEM (Cam Scan MV2300) and XRD (Philips Xpert pro) using $\text{Co } k\alpha$ radiation ($\lambda = 1.78892 \text{ \AA}$), respectively. The mean crystallite size and internal strain of the particles were calculated using Williamson–Hall plot for milled samples.⁸

3. Results and discussion

Fig. 1 shows SEM images of the as-received MoO_3 and graphite powders. As-received MoO_3 powder particles have lath type morphology with a mean length and thickness of $5\mu\text{m}$ and $2\mu\text{m}$, respectively.

Fig. 1. SEM images of the as-received (a) MoO_3 and (b) graphite powders.

Fig. 2 shows the X-ray diffraction patterns of a sample milled for various times. Analysis of the XRD patterns revealed that small fraction of MoO_3 reduced to MoO_2 after milling for 50 h and by further milling up to 165 h, MoO_3 was fully reduced to nano-crystalline MoO_2 . With prolonged milling to 200 h, the phase composition of the powder remained largely unchanged. Also, peak broadening occurred for the milled samples due to the crystallite refinement. In multiphase systems, milling causes intermixing of phases, which results in an increased interfacial surface area while shortening the diffusion path. These lead the reactions to occur at substantially lower temperatures and/or at higher rates than for normally mixed powders, resulting in a more rapid attainment of equilibrium within a milled system.⁹

Fig. 2. XRD patterns of the powder mixture milled for various times.

The mean crystallite size and internal strain for MoO_3 phase in 25 h milled sample calculated using the Williamson–Hall technique were 19 nm and 1.6%, respectively. Same parameters for MoO_2 phase in the sample milled for 200 h were 17.5 nm and 1.5%, respectively. The fact that the phase composition of the powder didn't change while the milling time increased from 165 h to 200 h suggests that the reduction reaction virtually stopped after 165 h of milling. The reflections corresponding to the residual carbon phase were not observed in the XRD patterns. This might be due to the fact that the carbon exists in an amorphous state in the samples.

Reduction of MoO_3 by carbon may take place according to the following reactions:

Fig. 3 shows the calculated values of ΔG of each reaction as a function of temperature. It is shown that, there is a thermodynamic driving force for the reaction between MoO_3 and carbon [$\Delta G_{(298\text{ K})} = -122.3$ (kJ/mol)]. Therefore, occurrence of the reaction 2 during ball milling is predictable. In contrast, there is a large thermodynamic barrier for the reaction 3, [$\Delta G_{(298\text{ K})} = +136.8$ (kJ/mol)]. Although ball milling can possibly overcome a thermodynamic barrier of low magnitude on the order of, 10–20 kJ/mol through creation of a large area of inter-phase interfaces and other structural defects in the powder, a barrier of above 100 kJ/mol in magnitude is too large for the ball

milling process to overcome.¹¹ Hence it would not be expected that the reaction between MoO_2 and carbon occur during ball milling at room temperature.

Fig. 3. Change of free energy (ΔG) of the reactions between the molybdenum oxides and carbon as a function of temperature: (a) reaction 2; (b) reaction 3, as specified in text.

Unlike the combustion reactions between MoO_3 and active metals such as Al (ΔG is more negative than -900 kJ/mol^{12}), reaction between MoO_3 and carbon during ball milling due to the much smaller thermodynamic driving force (ΔG is in the range from -120 to -150 kJ/mol) occurs at a very slow rate. The magnitude of the thermodynamic barrier for these reactions becomes less at higher temperatures, as shown in Fig. 3, but it appears that the temperature requires to be nearly 1100 K for the barrier to be sufficiently low for occurring reaction 3 during ball milling. This temperature is well beyond what the planetary ball mill can achieve.

Typical SEM images of the 25 and 200 h milled samples are shown in Fig. 4. As shown in Fig. 4 (a), 25 h milling of MoO_3 and carbon mixture is enough time to particles size of mixture becomes in nano-meter scale but there is not any phase transformation at this milling time. As molybdenum trioxide is the brittle component of the mixture, its particles are fragmented during milling and their size are reduced continuously. Formation of the fresh surfaces at this stage is another advantage of the fragmented particles. The newly created surfaces are appropriate sites for nucleation of MoO_2 after extended milling to 50 h. Fig. 4(b) shows morphology of synthesized MoO_2 after 200 milling. For longer milling time up to 200 h the change of particle size was not significant. However, the rate of agglomeration and fragmentation was equal and crystalline structure and particle size were constant.

Fig. 4. SEM images of the MoO_3 /graphite mixture milled for a) 25 h and b) 200 h.

4. Conclusions

The mechano-chemical reduction of MoO_3 with carbon was investigated in the present study and was shown that with extended milling to 165 h on mixture of MoO_3 and carbon, MoO_3 completely reduced to MoO_2 during high energy ball milling at ambient temperature but mechano-chemical reduction of MoO_2 to molybdenum metal does not occur during milling due to insufficient storage of internal energy in the MoO_2 and temperature raises accompanying collision events. Thermodynamic investigations also confirm the possibility of reduction of MoO_3 to MoO_2 during the milling operation at room temperature.

5. Acknowledgements

The financial support of this work by the Research Council of the University of Tehran is gratefully acknowledged. Also, the cooperation of Pars Molybdenum Company for supplying molybdenum oxide is appreciated.

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