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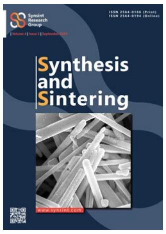

Research article

Synthesis of molybdenum carbide using mechanochemical and thermal approaches

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ABSTRACT

The carbothermic reduction of MoS_2 using Mg, an efficient sulfur scavenger, was carried out by two very different routes, i.e., mechanochemical reaction and heat treatment. The thermodynamic calculation results show that Mo_2C and MgS are the phases formed when the elements are combined, and carbothermic reduction of molybdenite takes place. XRD analysis data indicates no reaction occurred at 1, 2, and 5 h of milling by the mechanochemical method and the initial phases MoS_2, Mg, and C were identified. On the other hand, after 7 hours of milling, Mo_2C and MgS phases finally emerged. Through heat treatment, the desired Mo_2C and MgS phases were successfully prepared with the crystal diffraction spots obvious at 700, 800, and 900 °C, respectively. Both of these methods produced powders which were then washed with a 10% 1 M HCl solution, and as a result, a reasonable yield of pure molybdenum carbide was obtained.

KEYWORDS

Mechanochemical reaction
Molybdenite
Magnesium
Carbon
Molybdenum carbide

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1. Introduction

Molybdenum carbide (Mo_2C) is used due to its unique properties like its hardness, thermal stability, and catalytic activity. Also, molybdenum carbide is used as a catalyst in the production of petroleum, the application of hard coatings, and the replacement of precious metals in many chemical reactions. It is treated as a key material by the chemical industry because of its substantially high catalytic action, especially in hydrogenation and hydrodesulfurization reactions [1–3].

The primary source of molybdenum carbide that occurs naturally is molybdenite (MoS_2) [4]. Molybdenite is a mineral found in nature that goes through several processes, one of which includes chemical recovery, after which it may be utilized to get a pure molybdenum compound [5]. The analysis for molybdenum and molybdenite hence plays a very important role in the separation of molybdenum trioxide. After that, the last molybdenum trioxide is by the means of molybdenum carbide so metallic molybdenum can be produced, while such reactants as carbon or hydrogen gas are used. In any case, the traditional treatments also have their own environmental and commercial drawbacks such as SO_2 being formed during the smelting process and the difficulties that come with the high temperatures needed for the sublimation of MoO_3, which are then exacerbated by the high vapor pressure of MoO_3 and the sinterability of the sublimation oven [6, 7].

There are multiple methods of synthesizing molybdenum carbide (e.g., carbothermal reduction, chemical vapor deposition (CVD), and sol-gel techniques), which have developed. The carbothermal technique is a high-temperature process involving the reduction of molybdenum trioxide with carbon. This method, however, is characterized by long heating at temperatures higher than 1400 °C, therefore it is energy-consuming as well as likely to cause the production of grain growth and phase impurities. CVD and sol-gel techniques provide better control over the product's microstructure and composition. Still, they are often quite complex and expensive to meet industrial-scale manufacturing needs. Even though the techniques above can produce pure Mo_2C, the high operating costs, and environmental problems due to the chemicals precursors and by-products are the main reasons why they are not widely used [8–10].

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For the problems outlined above, scientists have found a way to reduce the problem through a direct process that uses sulfur-absorbing agents. This strategy tries to improve the production process and lower the environmental impact by using sulfur as a stable compound that will protect from the release of SO_2. An effective method is the direct reduction of molybdenite in the presence of absorbing agente, for example, magnesium (Mg) [11], aluminum (Al) [12], calcium oxide (CaO) [11, 13, 14], and magnesium oxide (MgO) [15]. The reaction can be shown as:

$$MoS_2 + 2C + 2CaO \rightarrow Mo + 2CaS + 2CO \text{ [14]} \quad (1)$$

Calcium oxide (CaO) acts as the sulfur sorbent. This process effectively traps sulfur as calcium sulfide (CaS), preventing its release into the atmosphere and making the process more environmentally friendly.

It is still evident that mechano-chemical methods which include high-energy ball milling can enhance the efficiency of the carbothermal reduction process. The ball milling process starts with the mechanical activation of the reactants, which means that they are transformed by size reduction and the creation of defects in the process. Such mechanical energy increases the chances of the carbon atoms diffusing into the molybdenum lattice. As a result, the carbide phase is also formed at lower temperatures and shorter reaction times compared to the traditional thermal methods. The benefits of ball milling are the production of nanostructured Mo_2C with a higher rate and a smaller amount of energy consumption, and improved reaction kinetics. This approach is one of the available and potentially industrial production of molybdenum carbide, but the solution comes with the removal of disadvantages of conventional methods with a proposal of better efficiency and environment friendliness [16].

Mechanochemical processing is a methodology that depends on high-energy ball milling, which not only accelerates the reaction kinetics but also promotes the formation of molybdenum carbide at lower temperatures and in shorter timescales when compared to thermal methods [17].

Besides, ball milling is a type of process in which the power of mechanical stress and friction is very high, which is due to the balls clashing with each other in the milling chamber. This mechanical energy is transported to the molybdenite crystal structure wherein it initially disrupts the perfect order of the structure, thus forming defects and finally fine particle size by and large. The resulting analysis favors the overall surface area increase and the resulting process accelerates the molybdenite reactivity, which makes it easy for carbon and sulfur to interact with absorbing agents. Milling time, speed, and reactant ratio are the variables that are normally adjusted to get a process of the finest quality. It means that one can get ultrafine particles of molybdenum carbide with an almost equal size distribution by ball milling.

This Mo_2C nanostructure has notable characteristics such as a large surface area and strong catalytic activity enabling it to be very profitable for the industry. Lower reagent temperatures, which reduce the minimum possible energy consumption, are one of the other important factors for the eco-friendliness and cost-effectiveness of the whole reaction [18].

This research employed magnesium as a sulfur scavenger to develop molybdenum carbide via two methods—mechanochemical and thermal. While other scientists used magnesium in molybdenum synthesis, this was the first time it was employed in both methods, particularly for Mo_2C production. Our work is different from other research in that it is a direct comparison of these two methods in terms of phase purity, reaction kinetics, and energy consumption. The mechanochemical method in particular consumed less energy due to mechanical activation, which made it possible to use the more eco-friendly and efficient homogenous method compared to the traditional high-temperature technique. This pioneering procedure presents a low-cost solution to the production of big quantities of Mo_2C products for industry use.

2. Materials and methods

In this experiment, molybdenite (purity>98%, particle size<80 µm), carbon (purity 99.9%, particle size<100 µm), and magnesium (purity 99.5%, particle size<200 µm) were used. The tests were performed using mechanochemical and heat treatment methods. In the mechanochemical method, five large stainless steel balls (diameter 2 cm, weight 18 g) and seven small stainless steel balls (diameter 1 cm, weight 14 g) were used. The ball-to-powder weight ratio was set to 10:1. Raw materials were first weighed with a stoichiometric ratio of 1:2:1 and milled (The Planetary Ball Mill PM 100 - Retsch) for 1, 2, 5, 7, and 10 hours at 300 rpm. The vial temperature was measured during the milling process to track possible exothermic reactions. As the direct temperature measurement of the powders included in the vial was impossible, the mill was stopped every 30 minutes, and the vial temperature was measured using a K-type thermocouple.

Firstly, a heat treatment method that included raw materials being ground to a stoichiometric ratio for 10 minutes in a planetary ball mill at 300 rpm was involved thermally. The mixture was then encapsulated in 316L stainless steel tubes to prevent oxidation, pressed from both sides, and heated in a box furnace at 700, 800, and 900 °C for 1 hour. The powders obtained from both methods were washed with 1 M HCl to remove MgS and produce pure molybdenum carbide. Finally, the structural changes in the products obtained from both methods were analyzed before and after acid washing using X-ray diffraction (XRD, Asenware model AW-XDM300, Cu target, Kα radiation, 40 kV, and 30 mA). Particle size and morphology were characterized using SEM (Mira3 TESCAN). Grain size calculations were made using the Williamson-Hall method [19].

3. Results and discussion

3.1. Thermodynamic and phase investigation

Via a thermodynamic analysis (HSC Chemistry Software version 5.1) [20], it is observed that reaction 2 has a negative change in Gibbs' free energy at 298 K, which means that it is energetically favorable to do it at room temperature. The enthalpy is getting lower, which is evidence the reaction is exothermic. The heat released might be enough to keep the process running after the original activation energy is provided. During the milling process, the heat generated usually brings about a considerable reduction in free energy. When a milling process is led to occur in a local environment of thermal energy, the materials exhibit a significant negative change in free energy, thus making them viable at room temperature, although kinetic factors may limit their occurrence.

$$2MoS_2 + 4Mg + C \rightarrow Mo_2C + 4MgS \quad (2)$$

$$\Delta G^0(298\ \text{K}) = -884\frac{\text{kJ}}{\text{mol}} \quad \Delta H\ (298\ \text{K}) = -881\frac{\text{kJ}}{\text{mol}} \quad (3)$$

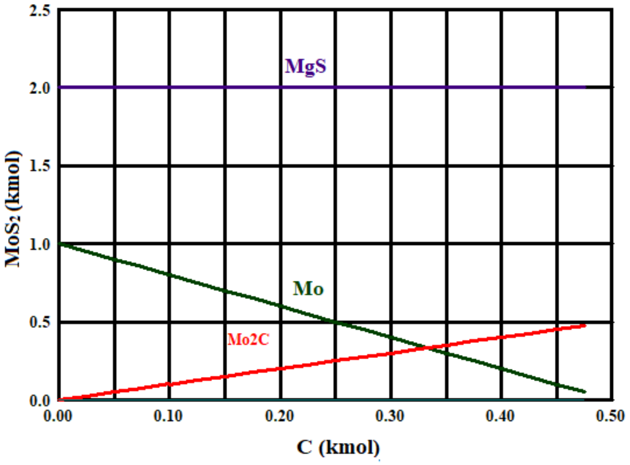

Fig. 1. Thermodynamic simulation of reactions between MoS_2, Mg, and C at 25 °C.

According to the Schaefer criterion [21], the adiabatic temperature of reaction 2 is found the standard way: the enthalpy of the reaction divided by the total heat capacity of the products in Kelvin units (Eq. 4). Thus, for reaction 2, the obtained value is 2226.9 K. If the adiabatic temperature (T_{ad}) of the reaction is over 2000 K as the Schaefer criterion articulates, then the reaction is meant to be a self-sustaining physical event [22]. According to the Schaefer criterion, it is obvious that reaction 2 occurred inside the ball mill and was immediately followed by self-propagating.

$$T_{ad} = \frac{-\Delta H^{0}_{298\ K}}{c_P} \approx 2226.9\ K \tag{4}$$

Fig. 1 reflects the equilibrium compounds that are expected to be present in the Mg-MoS_2-C system by the addition of carbon. The analysis points to only one main reaction: the conversion of molybdenite to molybdenum carbide (Mo_2C) with carbon. This implies that the ending of this reaction is 18.3 vol% molybdenum carbide and 81.7 vol% magnesium sulfide (MgS). These values came from the calculated densities of MgS and Mo_2C. The figure was devised by the HSC software. The chemical reaction path, as derived from the above model, shows that almost all the magnesium and carbon consumption shown in the system are allocated in the composition of molybdenum carbide. The completion of this reaction in the system is driven by the substantial change in Gibbs free energy that corresponds to the low equilibrium constant at ambient temperature.

While the process was demonstrated by continually monitoring the container temperature in the ball milling, the mechanism of action was examined. The data are plotted in Fig. 2. From this, we find that heating by ball collision can be observed by ball milling. Furthermore, after 400 min of milling, a clear rise in temperature is apparent, meaning that the reaction is initiated. This implies that the reaction starts during ball milling after active milling for about 400 minutes. The energy is released during the reaction because the reaction is exothermic. The necessary activation energy is given by mechanical impact and friction in the continuous mode of milling, which, if it is reached, allows the reaction to take place and heat to be produced, which in turn is the reason it carries on.

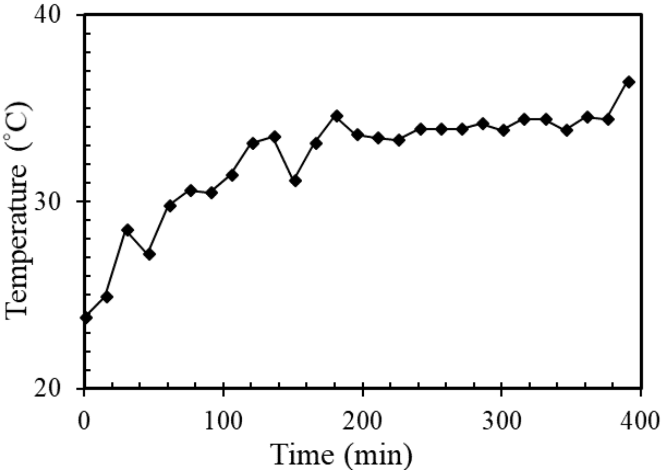

Fig. 2. Temperature profile of the $MoS_2 + C + Mg$ mixture during ball milling at 300 rpm.

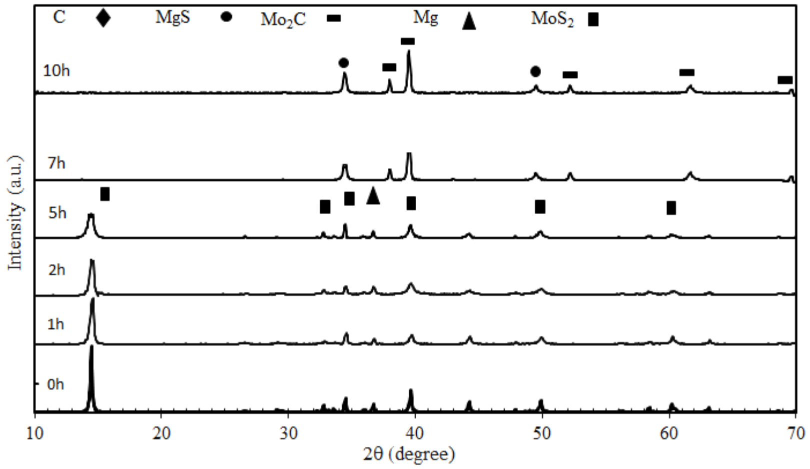

Fig. 3. XRD patterns of the as-received MoS_2-C-Mg powder mixture after 1, 2, 5, 7, and 10-hour ball milling.

More specifically, the powder mixture of Mg-MoS_2-C, while ball milling, undergoes compressing and sheering effects that create several defects like dislocations and grain boundaries which then facilitate interdiffusion. Not to forget, the rise in localized temperature caused by the kinetic energy of the colliding balls also helps the initial powder mixture turn into a very active state. Subsequently, the reaction could be achieved. When the reaction mentioned above was initiated, the released heat might be sufficient to keep the reaction going until the end. This is the mechanism mechanistically catalyzed self-propagating reaction, or MSR mode. The same modes of MSR during the synthesis of various compounds are also found in the literature [23].

X-ray diffraction was done to establish a reaction path during the process of ball milling.

Fig. 3 shows the XRD patterns of the ball-milled powder mixture as a function of the ball milling time: (a) 1 h, (b) 2 h, (c) 5 h, (d) 7 h, and (e) 10 h. Since the diffraction peaks of the unreacted raw materials are present after 1, 2, and 5 hours of the reaction time, the reaction has not taken place yet. After 7 h the reaction was thus finished, and the formation of Mo_2C became visible after 7 hours of milling (420 min). As explained before, the reaction did not take place until 400 min (6.6 h); the XRD patterns verify the course of the reaction.

There were no major differences in the phases when the ball milling time was increased to 10 hours, and only Mo_2C and MgS phases were recorded. After having examined the patterns of diffraction at various milling times, no mobilization or phase change was observed until the first 5 hours of mechanical activation passed. It was noted that the molybdenite peak intensities reduced and their widths increased as far as 5 hours of milling. These decreases in the width of the peaks and the increase in their intensity are believed to be the result of two processes namely the decline of the grain size and the increase of the lattice strain when milling was carried out over a longer period [17, 24–26].

As a result of the mechanical activation for 7 hours, the molybdenite peaks were no longer present, which means that the powder particles had a lot of defects and the internal energy had increased. This is evidence that prolonged milling not only leads to a decrease in grain size but also increases the number of internal defects and energy, which assists in the reactions as well as the phase transformations [27]. The phenomenon is also due to the increased density of dislocations and the formation of sub-boundaries as a result of the intense plastic deformation during milling. The dislocations reorganize over time and form sub-grains that later become smaller primary grains [25, 27, 28]. Also, we

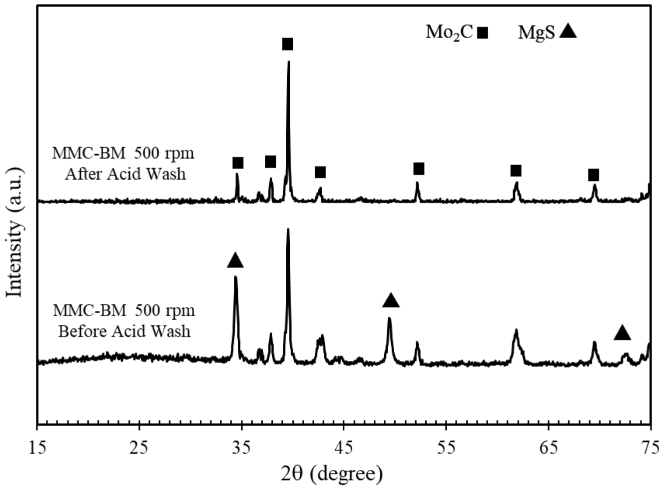

Fig. 4. XRD patterns of 10-hour ball milled powder before and after acid washing.

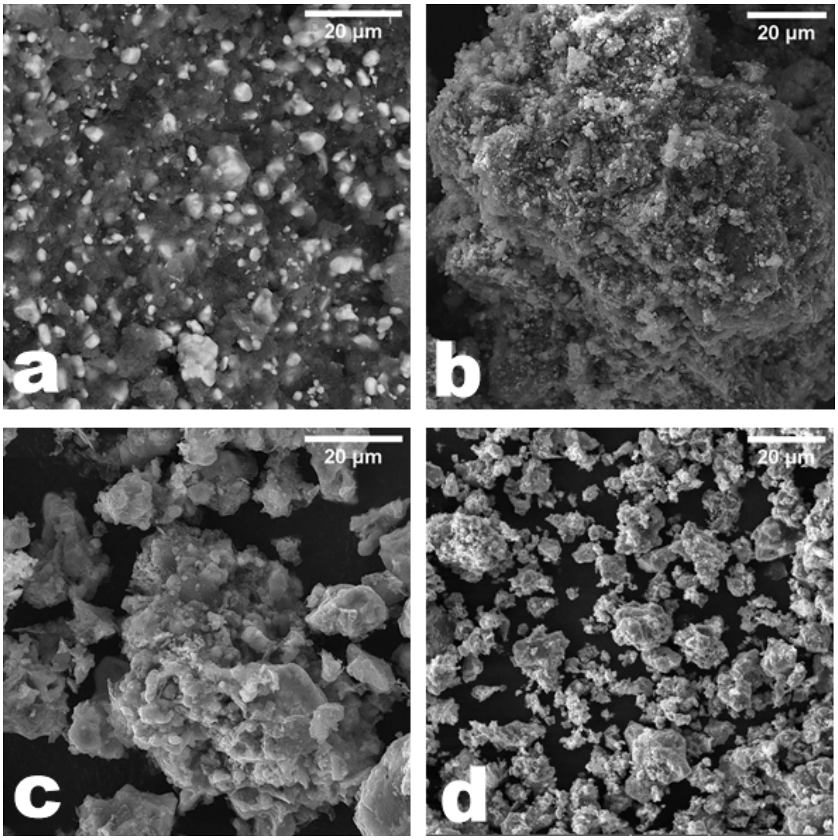

Fig. 5. SEM micrographs of the product after a & b) 7 hours and c & d) 10 hours of ball milling.

may obtain close and intimate contact with the Mg-MoS_2 and C phases. This process is clearly shown in the XRD patterns, where the broadening of peaks and the disappearance of some initial peaks signify a highly deflected and energetically enhanced state of the powder particles, which are responsible for the promotion of Mo_2C formation.

Cutting to the chase, Fig. 3 confirms the fact that with the increase of the milling time, the initial materials get fully converted into molybdenum carbide, thus, reflective of which milling time and the energy spent in mechanical interactions are important in the conversion process of the materials. Extending the milling time from 7 to 10 hours, a phase change cannot be detected in the XRD patterns, but maybe the Mo_2C and MgS peaks will be sharper in the 10-hour sample. The completion of the reaction can be credited to the increase in the crystallinity of the Mo_2C and MgS phases, as well as grain growth.

According to reaction 5, after the process of acid washing in 1 M HCl for 1 hour, MgS was completely removed, and thus the absolute purity of molybdenum carbide (Mo_2C) was produced.

$$Mo_2C + MgS + 2HCl \rightarrow Mo_2C + MgCl_2 + H_2S \quad (5)$$

Fig. 4 shows the XRD patterns of the powder mixture that was ball-milled for 10 hours before and after acid washing. This shows that the MgS was indeed leached, and a pure Mo_2C phase was formed.

Fig. 5 shows the SEM micrographs of the product after milling for 7 and 10 h at different magnifications. It is seen that molybdenum carbide prepared after 7 h of milling consists of larger particles in comparison to the ones after 10 h of milling. In particular, in Fig. 5a & b, for the sample ball milled for 7 h, molybdenum carbide appeared in a more massive agglomerated form. Fig. 5c & d, the 10 hours of milling demonstrate the molybdenum carbide changing from mass-like into somewhat fragmented, finely crushed pieces.

The gradual decrease in particle size and the rise in particle dispersion after 10 hours of milling show more breakup and improvement of the molybdenum carbide particles. It is of course that the further breakup is an aftermath of the long energy input provided by the continuous milling process, disintegrating the bigger particles into numerous tinier and uniformly distributed particles [27, 29].

The SEM analysis points out that the duration of milling is a crucial factor in the development of the particle structure. The longer milling time leads to the shattering of agglomerates and the emergence of small, well-laid-out particles.

This can improve the surface area and reactivity of the material, which is beneficial for various applications of molybdenum carbide.

3.2. Synthesis of molybdenum carbide by heat treatment

Fig. 6 shows the X-ray diffraction patterns of MoS_2 (molybdenite) carbon (C), and magnesium (Mg) mixed. The mixture was heated for 1 hour at three different temperatures (700 °C, 800 °C, and 900 °C) and then washed with acid. The profiles reveal that raising the temperature doesn't create a new phase. Also, X-ray diffraction pattern analysis indicates that as the temperature goes up, the peaks become sharper and stronger. This points to grain growth and means that at higher temperatures existing grains grow larger instead of new phases forming [30, 31].

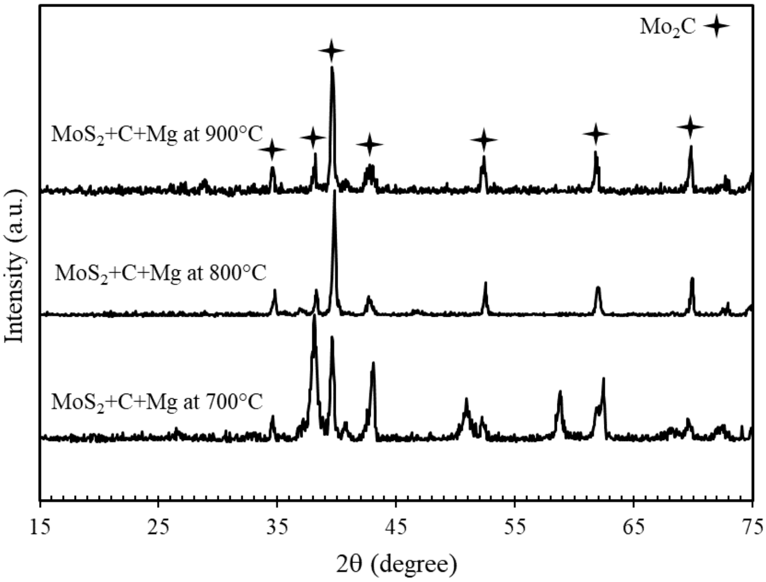

Fig. 6. XRD patterns of MoS_2 + C + Mg heated isothermally for 1 hour at 700 °C, 800 °C, and 900 °C.

According to the SEM images and the grain size calculations, 800 °C is the most excellent temperature at which a grain with the smallest size could be achieved in a measured grain size of 23.15 nm. This is indicated to be occurring at one temperature where there is an optimal point between recrystallization and grain boundary mobility is one of the most important aspects. It is the effect that causes the reduction in the grain size, and, at the same time, there is an increase in the uniformity.

Grain size calculations using the Williamson-Hall method (Eq. 6) where k is the shape factor (0.9), λ is the wavelength of the X-ray (0.15406 nm for Cu Kα radiation), β is the full width at half maximum (FWHM), θ is the Bragg angle, d is the crystallite size, and ϵ is the strain. This method determined the grain sizes as 47.5 nm at 700 °C, 23.15 nm at 800 °C, and 31 nm at 900 °C. These results suggest that 800 °C is the optimal temperature for achieving the smallest grain size. These results confirm that while increased temperature promotes grain growth, there is an optimal temperature (800 °C) for achieving the smallest grain size. Beyond this temperature, further increases lead to grain coarsening.

$$\beta \cos\theta = \frac{k\lambda}{d} + 2\varepsilon \sin\theta \tag{6}$$

4. Conclusions

Mechanical milling proved to be an effective method for creating fine, uniform particles of molybdenum carbide. The milling process resulted in notable grain refinement, as shown by the SEM micrographs and XRD patterns. The ideal duration for ball milling was determined to be 7 hours at a speed of 300 rpm, during which the complete reaction to form Mo_2C took place. Extending the milling time beyond this point did not lead to any further significant phase changes.

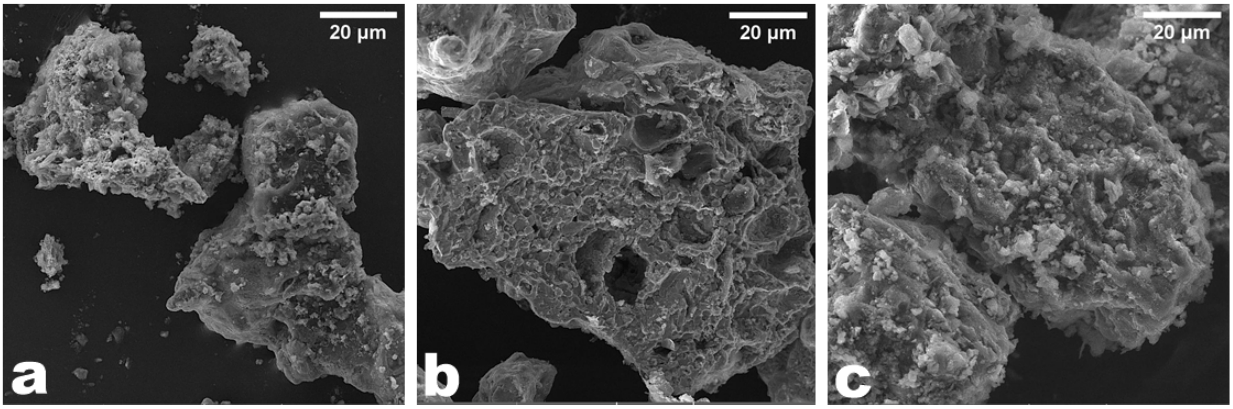

Fig. 7. SEM micrographs of MoS_2 + C + Mg after 1 hour of heating at a) 700 °C, b) 800 °C, and c) 900 °C and after acid washing.

The heat treatment of the MoS_2, C, and Mg mixture at different temperatures (700 °C, 800 °C, and 900 °C) highlighted how temperature affects grain growth and morphology. The SEM micrographs and XRD patterns indicated that 800 °C was the ideal temperature for achieving the smallest grain size of 23.15 nm.

The temperature has the ideal balance between recrystallization and grain boundary mobility, which is why the refined grains and the improvement of the material properties. In the case of higher temperatures, 900 °C, grain coarsening appears which shows that precise temperature control is necessary to prevent the grains grow unnecessarily. SEM analysis exhibited that mechanical milling enabled the production of lighter and more porous particles compared to the high-temperature synthesis method, which gave bigger and sintered grains because of the high adiabatic temperatures.

CRediT authorship contribution statement

Pegah Mohazab: Writing – original draft, Formal Analysis, Investigation, Methodology.

Samad Ghasemi: Writing – review & editing, Supervision.

Akbar Heidarpour: Writing – review & editing, Supervision.

Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

Declaration of competing interest

The authors declare no competing interests.

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