

## AN INVESTIGATION ON ALUMINOTHERMIC REDUCTION OF MoO<sub>3</sub> IN DOMESTIC MICROWAVE OVEN

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### Abstract

In the present study, feasibility of aluminothermic reduction of molybdenum oxide by microwave oven was studied. Furthermore, the effect of compaction pressure and the amount of used Al and CaO as flux on aluminothermic reduction of molybdenum oxide were investigated. Thermodynamic analysis of the corresponding reaction indicated that, aluminothermic reduction of MoO<sub>3</sub> was possible at all temperatures. XRD patterns and thermodynamic investigation of reaction products indicated that aluminothermic reduction of molybdenum oxide progressed through the formation of intermediate phases such as Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> and MoO<sub>2</sub>, where the final products were elemental Mo and Al<sub>2</sub>O<sub>3</sub>. Results revealed that by increasing the compaction pressure of the pellet, undesired phases of molybdenum dioxide (MoO<sub>2</sub>) and aluminum molybdate Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> can be detected among the final products. By increasing the amount of Al more than stoichiometric ratio, the intermediate phases, such as MoO<sub>2</sub>, were produced. The results indicated that by adding CaO to the MoO<sub>3</sub>-Al system, the unwanted molybdenum dioxide (MoO<sub>2</sub>) and aluminum molybdate (Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>) compounds were successfully reduced to Mo. In the present work, metallic molybdenum could easily and successfully be separated from Al<sub>2</sub>O<sub>3</sub> slag, as the side product of the reaction, in molten phase, based on the difference in their densities.

**Keywords:** Molybdenite; Molybdenum oxide; Aluminothermic reduction; Slag; Intermediate phase

### 1. Introduction

Molybdenite (MoS<sub>2</sub>) is the major source for production of molybdenum and its compounds [1]. There are several ways for extraction of molybdenum from its mineral source. The conventional method for producing molybdenum and its alloys is based on roasting of molybdenite, followed by the purification of the resultant oxide (MoO<sub>3</sub>) and finally reduction of the purified molybdenum oxide by H<sub>2</sub> [2-4]. This process has several disadvantages such as low recovery of molybdenum due to the loss of MoO<sub>3</sub> and MoO<sub>2</sub> during purification and the large number of processing steps [5-6]. These difficulties and disadvantages of roasting process have motivated the scientists to develop new methods for the production of molybdenum. Carbothermic reduction of MoO<sub>3</sub> is an alternative process for producing molybdenum metal and its carbide [7]. Recently, metallothermic reduction process has been suggested by various researchers for producing metallic molybdenum [8-11]. In the metallothermic reaction, an active metal reduced the molybdenum oxide and produced the molybdenum and oxide of active metal. Hoseinpour and et al used Zn for reduction of MoO<sub>3</sub> [12-13]. They

proposed that zincothermic reduction of molybdenum trioxide can be completed in two steps. In the first step, MoO<sub>3</sub> reduces to MoO<sub>2</sub> and then MoO<sub>2</sub> can be reduced to elemental molybdenum. Furthermore, Zn<sub>2</sub>Mo<sub>3</sub>O<sub>8</sub> phase can be formed as an unwanted intermediate phase. In the other study, research shows that, the increase of the microwave heating and reduction agent can complete the reaction and decrease the intermediate phases [14]. For separation of molybdenum metal from zinc oxide or magnesium oxide, HCl leaching can be used [15]. Manukyan et al. reported self-sustaining reduction and reaction pathway in a MoO<sub>3</sub>+Mg+C mixtures that may yield molybdenum or molybdenum carbide, depending on the process conditions [16-17]. In the previous works, the reduction of molybdenum trioxide by aluminum did not have any attention due to formation of aluminum oxide that had not solubility by HCl leaching [14]. On the other hand there is some research in which it has been shown that aluminothermic reduction reaction can be used successfully for producing metals from their oxide sources and alumina as one the reaction products can be easily separated in the form of slag. Yoshitaka et al. reported that aluminothermic reduction of chromium

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oxide was an exothermic autocatalytic reaction and a potential method for recovering of chromium from its oxide [18]. They showed that the chromium oxide could be reduced by aluminum to form molten chromium and oxide slag, formed on the metallic phase's surface which could be separated easily.

Table 1 shows the thermodynamic parameters for reduction of  $\text{MoO}_3$  by various active metallic elements.

According to Table 1, reaction of molybdenum trioxide with aluminum is highly exothermic, and it results in  $\text{Al}_2\text{O}_3$  and molybdenum metal with a density of about  $3.95 \text{ g/cm}^3$  and  $10.28 \text{ g/cm}^3$  at room temperature, respectively. Due to big difference between the densities of alumina and metallic molybdenum, it can be suggested that the separation of these two phases are probably feasible. However, no reports were found on the reduction of molybdenum trioxide by aluminum, and feasibility of separation of the reaction products.

In the present work, aluminothermic reduction of  $\text{MoO}_3$  was investigated. Initial activation energy to start the reaction was supplied by using a microwave oven and self-sustainability of the reduction reaction was studied. In the next step, feasibility of separation of reduction reaction products, including alumina and metallic molybdenum, based on difference in their densities, was investigated.

## 2. Experimental

### 2.1. Materials

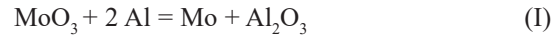
Molybdenum oxide powder (98% purity and -325 mesh size) from Sarcheshmeh- Kerman- Iran industry, aluminum oxide (99 % purity) from MERCK company and aluminum (99% purity) from UNI CHEM company in the size range of less than  $45 \mu\text{m}$  were used as raw materials. Calcium oxide ( $\text{CaO}$ ) from MERCK company was used to form a slag ( $\text{CaO}.\text{Al}_2\text{O}_3$ ) with relatively low melting temperature and viscosity.

**Table 1.** Thermodynamic assessments for reduction of  $\text{MoO}_3$  by various elements [15, 17, 19-20]

Reduce agent	Reduction reaction	$\Delta H_{298}^\circ$ (KJ)	$\Delta G_{298}^\circ$ (KJ)	Log [Keq] T=298 K
Zn	$\text{MoO}_3 + 3\text{Zn} = \text{Mo} + 3\text{ZnO}$	-306.899	-293.636	51.47
Si	$\text{MoO}_3 + 1.5\text{Si} = \text{Mo} + 1.5 \text{SiO}_2$	-621.68	-617.175	108.9
Al	$\text{MoO}_3 + 2\text{Al} = \text{Mo} + \text{Al}_2\text{O}_3$	-931.089	-914.791	160.36
Mg	$\text{MoO}_3 + 3\text{Mg} = \text{Mo} + 3\text{MgO}$	-1060.198	-1040.575	182.411

## 2.2. Apparatus and procedure

In each experiment, the mixture of  $\text{MoO}_3$  and Al powders, presented in reaction (I), was blended by using an attritor.



Then 10 g of each blended powder was pressed uniaxially under three different pressures of 40, 70, and 100 MPa to obtain pellets with different green densities, for studying the effect of green density on the reaction.

An 800 W microwave oven was used for ignition of prepared pellets by exposing them to the microwave radiation about 10 s.

To solve the problem of sublimation of  $\text{MoO}_3$ ,  $\text{CaO}$  was used to react with  $\text{MoO}_3$  to form  $\text{CaMoO}_4$ , stabilize  $\text{MoO}_3$ , and prevent sublimation of  $\text{MoO}_3$ .

The raw and the final products of reduction reaction were analyzed by a Philips X-pert X-ray diffractometer using Cu  $K\alpha$  radiation. A scanning electron microscope (SEM), including EDX analyzer, was used to study the reaction products.

## 3. Results and discussion

### 3.1. Investigation of thermodynamic parameters in metallurgical reduction of $\text{MoO}_3$

Thermodynamic calculation of different reactions introduced in Table 1 is shown in Table 2 [14, 19, 23].

The Eq. 1 can be used for calculation of adiabatic temperature ( $T_{ad}$ ) of the reaction I

$$-\Delta H_r^{1173} = \int_{1173}^{T_m^{Al_2O_3}} (C_p^{Al_2O_3(s)} + C_p^{Mo(s)})dT + \Delta H_m^{Al_2O_3} + \int_{T_m^{Al_2O_3}}^{T_m^{Mo}} (C_p^{Al_2O_3(l)} + C_p^{Mo(s)})dT + \Delta H_m^{Mo} + \int_{T_m^{Mo}}^{T_{ad}} (C_p^{Al_2O_3(l)} + C_p^{Mo(s)})dT \quad (1)$$

Where  $C_p$  is the heat capacity of the substances in 1 atm,  $\Delta H_m$  is the latent heat of melting, and 1173 is the ignition temperature of reaction that is calculated from the thermal analysis. According to Tables 1 and 2, the aluminothermic reduction of molybdenum trioxide is possible at all temperatures regarding the thermodynamic values. As Table 2 and equation (1) show, the adiabatic temperature of the reaction (I) is about 5956 K and  $\Delta H_{298}^\circ / C_p$  is 9094 K which shows that this reaction is a SHS reaction ( $T_{ad} > 1800 \text{ K}$  for SHS reactions) [14]. Tables 1 and 2 show that aluminothermic reduction of  $\text{MoO}_3$  against zincothermic, silicothermic, and magnesium carbothermic reaction has a higher  $\Delta H_r$ , higher negative value of  $\Delta G_r^\circ$ , and high  $T_{ad}$  values that will

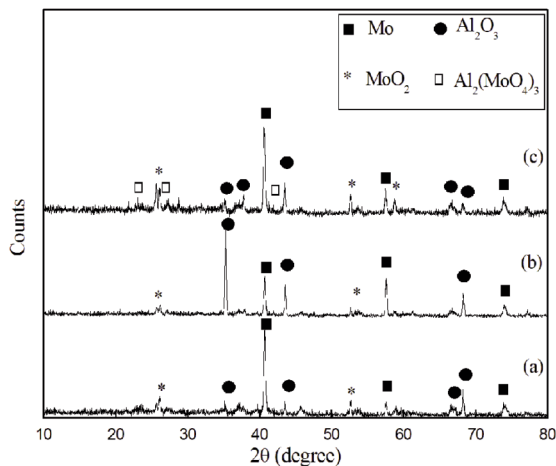


cause all products to melt.

### 3.2. The products of aluminothermic reduction of molybdenum trioxide

Fig. 1 indicates the XRD patterns of the combustion products of the compacted mixed powders of MoO<sub>3</sub> and aluminum in microwave.

The XRD patterns of the combustion products show formation of elemental molybdenum and aluminum oxide, furthermore, two other intermediate phases can be detected among the products. As shown in Fig. 1, by increasing the compaction pressure of the pellets, the undesired phases of molybdenum dioxide (MoO<sub>2</sub>) and aluminum molybdate Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> can be more easily detected among the products. The presence of both MoO<sub>2</sub> and Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> phases indicates that the aluminothermic reduction was



**Figure 1.** The effect of die pressure on XRD patterns of the synthesized products after combustion in microwave oven. (a: P= 40 MPa, b: P= 70 MPa, and c: P= 100 MPa)

**Table 2.** Thermodynamic assessments for reduction of MoO<sub>3</sub> by Al, Zn and Mg+C

Reduce agent	Reduction reaction	Adiabatic temperature T <sub>ad</sub> (K)	ΔH <sup>o</sup> <sub>298</sub> /C <sub>p</sub> (K) (Merzhanov's criterion)	Ref.
Zn	MoO <sub>3</sub> +3Zn=Mo+3ZnO	1939	--	[14, 15]
Al	MoO <sub>3</sub> +2Al=Mo+Al <sub>2</sub> O <sub>3</sub>	5956	9094	Present work
Mg + C	2MoO <sub>3</sub> + 5Mg + 2C = 5MgO + Mo <sub>2</sub> C + CO	3969.85	--	[23]
	2MoO <sub>3</sub> + 4Mg + 3C = 4MgO + Mo <sub>2</sub> C + 2CO	3257.93		
	2MoO <sub>3</sub> + 3Mg + 4C = 3MgO + Mo <sub>2</sub> C + 3CO	2526.03	--	
	2MoO <sub>3</sub> + 2Mg + 5C = 2MgO + Mo <sub>2</sub> C + 4CO	1132.4		

incomplete. By increasing the compaction pressure of the pellets, green density of the pellets was increased and the remained porosity in the pellets decreased.

Density and porosity of the compacted raw materials was calculated and presented in Table 3 after pressing in a die by applying different pressures.

As is shown in Table 3, increasing the compaction pressure leads to decreasing in remained porosities and much more mechanical interlocking between the particles, and much more contacts points/area between the metallic soft/deformable Al particles that cause more metallic like properties for the pellet as well. These events not only led to more reflection of microwave radiation, but also it caused some difficulties in Al molten phase penetration during the reduction reaction. For the samples prepared by applying low pressure, it could be supposed that Al would be able to penetrate more easily to the point of reaction, while in the samples prepared by applying high pressure, migration of Al, as reducing agent, was much more difficult and therefore more intermediate phases and incomplete reaction could be expected. The same phenomena was also well known in liquid phase sintering process, where low density of green body was preferred for easier liquid phase penetration [24].

### 3.3. Effect of the amount of Al, as reduction agent, on the combustion products

In the case of reduction of MoO<sub>3</sub> by Zn carried out

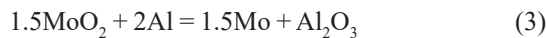
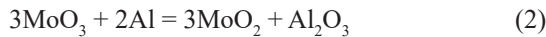
**Table 3.** Density and porosity of compacted raw materials after pressing in a die at different pressures

Mixing of MoO <sub>3</sub> +Al	P=40 MPa	P=70 MPa	P=100 MPa
Green density(g/ cm <sup>3</sup> )	2.57	2.92	3.07
Porosity (%)	33.5	24.9	21

by Hoseinpur and et. all [14], two methods for removing the intermediate phases, such as  $Zn_2Mo_3O_8$ , and completion of the reaction were applied. These two methods were increasing the heating of microwave and initial amount of Zn [14]. In the present study, using Al more than stoichiometric ratio was examined to see if it was possible to remove the intermediate phases and obtain the final products.

According to the reaction (1), the stoichiometric ratio of Al/MoO<sub>3</sub> was equal to 2 ( $\alpha=2$ ). Fig. 2 shows the XRD patterns of the products after combustion of mixed powders of MoO<sub>3</sub> and aluminum in microwave for  $\alpha=2$  (stoichiometric ratio),  $\alpha=3$  (50% excess Al), and  $\alpha=4$  (100% excess Al). The applied pressure for preparation of these pellets was 70 MPa.

According to Fig. 2, it is seen that by increasing the amount of Al more than stoichiometric, the intermediate phases, such as MoO<sub>2</sub>, was produced. The formation of MoO<sub>2</sub> and Mo indicates that reduction of MoO<sub>3</sub> by Al in reaction (1) could be divided in two steps. In the first, MoO<sub>3</sub> could be reduced to molybdenum dioxide (MoO<sub>2</sub>) and finally MoO<sub>2</sub> could be reduced by Al according to reaction (3).

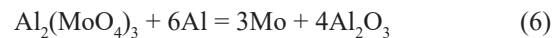


The XRD patterns in Fig.1 did not show any unreacted MoO<sub>3</sub> phase in the final products that further inferred that reaction (2) was completed. However, the second step, (reaction (3)) was incomplete, due to the presence of MoO<sub>2</sub> among the products. The produced Al<sub>2</sub>O<sub>3</sub> could be the reason, between the MoO<sub>2</sub> and Al, that the reaction (3) stopped [15]. This means, when MoO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were produced in reaction (2), Al<sub>2</sub>O<sub>3</sub> separated Al and

MoO<sub>2</sub> from each other and slowed or even terminated the reaction (3). Therefore, it can be concluded that during the aluminothermic reduction, the first step (reaction (2)), occurred immediately. However, MoO<sub>3</sub> also reacted with aluminum oxide to form aluminum molybdate, according to reaction (4), to produce another intermediate phase [22].



It should be noted that the Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> was an intermediate composition that remained among the final products. Here, two different paths for the reduction of Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> occurred. In the first path, according to reaction (5), Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> dissociated to molybdenum dioxide and aluminum oxide, then molybdenum dioxide was reduced to molybdenum with the reaction (3). In the second path, Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> was reduced to molybdenum metal regarding to reaction (6).



By increasing  $\alpha$ , the mode of reaction was changed from progressing mode to explosive mode, therefore, by starting the reaction, MoO<sub>3</sub> was reduced by Al (reaction (2,4)), but the produced particles moved away from each other due to explosion. Therefore, the chance of reduction of MoO<sub>2</sub> decreased and MoO<sub>2</sub> and Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> increased by increasing the amount of Al [24]. In this condition the reactions (3), (5), and (6) were not completed and the intermediate phases including MoO<sub>2</sub> and Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> appeared in the combustion products. The mechanism and kinetics of aluminothermic reduction of molybdenum trioxide was studied by Sheybani et al [27]. Simultaneous thermal analysis (STA) under argon atmosphere with a heating rate of 10 °C/ min was carried out and the kinetics of reduction reaction was investigated using Coats-Redfern method. The kinetic model for the aluminothermic reduction of molybdenum trioxide was determined as chemical control [27].

### 3.4 Effect of CaO addition on the aluminothermic reduction of MoO<sub>3</sub>

One of the main problems in aluminothermic reduction of molybdenum trioxide was the sublimation of molybdenum trioxide [21]. The other problem was the formation of Al<sub>2</sub>O<sub>3</sub> as a final product that did not show solubility by HCl leaching [15, 17, 23].

This problem was solved by adding CaO to the raw materials [21-22]. In the presence of CaO, calcium molybdate was formed [22]. Calcium

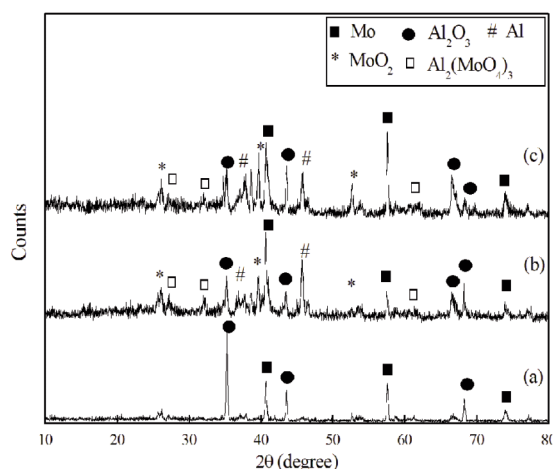


Figure 2. XRD patterns of the synthesized products after combustion in microwave for (a)  $\alpha=2$ , (b)  $\alpha=3$  and (c)  $\alpha=4$

molybdate was stable at reaction temperature and was easily reduced by Al in the process [22]. Finally, a slag with lower melting point and lower density than  $Al_2O_3$  was formed [22].

Fig. 3 shows the phase diagram of CaO- $Al_2O_3$  system, by addition of CaO to the  $MoO_3$ -Al system. Synthesized  $Al_2O_3$  reacted with CaO and formed a phase, such as  $CaO.Al_2O_3$ , that had a lower density and lower melting point than the one which can be separated in the form of melted phase. Under this condition, a system including two components, molten slag and molten metal (Mo), was formed.

In the presence of CaO, the chemical reaction between  $MoO_3$  and CaO occurred at a low temperature according to the following reaction [21]:



The formation of  $CaMoO_4$  stabilized  $MoO_3$  and

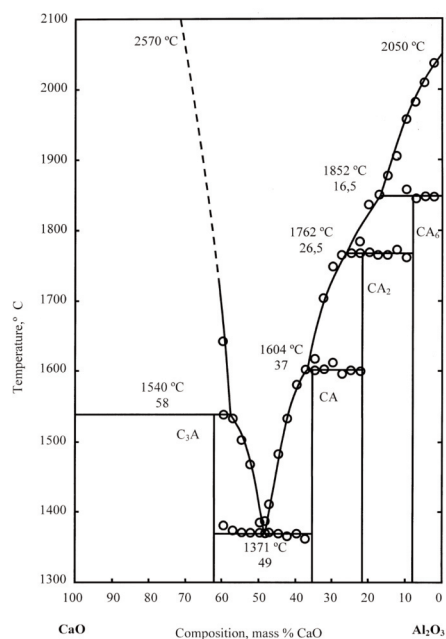


Figure 3. Phase diagram of the CaO -  $Al_2O_3$  system [25]

Table 4. Thermodynamic parameters of reactions (7) and (8) in different temperatures [19, 20]

Reaction	T(°C)	$\Delta H^\circ$ (kJ)	$\Delta G^\circ$ (kJ)	Log K(T)
$MoO_3 + CaO = CaMoO_4$	400	-163.018	-167.077	12.96
	600	-163.101	-168.27	11.329
	800	-163.295	-169.437	9.064
	1000	-215.016	-161.324	6.619
$CaMoO_4 + 2 Al = Mo + CaO.Al_2O_3$	400	-786.23	-740.546	57.46
	600	-798.04	-725.34	43.39
	800	-834.6	-703.79	34.25
	1000	-849.95	-678.08	27.82

prevented sublimation of  $MoO_3$ .

In the second step calcium molybdate was reduced by Al to Mo and  $CaO.Al_2O_3$  according to reaction (8) [22].



The thermodynamic parameters of reactions (7) and (8) in different temperatures are shown in Table 4, which confirmed the feasibility of reactions (7) and (8) due to their high negative values of  $\Delta G^\circ$  and  $\Delta H^\circ$ .

Fig. 4 shows the XRD patterns for  $MoO_3$ -CaO mixtures with 1:1 mole ratio. According to reaction (7), they reacted at different temperatures for 30 min. It was obvious that  $MoO_3$  reacted with CaO to form calcium molybdate ( $CaMoO_4$ ). According to Fig. 4, at 600 °C, unreacted  $MoO_3$  and CaO were detected in the products after 30 min of heating, but by increasing temperature to 800 °C, the unreacted materials were decreased and  $CaMoO_4$  was produced completely.

Fig. 5 shows the XRD patterns of the synthesized products after combustion of mixed powders of  $MoO_3$ , aluminum (with stoichiometric mole ratio),

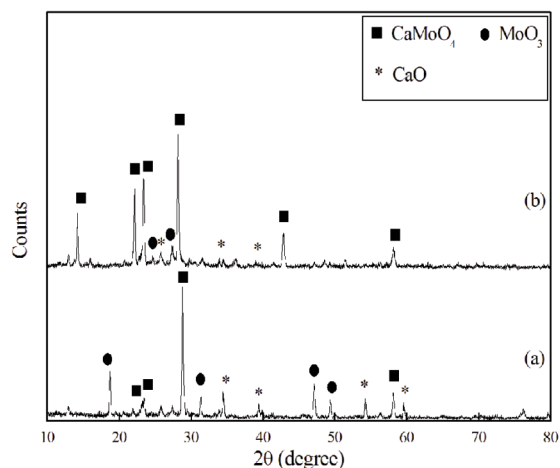


Figure 4. XRD patterns for  $MoO_3$ -CaO mixtures reacted at different temperatures for 30 min. (a):  $T = 600^\circ C$  (b):  $T = 800^\circ C$

and necessary amount of CaO for formation of  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  phase in microwave. The necessary amount of CaO was calculated from the produce  $\text{Al}_2\text{O}_3$  that was balanced to produce  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ . The applied pressure for preparation of the pellets was 70 MPa.

According to Fig. 5, by addition of CaO to the system,  $\text{Al}_2\text{O}_3$  reacted with CaO and formed a  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  phase that had a lower density and melting point [25, 26] so it could be separated easily from the heavy molten Mo phase. Figures 6 and 7 show the SEM images of the products of aluminothermic reduction of  $\text{MoO}_3$  in microwave with and without addition of CaO.

According to Figures 6 and 7, by addition of CaO, alumina phase with cubic crystal structure was eliminated and a new phase appeared in the products.

Therefore, by addition of CaO, three problems can be solved that are shown in Fig. 8

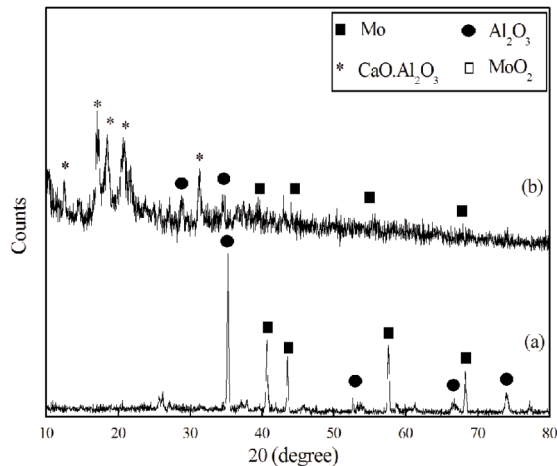


Figure 5. The XRD patterns of the synthesized products after combustion of mixed powder. (a): without CaO (b) with additional CaO

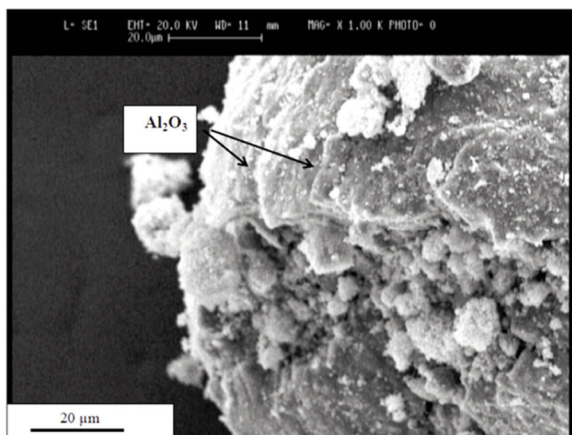


Figure 6. SEM image from the slag of aluminothermic reduction of  $\text{MoO}_3$  in microwave without addition of CaO

### 3.5. Separation of products after reduction of $\text{MoO}_3$ by Al without CaO addition

In the aluminothermic reduction of molybdenum trioxide,  $\text{Al}_2\text{O}_3$  was formed according to reaction (I) that did not show solubility by HCl leaching. But in the case of zincothermic and magnesiothermic, ZnO and MgO were produced that had a good solubility with HCl. [16-17]. In the present work a simple method for removing  $\text{Al}_2\text{O}_3$  from the molybdenum metal was introduced. According to reaction (I), Mo and  $\text{Al}_2\text{O}_3$  were the final products of the reaction with large difference in their densities. The density of molybdenum metal was  $10.28 \text{ g/cm}^3$  and  $\text{Al}_2\text{O}_3$  had a density about  $3.95 \text{ g/cm}^3$  at room temperature. The adiabatic temperature and  $\Delta H$  of the reaction (I) is presented in Table 3. Based on an investigation carried out by Sheybani et al., it can be seen that the aluminothermic reduction of  $\text{MoO}_3$  was characterized by three peaks in DSC curves. The second and third peaks occurred at 850 and 1100 °C, and the first peak was an endothermic one that occurred at about 660 °C due to the melting of Al powder. The second and third peaks occurred due to the exothermic reactions. This means that aluminothermic reduction of molybdenum trioxide was advanced through the two steps [27].

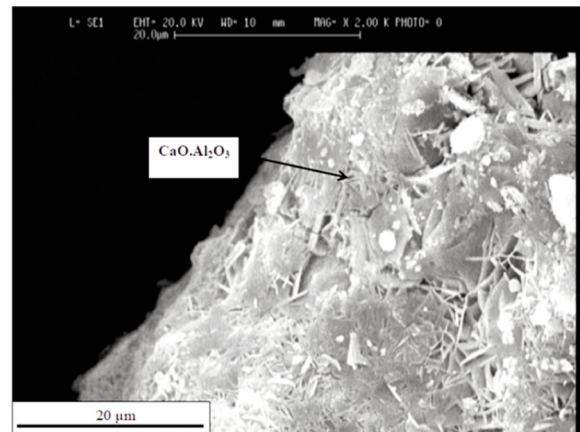


Figure 7. SEM image from the slag of aluminothermic reduction of  $\text{MoO}_3$  in microwave with addition of CaO

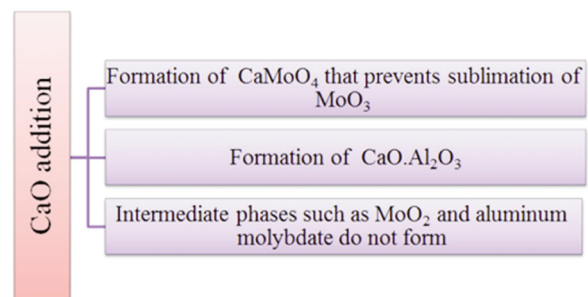


Figure 8. Advantage of addition of CaO to the system of  $\text{MoO}_3$ -Al

Due to the high adiabatic temperature of the reaction and high amount of heat of reaction, all products were produced in the liquid state, and a system containing of slag ( $\text{Al}_2\text{O}_3$ ) and melt (Mo metal) that could be easily separated was formed. Fig. 9 shows the slag and melt formed during the aluminothermic reduction of molybdenum oxide.

Figures 10 and 11 show the SEM image and EDS analysis of the formed metallic compound and slag as the products of aluminothermic reduction of molybdenum oxide by metallic aluminum.

Regarding Fig. 10 and Fig. 11, it can be seen that the molybdenum oxide was reduced by aluminum to metallic molybdenum and a slag, based on aluminum oxide. According to Fig. 10 (a), it can be seen that  $\text{Al}_2\text{O}_3$  was completely separated during the reduction and melting process and only the molybdenum peak was detected. This is a clear evidence for the production of pure elemental molybdenum during the current research. Regarding Fig. 11 (a), the peaks of Al and O in the EDS analysis and no evidence of molybdenum metal in slag could be seen. Therefore, the slag mainly included  $\text{Al}_2\text{O}_3$ . The SEM images in Figures 10 and 11 show existence of some porosities in the metallic molybdenum and slag. To compare the density of products (metallic molybdenum and slag), the density of products was measured with Archimedes method. Table 5 shows the obtained densities of the product compounds and compare them with theoretical density.

According to Table 5, the density of metallic compound was almost the same as the theoretical density of molybdenum metal, and for the slag, it was near to the theoretical density of aluminum oxide.



Figure 9. (a) Metallic product (b) Slag and (c) Metallic product and slag before separation

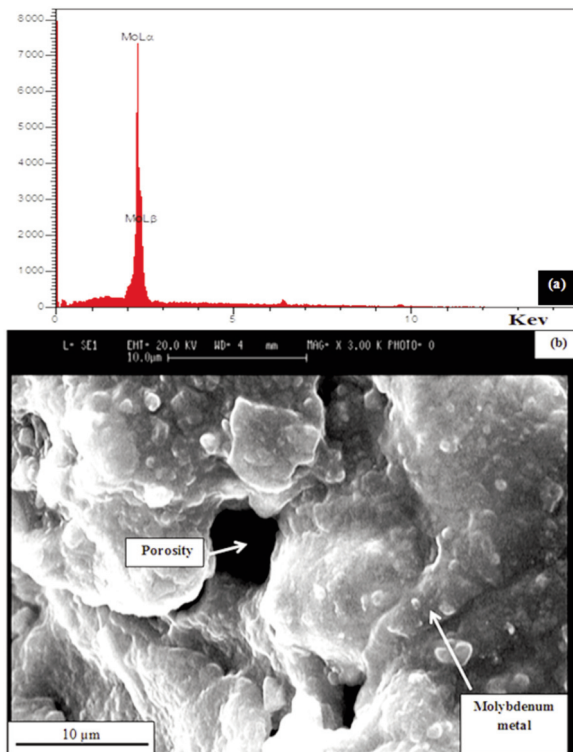


Figure 10. (a) EDS analysis and (b) SEM observation of metallic compound of aluminothermic reduction of molybdenum oxide

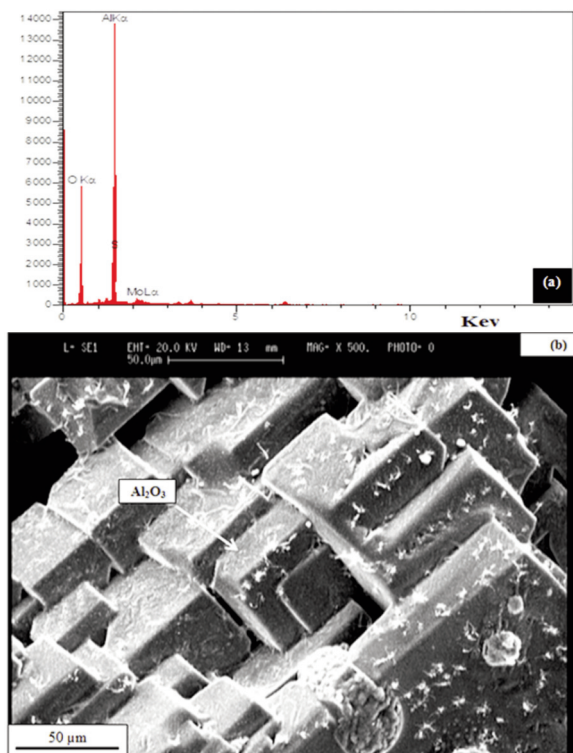


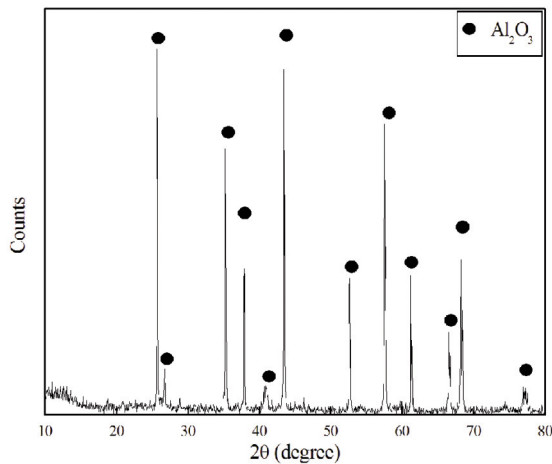
Figure 11. (a) EDS analysis and (b) SEM observation of slag of aluminothermic reduction of molybdenum oxide

The difference between apparent density and theoretical density is probably due to the existence of some porosities that are shown in SEM images presented in Figures 10(b) and 11 (b).

The XRD pattern of the formed slag that is shown in Fig. 12 was also an indication of creation of  $Al_2O_3$  (with Ref. pattern 01-081-2266) as the main phase of formed slag.

**Table 5.** Densities of product compounds in comparison with their theoretical density

Product	Apparent density(g/cm <sup>3</sup> )	Theoretical density(g/cm <sup>3</sup> ) at room temperature
Metallic compound	8.7	Mo = 10.3
Slag	3.4	$Al_2O_3 = 3.9$



**Figure 12.** XRD pattern of slag compound of aluminothermic reduction of molybdenum oxide

#### 4. Conclusions

The main findings of this research can be summarized as follow:

1 - The thermodynamic investigations showed that aluminothermic reduction of  $MoO_3$  was possible at all temperatures due to the negative value of  $\Delta G^\circ$

2 - The possible stages of aluminothermic reduction of molybdenum trioxide were through the formation of  $MoO_2$  and  $Al_2(MoO_4)_3$  as intermediate phases and the final products of the reaction were Mo and  $Al_2O_3$ .

3 - By increasing the applied pressure used for compacting  $MoO_3$  and Al mixed powder, amount of undesired phases of molybdenum dioxide ( $MoO_2$ ) and aluminum molybdate  $Al_2(MoO_4)_3$  increased in the products possibly due to the decrease in porosities.

4 - By increasing the amount of Al more than stoichiometric amount, undesired phases

molybdenum dioxide ( $MoO_2$ ) and aluminum molybdate  $Al_2(MoO_4)_3$  increased due to conversion of reaction to explosive mode.

5 - By addition of CaO to the  $MoO_3$ -Al system, a compound such as  $CaO.Al_2O_3$  was formed which could solve the problem of sublimation of  $MoO_3$  and creation of undesired phases of molybdenum dioxide ( $MoO_2$ ) and aluminum molybdate  $Al_2(MoO_4)_3$ .

6 - Due to the high values of  $T_{ad}$  and  $\Delta H^\circ$  of aluminothermic reduction of molybdenum oxide, all products were formed in liquid state, with a great difference in densities of products that can be separated from each other easily.

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#### References

- [1] M.h. Golmakani, J. Vahdati khaki, A. Babakhani, J. Min. Metall. Sect. B-Metall., 54 (2) B (2018) 233 – 241.
- [2] B. Hu, B.Yao, J. Wang, J. R. Zhao, F. F. Min, Y. Du, J. Min. Metall. Sect. B-Metall., 53 (2) B (2017) 95 – 106.
- [3] J. Dang, G.H. Zhang, K.C. Chou, R.G. Reddy, Y. He, Y. Sun, Int. J. Refract. Met. Hard Mater., 41 (2013) 216-223.
- [4] I. Wilkomirsky, A. Otero, E. Balladares, Metall. Mater. Trans. B, 63 (2010) 63-67.
- [5] M. Afsahi, M. Sohrabi, R. Vasant Kumar, H. Ale Ebrahim, Thermochem. Acta, 473 (2008) 61-67.
- [6] W.V. Schulmeyer, H. M. Ortner, Int. J. Refract. Met. Hard Mater., 20 (2002) 261-269.
- [7] Z. Hung, L. Zheng, J. Iron Steel Res. Int., 21 (2013) 51-56.
- [8] S. Bakhshandeh, N. Setoudeh, M. Ali Askari Zamani, A. Mohassel, J. Min. Metall. Sect. B-Metall., 54 (3) B (2018) 313 – 322.
- [9] A. Manjari, P. Ravikumar, J. Magn. Mag. Mater., 418 (2016) 253-259.
- [10] G.D. Sun, G.H. Zhang, S. Jiao, K.C. Chou, J. Phys. Chem. C, 122 (2018) 10231-10239.
- [11] J. Yonglin, L. Bingguo, L. Peng, Z. Libo, Metall. Mater. Trans. B, 16 (2017) 213-220.
- [12] S.K. Ko, C.W. Won, S.S. Cho, B.S. Chun, Metall. Mater. Trans. B, 27 (1998) 315-318.
- [13] D. Davtyan, K. Manukyan, R. Mnatsakanyan, S. Kharatyan, Int. J. Refract. Met. Hard Mater., 28 (2010) 601-604.
- [14] A. Hoseinpour, M.Sh. Bafghi, J.V. Khaki, Int. J. Refract. Met. Hard Mater., 50 (2015) 191-196.
- [15] K. Manukyan, R. Mnatsakanyan, S. Kharatyan, Int. J. Refract. Met. Hard Mater., 28 (2010) 601-604.
- [16] K. Manukyan, S. Aydinian, A. Aghajanyan, Y. Grigoryan, O. Niazyan, S. Kharatyan, Int. J. Refract. Met. Hard Mater., 31 (2012) 28-32.
- [17] S.V. Aydinian, Z. Manukyan, Mater. Sci. Eng. B, 172 (2010) 267-271.



- [18] K. Yoshitak, J. Yang, Metall. Mater. Trans. B, 127 (2007) 271-276.
- [19] C.K. Gupta, Extractive metallurgy of molybdenum, CRC press, USA, 1992.
- [20] A. Roine, "Outokumpu HSC chemistry software," vol. 5.1, 2002.
- [21] Z. Hung, L. Zheng, J. Iron Steel Res. Int., 13 (2013) 51-56.
- [22] O.K. Mehra, C.K. Gupta, Metall. Trans., 4 (1992) 691-694.
- [23] Y. Wang, L. Wang, K.C. Chou, J. Min. Metall. Sect. B-Metall., 51 (1) B (2015) 17 - 24.
- [24] R-M German, Liquid phase sintering, Springer Science+Business Media, New York, 1985.
- [25] H. Doweidar, J. Non-Cryst. Solids, 471 (2017) 344-348.
- [26] V.E. Sokol'skiia, D.V. Prutskovb, V.M. Buskob, V.P. Kazimirova, O.S. Roika, A.D. Chyrkina, V.I. Galinich, I.A. Goncharovc, J. Min. Metall. Sect. B-Metall., 54 (2) B (2018) 133 - 141.
- [27] K. Sheybani, M.H. Paydar, M.H. Shariat, Trans. Indian Inst. Met., 73 (202) 2875-2888.

## ISPITIVANJE ALUMINOTERMIJSKE REDUKCIJE $\text{MoO}_3$ U MIKROTALASNOJ PEĆNICI

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### Apstrakt

U ovom radu je ispitivana izvodljivost aluminotermijske redukcije molbiden oksida u mikrotalasnoj pećnici. Pored toga je ispitan i uticaj pritiska prilikom sabijanja, kao i količina upotrebljenog Al i CaO u svojstvu reagensa za aluminotermijsku redukciju molbiden oksida. Termodinamička analiza odgovarajuće reakcije je pokazala da je aluminotermijska redukcija  $\text{MoO}_3$  moguća na svim temperaturama. XRD obrasci i termodinamičko ispitivanje proizvoda reakcije su pokazali da je aluminotermijska redukcija molbiden oksida napredovala formiranjem prelaznih faza kao što su  $\text{Al}_2(\text{MoO}_4)_3$  i  $\text{MoO}_2$ , dok su konačni proizvodi bili elementarni Mo i  $\text{Al}_2\text{O}_3$ . Rezultati su pokazali da se povećanjem pritiska prilikom sabijanja peleta mogu detektovati neželjene faze molbiden-dioksida ( $\text{MoO}_2$ ) i aluminijum molbidata  $\text{Al}_2(\text{MoO}_4)_3$  među finalnim proizvodima. Povećanjem količine Al iznad vrednosti stehiometrijskog odnosa dolazi do stvaranja prelaznih faza kao što je  $\text{MoO}_2$ . Rezultati su takođe pokazali da se dodavanjem CaO u  $\text{MoO}_3$ -Al sistem neželjene faze molbiden-dioksida ( $\text{MoO}_2$ ) i jedinjenja aluminijum molbidata ( $\text{Al}_2(\text{MoO}_4)_3$ ) uspešno redukuju u Mo. U ovom radu je metalni molbiden lako i usepešno izdvojen iz  $\text{Al}_2\text{O}_3$  šljake kao sporedni proizvod reakcije, u rastopljenoj fazi i na osnovu razlike u njihovoj gustini.

**Ključne reči:** Molbidenit; Molbiden oksid; Aluminotermijska redukcija; Šljaka; Prelazna faza

