

Synthesis of Molybdenum from Molybdenite by Mechanical Activation

Behrooz Ghasemi⁺ and Behzad Nategh

Department of materials and metallurgy, University of Semnan, iran

Abstract. Common approaches for the synthesis of molybdenum from molybdenite are problematic and limited. This work evaluates the feasibility of a simple mechanochemical processing method for molybdenum production that uses mechanical activation, milling additives, and heating. First, mechanical activation was applied to molybdenite powder at ambient temperature for various durations. In next step, the effect of using an additive during milling was explored thermodynamically and experimentally. The results were studied using X-ray diffraction analysis, differential thermal analysis, and scanning electron microscopy. It was found that the mechanical milling alone is not sufficient for yielding molybdenum and an appropriate additive is necessary. Subsequent heating of the milled product enhanced the formation of molybdenum.

Keywords: Molybdenum; Molybdenite; Mechanochemical synthesis; Additive

1. Introduction

Molybdenum is a refractory metal with excellent high temperature properties and has many applications. It is used as an alloying element in the steel industry for structural pipelines, steel tools, stainless steels, and high-temperature super alloys [1]. It is also used as a component in paint pigments, chemical catalysts, soil supplements, and a wide variety of petrochemical and pharmaceutical reactants [2]. Molybdenum is found in minerals such as wulfenite (PbMoO_4) and powellite (CaMoO_4). The chief source of molybdenum is molybdenite, which is a mineral of molybdenum disulfide (MoS_2). The most common production method for molybdenum is flotation beneficiation of molybdenite, which yields a high-grade concentrate containing about 90–95% MoS_2 . The concentrate is roasted to drive off sulfur to yield molybdenum trioxide (MoO_3). Leaching and further processing of MoO_3 yields ammonium molybdate, which is reduced to molybdenum metal powder using hydrogen. This method requires high temperature and pressure and a large amount of equipment, and causes environmental pollution, leading many researchers to suggest new methods for Mo extraction [1,2]. Combustion synthesis of molybdenite with aluminum, lead, tin, and zinc has been investigated [3]. Mechanical activation is a simple and useful technique to synthesize both equilibrium and non-equilibrium materials. It is also economical with important technical advantages [4,5]. The term “mechanical activation” was coined by Smekal in 1942, and refers to a process in which the reaction ability of a material is increased without changing the material. If the activation causes changes in the composition and structure of the material, then the process is referred to as a mechanochemical reaction [6,7]. Mechanical activation increases the area of contact between the reactant powder particles due to reduction in particle size and allows fresh surfaces to come into contact. This allows reduction to proceed without the necessity for diffusion through the product layer. As a consequence, solid-state reactions that normally require high temperatures occur at lower temperature during mechanochemical synthesis without any externally applied heat. In addition, induced high defect densities favor the diffusion process [8]. The effect of mechanical activation was studied on many ore concentrates in order to determine an appropriate technological flow sheet [7]. Kano et al. [9] used mechanical activation for the reduction of metallic tungsten from tungsten oxide (WO_3), which has similar problems. Hu et al. [10] investigated the effect of mechanical activation on molybdenite by studying the oxidation behavior and structural changes of nonactivated and mechanically activated molybdenite. They concluded that the effect of mechanical activation on molybdenite is small, and

⁺ Corresponding author. Tel.: +98 912 2055283 , Fax: +98 231 335 4119
E- mail address: bghasemi@semnan.ac.ir

they attributed the effect to the special structure of molybdenite and its special change of morphology during mechanical activation [9,10]. The aim of this work is to evaluate the feasibility of a simple process to synthesize molybdenum from molybdenite using mechanical activation with additive utilization.

2. Experimental

Molybdenite powder (with a purity greater than 98% and a particle size less than 50 μm) was used with manganese (with a purity greater than 99% and a particle size less than 63 μm) as an additive. Ball milling was performed in a planetary mill (PMU1) with T4 Steel cylindrical vials in air at room temperature. Hardened steel milling balls with two diameters, 7 mm and 10 mm, were chosen to increase the collision efficiency. The ball to powder weight ratio (BPR) and speed were set to 20:1 (18 balls of each diameter) and 250 rpm, respectively, in all experiments. Ethanol was used as a process control agent with a quantity as much as 1.5% wt of total powder mass. All mechanical treatments were performed for several milling times (30, 45, and 60 h) on molybdenite without any additives to investigate the occurrence of the solid state reaction of MoS_2 and O_2 through Eq. (1):



In next step, treatments were carried out in similar milling times in the presence of manganese additive, having higher sulfidation and lower oxidation affinity. In all experiments, 7.5 g of MoS_2 and 2.5 g of Mn were used according to the stoichiometry of Eq. (2).



The formation of phases during milling was followed by X-ray powder diffraction analysis (XRD). XRD patterns were recorded using a Bruker AXS D4 Endeavor diffractometer operating with $\text{Cu K}\alpha$ radiation source. In order to examine the changes in the milled powders during heat treatment, a sample of the milled powders was tested using a multifunctional thermal analyzer (model Netzsch STA 409) under a flowing Ar atmosphere while the temperature was changed at $10\text{ }^\circ\text{C min}^{-1}$. Microstructural analysis was performed using scanning electron microscopy (model VEGA, TESCAN).

3. Results and Discussion

As the first step, a milling process was performed on molybdenite powder without additives for 30, 45, and 60 h. Fig. 1 shows X-ray diffractions for the milled samples. In all samples, molybdenite and molybdenum oxide peaks are observed. The appearance of MoO_3 peaks can be derived from the following reaction:



Considering the large negative free energy change, the reaction is highly possible at room temperature but it is not completed even after 60 h. At 30 h of mechanical milling, molybdenum peaks were not observed and only peaks of molybdenite and molybdenum oxide derived from reaction (3) were observed. After 45 h of milling, chemical reaction (1) can occur and the reaction product (Mo) is produced locally. Increasing the milling time to 60 h lead to the same reaction with little increase in the intensity of molybdenum peaks. In next step, a milling process was used with manganese as an additive.

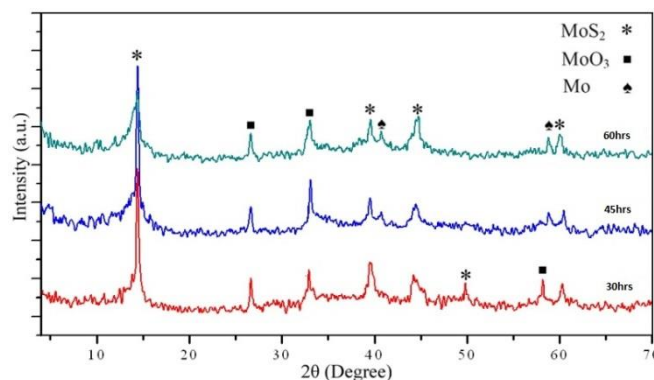


Fig.1 : X – ray diffractions at milling times 30,45,60 h and without additive

Fig. 2 shows X-ray diffraction patterns for the samples milled with manganese for 30, 45, and 60 h, and as - milled powder mixture. For 30 h of milling, the main result is a decrease in molybdenite and manganese peak intensities and the appearance of molybdenum and molybdenum oxide peaks, which can be predicted as a result of reactions (2) and (3), as shown in Fig. 2-b. In the sample with 45 h of mechanical milling (Fig. 2-c), the decrease in MoS₂ peak intensity continues such that amorphous states become possible. In this sample, peaks of other forms of molybdenum sulfide appeared, such as Mo₂S₃, which was not observed in the previous experiments. It is supposed that Mo₂S₃ is stable at temperatures higher than 630 °C and is dissociated to molybdenite and molybdenum at this temperature. It is probable that a long milling time can transform the unstable sulfide into a meta-stable state. After 60 h of mechanical milling (Fig. 2-d), the reappearance of most of the peaks clearly suggest crystallization of the molybdenite phase. An increases in intensity was observed for peaks of Mn, MnS, and Mo₂S₃. It is expected that the reaction of molybdenite with manganese occurs faster, considering the large negative free energy change.

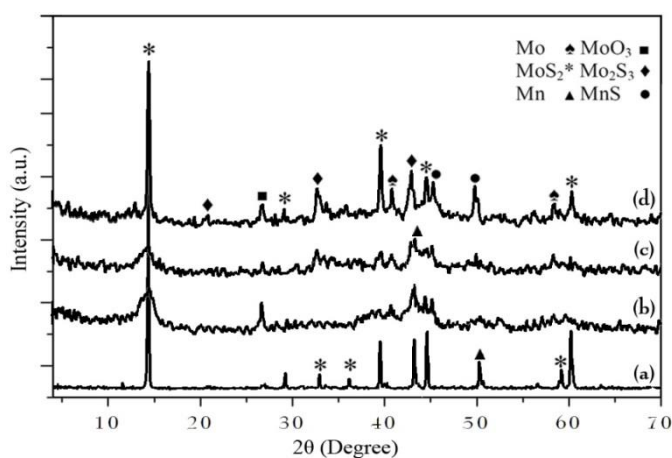


Fig.2: X – ray diffractions with manganese additive a) As–milled b) 30h c) 45 h d) 60 h.

Powder mixture micrographs after 30 and 60 h of milling (Fig. 3) clearly show grinding of particles. In Fig. 3-a, the particles are laminated, which is a result of sequence fractures in mechanical activation. In Fig. 3-b, the particles are smaller and more concentric, which is caused by a long milling time.

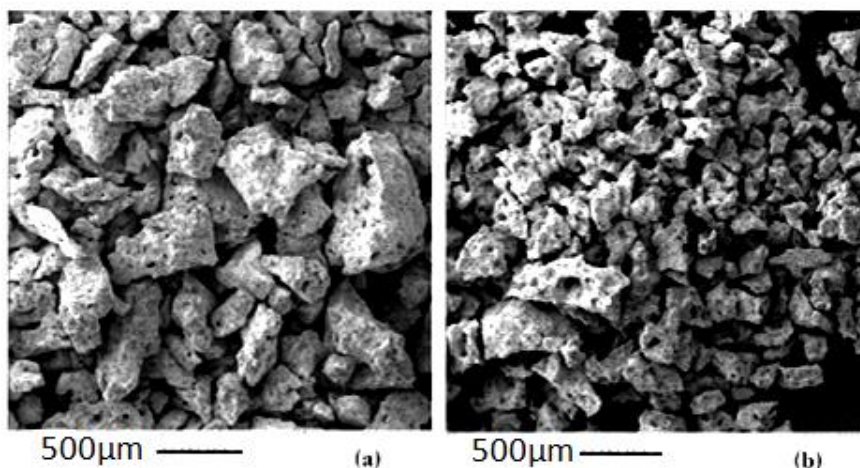


Fig.3 : SEM micrographs of powder mixture after a) 30 h milling b) 60 h milling.

The milling process with or without an additive does not produce significant amounts of molybdenum. In the third step, two samples with 30 h of milling (with and without an additive) are heated in DTA analysis. Fig. 4 shows DTA curves for samples milled for 30 h. With an additive, exothermic peaks at 500 and 700 °C are observed (Fig. 4-a). The first exothermic peak can be attributed to relaxation of the material structure because mechanical milling produces unstable and distorted structures [11,12]. The second exothermic peak can be attributed to occurrence of reaction (2) because of a high affinity of manganese to sulfur and the formation of meta-stable sulfides. In DTA analysis of a sample with 30 h milling and no manganese additive, no specific event is observed after heating to 1200 °C (Fig. 4-b). For further investigation, X-ray diffraction was performed on these samples.

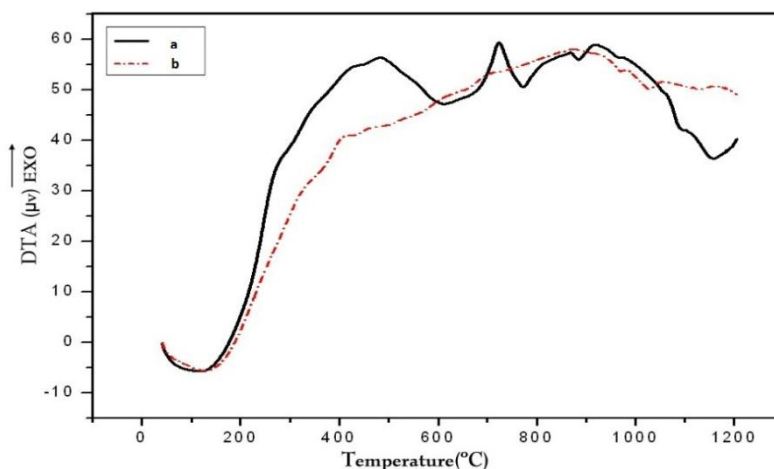


Fig.4: DTA curves for samples with 30h milling a) with manganese additive b) without additive.

Fig. 5 shows the results of the X-ray diffraction studies. In Fig. 5-a, it is observed that heating molybdenite with 30 h of milling in the presence of manganese produces significant amounts of molybdenum. However, after heating a sample with 30 h of milling without manganese, only molybdenite peaks are observed (Fig. 5-b). Therefore, molybdenite reacts faster to yield molybdenum when it is milled with manganese than when milled without manganese. The role of manganese in the progression of the reaction is a result of the high affinity of manganese to sulfur, which causes the formation of sulfide and production of molybdenum.

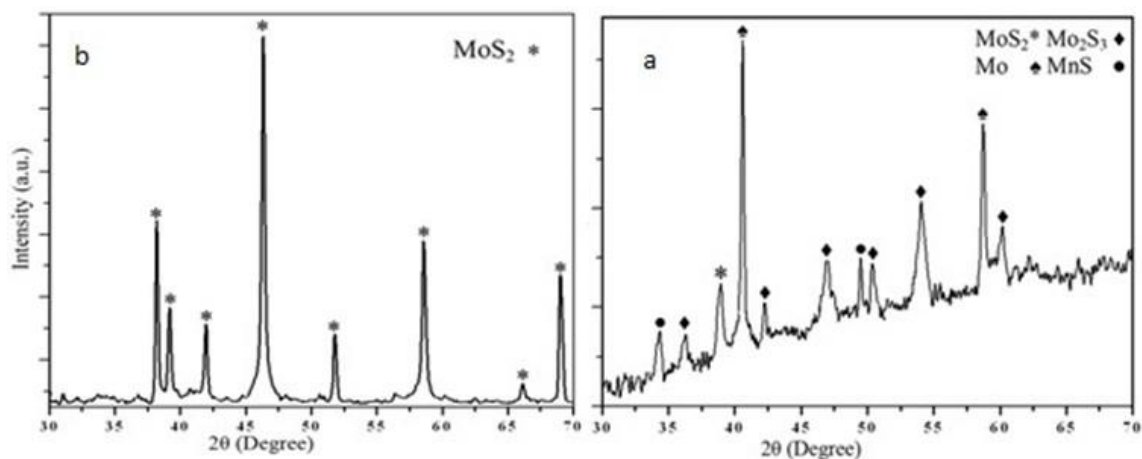


Fig.5: X- ray diffractions for samples with 30h milling after heating to 1200 °C a) with presence manganese additive b) no presence manganese additive

4. Conclusion

In this research, the possibility of molybdenum production from molybdenite using mechanical milling is investigated. To accomplish this, molybdenite powder was milled with and without manganese. Results demonstrate that molybdenum peaks are observed after 45 h of molybdenite milling without manganese. After 60 h of milling, the intensity of molybdenum peaks slightly increases. However, when milled with manganese, molybdenum peaks are observed after 30 h of milling, and their intensity increases with the milling time. DTA analysis of milled samples heated equally to 1200 °C shows that presence of manganese as an additive results in significantly higher amounts of molybdenum production.

5. References

- [1]. C. K. Gupta, Extractive metallurgy of Molybdenum, CRC Press, 1992.
- [2]. A. Sutulov, International Molybdenum encyclopedia (1778-1978)", Vol. 2, 1978, Internet, Santiago.
- [3]. B.D Stojanovic, A.Z. Simoes, C.O. Paiva-Santos, C. Jovalekic, V.V. Mitic, J.A. Varela, Mechanochemical synthesis of barium titanate, J. European Ceramic Society 25, 1985-1989, 2005.
- [4]. C. Suryanarayana, Mechanical alloying and milling, Marcel Dekker, New York, 2004.
- [5]. C. Suryanarayana, In: Powder metal technologies and applications. ASM Handbook, vol. 7, ASM International, Materials Park, OH, 1988.
- [6]. P. Balaz, Mechanical activation in hydrometallurgy, Int. J. Miner. Process 72, 2003, 341-354.
- [7]. C. Suryanarayana, Mechanical alloying and milling, Progress in Materials Science 46, 2001, 1-84.
- [8]. M.S. El-Eskandarany, Mechanical alloying for fabrication of advanced engineering materials, 2001, New York, Noyes.
- [9]. J. Kano, E. Kobayashi, W. Tongamp, S. Miyagi, F. Saito, Reduction of WO_3 to W-metal by mechanochemical reaction, Journal of Alloys and Compounds, 2009.
- [10]. H. Hu, Q. Chen, Z. Yin, G. Gotlstein, P. Zhang, G. Guo, Structural change of mechanically activated Molybdenite and the effect of mechanical activation on Molybdenite, J. of Metallurgical and materials transactions B 35, 2004, 1203-1207.
- [11]. P.C. Kang, Z. Yin, O. Celestine, Effect of milling time on phase transition and grain growth during the annealing process of MA powders, I., Materials Science and Engineering A 395, 167-172, 2005.
- [12]. P. Kang, Z. Yin, Phase formation during annealing as-milled powders of molybdenum disilicide, I. Materials Letters 57, 4412-4417, 2003.



Behrooz ghasemi, Date of birth 29/08/1966, Makoo city- Iran. Master's Degree in Metallurgical Engineering, Materials Identification and Selection, awarded by Tehran University in 1995 and PhD in Metallurgical Engineering at Iran University of Science and Technology in 2006-2007 in filed synthesis of materials. working experience: Instructing at Shahid Bahonar University, Kerman as a Faculty Member since 1996 – 2001, Conducting research at Forging and Casting of Steel -Tehran, Conducting research at Sarcheshmeh Copper Complex, Kerman, Instructing at Semnan University, as a Faculty Member since 2006- 2007. Interesting and current research is about ,synthesis of materials, thermodynamics and kinetics of materials.