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Direct Production of Ferromolybdenum from Molybdenite by Combustion Synthesis Reaction in the Presence of Aluminum

Suhrab Nikjo Qaisari[1] and Zabiullah Haidari[2]
[1]Department of Chemical Engineering, Faculty of Engineering, Faryab University, Maymana, Faryab 1801, AFGHANISTAN.
[2]Department of Drawing and Descriptive Geometry, Construction Faculty, Kabul Polytechnic University, Kabul 1001, AFGHANISTAN.

[1]Corresponding Author: suhrab.nikjo2021@gmail.com

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ABSTRACT

In this research, a new method for the direct and in-situ production of ferromolybdenum alloy by the combined aluminothermic reduction of molybdenum sulfide (MoS) and iron oxide Fe_2O_3 has been introduced and its feasibility has been investigated. Also, in order to investigate the effect of the presence or absence of a desulfurizer on the chemical composition and purity of the product, lime (CaO) and magnesia (MgO) have been used as desulfurizers. Preliminary investigations showed that the heat of reduction of molybdenum sulfide by aluminum is very high. Their reaction can be carried out as a self-promoting combustion synthesis reaction (Self-propagating high-temperature synthesis). Also, preliminary results showed that increasing the amount of iron oxide in the composition of raw materials increases the heat produced by the reaction, which results in the melting of FERROMOLYBDENUM as a reaction product. In order to examine the synthesized phases and analyze the obtained results, the images taken by the scanning electron microscope (scanning electrode microscope) and the data obtained from the analysis (Energy-dispersive spectroscopy) were used. Also, X-Ray Diffraction Analysis was used to analyze the formed slag. The results indicate that the reaction carried out in the presence of magnesia as a desulfurizer is a more successful system in absorbing sulfur from the produced alloy.

Keywords- Direct reduction, aluminothermic reduction, ferromolybdenum, combustion synthesis and molybdenite.

I. INTRODUCTION

Molybdenum is a rare and valuable metal that is used in various industries such as steel production, electrical industries.

It is used in electronics, nuclear energy and oil. This metal is one of the important alloy elements in steels, which plays a great role in increasing their mechanical and physical properties. In steels, the increase of molybdenum causes the uniformity of the microscopic structure, increase of hardenability and prevention of brittleness after turning. In addition, molybdenum increases creep resistance, hot hardness and strength at high temperatures. More than eighty percent of the consumption of molybdenum element is in various types of stainless steels and super alloys, low alloy steels, as well as tool and casting steels, and about twenty percent of it is used in the form of molybdenum chemical and metal compounds [1].

Molybdenite is the main source of molybdenum production, which is one of the ores that exist in the country and is one of the most important side products of copper factories. Due to the great importance of molybdenum in various industries, its extraction in the country seems to be an economic and necessary matter. At present, the traditional method of producing Ferro-molybdenum from molybdenite, which after decades is still the most common method for this purpose, consists of a process step called Annealing stage on processed and purified molybdenite ore and production of molybdenum trioxide and then performing melting operations under special conditions and in the presence of reductants such as aluminum and obtaining Ferromolybdenum alloy [1, 2]. The general goal of the upcoming research is to provide a new method for producing Ferromolybdenum, which can solve the problems of the conventional method by removing the quenching step and directly reducing molybdenum disulfide to metal. To solve the production of this alloy to a large extent and in the absence of a suitable industrial substitute for this method, it can be proposed as an industrial method. For this purpose, the use of thermite reactions to perform the simultaneous reduction process of molybdenum sulfide and iron oxide in the presence of metallic aluminum and in-situ production of Ferromolybdenum has been proposed.

Some chemical reactions, which are known as thermite reactions, produce a considerable amount of heat when they are carried out. The heat produced in these reactions is sometimes to such an extent that if the reaction starts in one corner of the raw materials, the resulting heat can provide the necessary activation energy for the adjacent layers and therefore the reaction can spread to other points. The reaction of iron and aluminum oxide is an example of this reaction. This property of thermite reactions is used in the process of combustion synthesis. Combustion synthesis is a new method for the production and synthesis of ceramics, compounds and metal alloys and composite materials [2]. The traditional methods of producing metal alloys require the use of furnaces with high temperature and long time, which increases the price of these materials, but the interesting feature of the new method, such as low energy consumption and high speed, has made it very useful after a short period of use. Be noticed.

II. METHODOLOGY

In this research, the studies of several books about the combustion synthesis process for the production of Ferromolybdenum alloy directly from its sulfide ore have been used. In order to produce an alloy with a better chemical composition and higher purity, it is suggested to use appropriate desulfurization in the reaction, which can absorb the sulfur in the alloy during the reaction and enter the reaction slag as a solid product. Also, another point that is important to mention is that one of the big problems is the traditional method of producing toxic sulphide gases and causing environmental pollution, which is due to the significant need that the world currently has to use environmental materials. Better industrial methods one of the important goals in advancing this research has been to prevent the release of sulfur as a gas in the environment and trap it in the form of solid products.

III. RESULT DISCUSION

3.1. Combustion synthesis process:

Combustion synthesis is a term used to describe a process that first contains raw materials, and when the materials are ignited due to the heat released from the reaction, the raw materials are automatically transformed into products. Other terms such as gasless combustion, self-promoting combustion and self-promoting exothermic reactions are used to describe similar processes [2].

In this method, different powders are mixed and compressed. Then this compressed mixture is ignited in air or a neutral atmosphere and by performing an exothermic chemical reaction, the combustion front is created. When this front passes through the reactants, products are produced (Figure 1). Primary heat can be provided by factors such as electric spark, induction, laser, hot wire, furnace or any other heat source. Another method of generating primary heat is using It is from the microwave. In this method, the heat starts to increase from the inside and is transferred to the surface of the part, which prevents the part from breaking due to the stresses caused by the contraction. A significant point in the microwave is the increase in the absorption of waves due to rising. It is the temperature that can be effective in increasing the temperature. High temperature, high speed of heating and cooling, and high speed of the progress of the combustion front are some of the significant points of this process [2, 3].

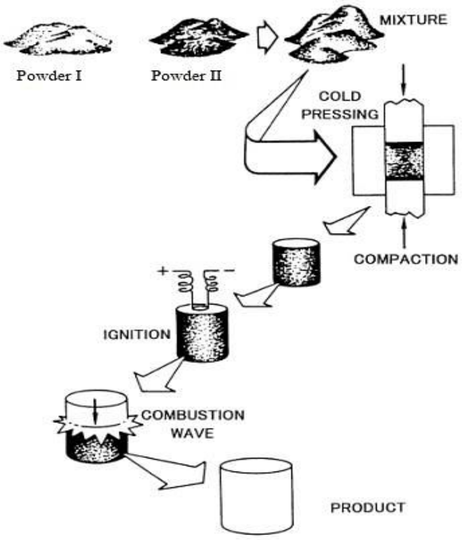

Figure 1: **A schematic of the combustion synthesis reaction and the production of the final product from the initial powders [4]**.

Combustion synthesis is a process in which two or more substances with a negative heat of mixing, when If they are heated enough, they start to mix on an atomic scale and release heat in this process [5]. The heat produced in these reactions is sometimes to such an extent that if the reaction starts in one corner of the raw materials, the resulting heat can provide the necessary activation energy for the adjacent layers and therefore the reaction can be transferred to other points. Combustion synthesis is a new method for producing ceramics, intermetallic compounds and composite materials.

Traditional methods of producing refractory and ceramic compounds require the use of furnaces with high temperature and long time, which increases the price of these materials, but the interesting features of the new method, such as low energy consumption and high speed, have made it possible after a short period of introduction It is very interesting. Since the introduction of the combustion synthesis method, various materials have been produced by this method, among which titanium carbide and its compacts can be mentioned. Combustion synthesis method is superior to traditional methods in many ways [6-7]. The most important advantage of this method is the spontaneous production of the energy required for the process and low energy consumption. Some of the other advantages of the combustion synthesis method are:

1. Low energy consumption: The production of ceramic materials using common methods requires spending a lot of time and energy, and these methods are performed using an external energy source (furnace) at high temperature and for a long time. Therefore, the products of these methods become expensive. But in the combustion synthesis method, the reaction starts by heating a small area of the sample where the heat required for this work is negligible. When the reactions start in this area, they continue and progress spontaneously.
2. Production efficiency: the high speed of the reactions causes all the raw materials to be converted in a short period of time be produced, the result of which is very high production efficiency.
3. Ease of the method and cheapness of the equipment: The equipment of the combustion synthesis method is simple and cheap, and it is easy to work with them. For this reason, the development and training of this method on an industrial scale is easily possible.
4. High quality of products: It is claimed that the quality of products produced by the combustion synthesis method is better than other production methods. The high purity of the products due to the high evaporation of impurities at the combustion temperature is one of the characteristics of the products of this method.
5. The possibility of producing different forms: the products produced by the combustion synthesis method can be diverse. The reaction product can be in powder form. The powders produced by this method can be used as a final product (for example, TiC for use in abrasive materials) or they can be made into the desired shape and density in the next step, for example, through powder metallurgy. Due to the presence of porosity in the products of this process, they can be used as ceramic filters. However, compact products with high density can also be produced. If the combustion temperature is higher than the melting temperature of one of the components, casting parts can also be produced with this method.
6. Non-equilibrium nature: The non-equilibrium nature of the combustion synthesis method has made it possible to produce quasi-stable phases and non-equilibrium structures such as FGM target materials due to the availability of a high temperature gradient.
7. Reduction of separation: Due to the fast reaction time, the separation between background and amplifying phase happens less [8, 9].

3.2. Classification of combustion synthesis reactions:

1. Processes in which combustion occurs in layers (diffusion synthesis mode).
2. Processes in which combustion occurs as a whole (volume) (explosive synthesis mode).

Diffusion synthesis mode occurs when the reactions are ignited in a small area of the surface and then the combustion wave spontaneously passes through this compressed sample. This type of combustion is called self-promoting synthesis of high temperature, which usually occurs in systems where the enthalpy of reactions is high (Figure 2).

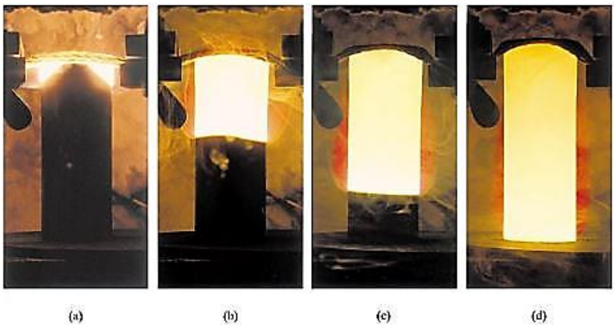

Figure 2: Sequential images of the combustion synthesis reaction in the self-promoting mode (SHS)

In the picture, Figure 3: Schematic of the combustion synthesis reaction in two modes of self-progressive synthesis and we observe explosive synthesis.

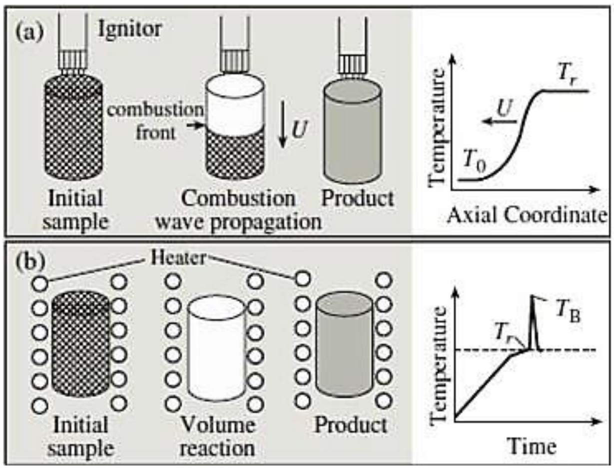

Figure 3: Schematic of combustion synthesis method a) self-propelling mode b) thermal explosion mode [10].

But in cases where the heat of the reactions is not high (such as the formation of intermetallic compounds), the whole sample before Combustion is preheated quickly and then the reaction starts simultaneously in all samples and is completed within a few seconds [11]. This type of combustion is also called thermal explosion.

3.3 Molybdenite:

Molybdenite ore or molybdenum disulfide is a modified granite whose most important deposits are located in Colorado, USA. The molybdenite crystal network is hexagonal, in which each molybdenum atom is surrounded by a triangular prism of sulfur atoms at a distance of 41/2 angstroms, so that the formation of intermediate layers of molybdenum and sulfur atoms in the form of a sandwich structure like S-Mo-S. They give the crystallographic model of molybdenite is shown in (Figure 4).

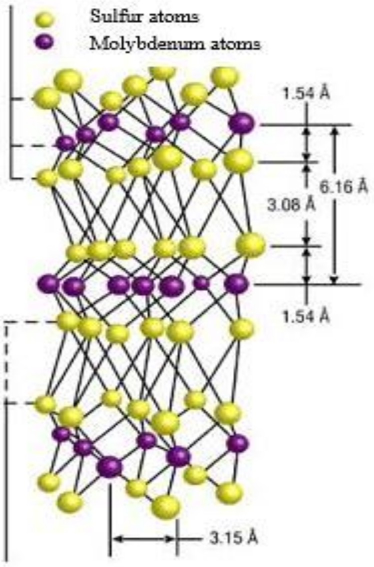

Figure 4: Crystallographic model of molybdenite [12]

3.4. An overview of the production methods of ferromolybdenum:

Due to the importance of molybdenum, the extraction and production processes of this alloy have always been of interest, so that many industrial and laboratory methods have been used to extract it from molybdenite. The traditional method used to produce Ferromolybdenum from molybdenite, which is still the most common industrial method for this purpose after decades, is a process step on molybdenite ore (MoS_2) (processed and purified, under The stage of smelting and production of molybdenum trioxide (MoO_3) and then performing smelting operations under special conditions and obtaining Ferromolybdenum. In this chapter, the conventional and industrial method of producing this alloy from the ore concentration stages to the end is described first, and then we will have an overview. On other methods of producing Ferromolybdenum.

3.5. Production of molybdenite: Concentration

Molybdenite stones are extracted by underground and open pit methods. A molybdenum ore, For example, they have 0.25 to 0.5% molybdenum and secondary rocks (copper) have on average 0.3 to 1% copper and 0.01 to 0.05% molybdenum. By flotation, molybdenite concentrate with an industrial grade of 90 to 95% is obtained. In flotation, crushed stones are mixed in water, then collecting oil and chemicals are added to selectively wet the stone particles. Unwetted copper and molybdenum particles are transported to the surface of the flotation cell by air bubbles, while the rock particles remain settled or suspended. A foaming agent is used to stabilize the bubbles (which carry sulfides) to facilitate the defoaming operation from the surface. Molybdenite flotation is spontaneous, which is called natural flotation. Other minerals such as CuS, which are usually associated with ores containing molybdenite, are also natural floaters. For this reason, the flotation process to produce - Molybdenum from the main molybdenum minerals is different from its secondary sources. The economic aspects of the process are influenced by factors such as crushing method, slurry density and the use of reactive factors [13].

3.6. Recovery from main mines:

Although the pulverization methods are different, the goal of all of them is to break the rock to release molybdenite. For example, in Climax mine, it uses four stages of crushing along with sanding and ball mills along with classified hydro cyclones to produce flotation feed. Usually, an initial crushing to prepare a concentrate with a molybdenum grade of 2.5 to 5% is acceptable in the first stage of flotation, but in the next stages, the grade of this concentrate is increased by further crushing and flotation of the cleaner. Further crushing and cleaning steps are carried out to obtain concentrates with the desired degree of freedom. For example, 6 stages of scrubber flotation are performed at the Thompson Creek plant, 5 stages at Climax and 4 stages at Henderson. Unfloated material at the output of the last step returns to the previous cleaning steps in the form of an opposite flow. Overall recovery is generally 85%. In each flotation stage, molybdenite particles are floated and collected, and impurities are transferred out of the cell by adding additives. Simple hydrocarbon collectors such as kerosene and cooking oil can be used. From pine oil, which has both emulsifying and astringent properties.

It is used as a floor covering. Of lime and sodium carbonate to control the alkaline state, usually in pH = 5.8 is used. Pollution also by controlling the pH at an optimal level and adding agents Precipitant such as (Noke) (The product formed from the reaction of stoichiometric amounts of sodium hydroxide and phosphorus Penta sulfide) and sodium cyanide are separated [13].

3.7. Concentrate processing:

Production concentrate is used for two purposes,
- Direct use
- Production of molybdenum opium seed

Some commercial grade molybdenite is further subjected to grinding and flotation operations to produce molybdenum disulfide with lubricating grade (2MoS with 99% purity). The remaining oil and water from flotation is removed by contacting the concentrate with neutral gas. This high purity product is added to greases and oils as a solid lubricant [13].

The main commercial product of molybdenum is molybdenum trioxide (3MoO). In addition to being the main compound for adding molybdenum to steel, it is the starting compound for obtaining other molybdenum products, such as ammonium dimolybdate, pure molybdenum trioxide, sodium molybdate, molybdenum metal and Ferromolybdenum. Molybdenite it is converted into molybdenum trioxide by heating in the presence of air in a layer furnace or a fluidized bed. The obtained product contains less than 0.1% sulfur. The upper layers are mainly used for burning oil and evaporating the water in molybdenite. Fossil fuels are usually used in this area-to ensure stable temperature control. The temperature in this area is between 600 and 700 degrees Celsius.

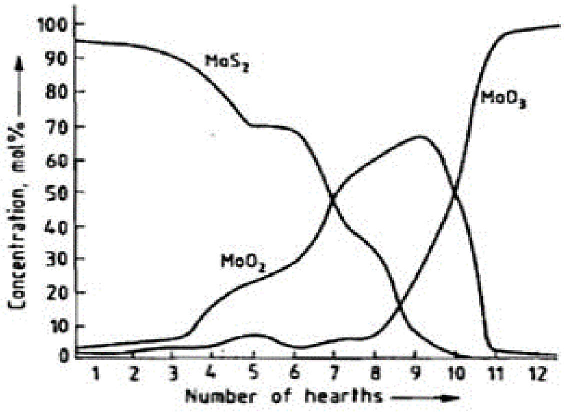

Figure 5: Molybdenum sulphide and oxide composition in stratified furnace heating [13]

Sulfur in the middle layers is removed by oxidation:
$2MoS_2 + 7O_2 = 2MoO_3 + 4SO_2$ 1
$MoS_2 + 6MoO_3 = 7MoO_2 + 2SO_2$ 2
$2MoO_2 + O_2 = 2MoO_3$ 3

3.8 Molybdenite oxidation:

At this stage, air oxygen at a temperature of more than 400 degrees Celsius comes into contact with molybdenite and turns it into molybdenum trioxide as a result of a highly exothermic and irreversible reaction. At this stage, a thin layer of oxide is formed on the surface of sulfide, and the progress of the reaction is related to the structure of the oxide layer, the speed of oxygen penetration into the common phase, and the release of sulfur dioxide from the common phase of the layer. At low temperatures (about 400 degrees), a porous oxide layer is formed.

3.9 Mutual reaction between system components during heating and production of molybdenum dioxide:

Solid components of the system in contact with sulfur dioxide and sulfur gas according to the following reactions to the dioxide Molybdenum becomes:

$MoS_2 + 3O_2 = MoO_2 + 2SO_2$ 4
$4MoO_3 + S_2 = 4MoO_2 + 2SO_2$ 5
$2MoS_2 + 2SO_2 = 2MoO_2 + 3S_2$ 6

Since molybdenum dioxide is insoluble in ammonia solutions and in the next stages of extraction, it reduces molybdenum recovery, its formation should be prevented. Although molybdenum dioxide production reactions have a high speed at temperatures over 600 degrees Celsius, but annealing at high temperatures causes severe sintering of the product and causes application problems. Therefore, annealing should be done at temperatures lower than 600 degrees.

3.10 Dissolving sulfide of other metals in the ore:

The sulfides of copper, iron, rosin and lead in the ore also turn into oxide or sulfate during molybdenite quenching in the range of 550 to 600 degrees. If molybdenite contains calcium carbonate, it is also possible to form calcium sulfate:
$CaCO_3 + SO_3 = CaSO_4 + CO_2$ 7

3.11 Formation of molybdate carbonate:

As a result of the reaction between molybdenum trioxide and oxides, sulfates and carbonates in the system, it is possible there is the formation of molybdate compounds:
$MoO_3 + MO = MMoO_4$ 8
$MoO_3 + MSO_4 = MMoO_4 + SO_3$ 9
$MoO_3 + MCO_3 = MMoO_4 + CO_2$ 10

M can be metals such as calcium, copper, zinc, iron, lead, etc. Molybdenum trioxide with compounds like calcium molybdate and copper molybdate, it forms a eutectic with a low melting point and causes sintering. The products become liquid. Therefore, the formation of these compounds should be prevented as much as possible. Lead and calcium molybdates are very little soluble in ammonia solutions and therefore reduce the process recovery in molybdenum purification stages. Therefore, the formation of these compounds should be prevented during cooling.

3.12 Leaching to remove impurities:

In many cases, a chemical leaching step is required before quenching to remove non-ferrous impurities that are problematic in steelmaking. There are three leaching processes as follows:
- Sodium cyanide leaching agent, which is used to remove gold and copper.
- Iron chloride (III) (to remove copper, lead and calcium.
- Hydrochloric acid to remove lead and bismuth [13].

3.13 Purification of molybdenum trioxide:

Pure molybdenum trioxide can be produced from industrial grade 3MoO in two ways:
1- Calcination of ammonium dimolybdate (ADM)

2- Sublimation

$MoO_3 + 2NH_3 + H_2O = (NH_4)_2MoO_4$ 11

$2(NH_4)_2MoO_4 = (NH_4)2Mo_2O_7 + 2NH_3 + H_2O$ 12

Ammonium dimolybdate crystals are recovered by centrifuge and then dried. Pure MoO_3 is produced by calcining ammonium dimolybdate in a rotating furnace that is indirectly heated at temperatures above 420 degrees Celsius [13].

3.14. Sublimation method:

Pure molybdenum trioxide can also be produced by sublimation. The oxide passes under an electric element as a thin layer in a donut-shaped furnace and is heated to a temperature of 1100-1200 degrees Celsius. The air flow passes over the heated surface and collects the vaporized MoO_3, and gangue and other non-volatile metal impurities remain in place. The charge on the furnace passes only one pass through the heating sub-elements. The remaining solid, which is still rich in molybdenum, is drained and used for steelmaking. Sublimation efficiency is about 60% to 70%. The obtained sublimation vapor is cooled, condensed and packaged after cooling.

Molybdenum oxides that are obtained through these two methods of ammonium dimolybdate calcination and sublimation, they have a high purity (9.99%). In comparison with the ADM calcination method, the pure oxides have less alkaline impurities, but they have more silicon, iron, lead and tin. They are also smaller and needle-shaped [13].

3.15. Raw materials for the experiment:

The raw materials used in this research were the primary compounds of the combustion synthesis reaction, all of which were used in powder form. In this research, combustion synthesis has been carried out on the $Fe_2O_3/Al/MoS_2$ system along with the desulfurization additives with the composition of CaO and Mgo. Therefore, the powders used as raw materials for the reactions can be expressed as follows:

- Molybdenite concentrate (MoS_2) with a composition of 8.92% molybdenite, 0.1% iron, 0.42% copper, 3.8% moisture and 0.2% oil,
- Hematite iron oxide powder (Fe_2O_3) (81% purity,
- Aluminum powder with 96% purity,
- Lime powder (CaO) with a purity of more than 90%,
- Magnesium oxide (MgO) powder (5.98% purity.

3.16 Devices and tools used:

- Microwave device:

In this research, a laboratory microwave device has been used to provide the primary energy needed to start the synthesis-combustion reaction. To conduct experiments, the microwave mode of the device and its maximum power have been used.

- X-ray diffraction (XRD):
- Scanning electron microscope (SEM):
- Resistance heating device (oven) to dry the moisture of the used powders.
- Hydraulic press machine for pressing powders under proper pressure and preparing tablets with desired dimensions.
- Laboratory digital scale with an accuracy of 0.01 grams.
- Molds and molds made of stainless steel to prepare tablets in the press machine.
- Laboratory containers.

3.17 Method of direct production of ferromolybdenum from molybdenite by combustion synthesis reaction:

In this research, a new method for extracting molybdenum from molybdenite is presented. The product obtained in this method is a Ferro-molybdenum alloy, which is obtained by the metallothermic reduction reaction of molybdenite and iron oxide, which proceeds as a synthesis-combustion reaction in the presence of aluminum and sulfur absorbents such as lime (CaO) and magnesia (MgO).

The primary heat for the start of the combustion synthesis reaction is provided by the microwave environment. Usually, in steelmaking, in order to add alloy elements such as molybdenum, their alloy is used to lower the melting point of the added element. For this purpose, Ferromolybdenum is widely used in steelmaking.

IV. CONCLUSION

Based on the research and study about this research, it is possible to perform molybdenite reduction reaction by aluminum and in the presence of iron oxide for all three systems without desulfurization, with lime desulfurization (CaO) and with magnesia (MgO) desulfurization in the form of a combustion synthesis reaction. It is possible to directly and in situ produce Ferromolybdenum with different weight percentages of molybdenum from 10% to 60% by weight from molybdenite, by alumino thermal reduction reaction and in the presence of hematite iron oxide.

REFERENCES

[1] S.L. Kharatyan, A.R.S., "SHS densification of complex silicides: promising materials for the electronics and electrotechnical industries", International Journal of SHS, 332-323, 1993.

[2] W. Lin, L.H., Y. Berta, R. Speyer, "Combustion gas corrosion resistance of heat exchange materials and refractories for glass furnaces at high temperature", Ceram. Soc. Bull, 78-72, 1994.

[3] Clarke, D.R., "High-temperature deformation of a polycrystalline alumina containing an intergranular glass phase", Journal of Materials Science, 20, -1321 1332, 1985.

[4] Akino, A., "Fundamental aspects of the heterogeneous flame in the self-propagating high-temperature synthesis (SHS) process", Progress in Energy and Combustion Science, 27, 74-1, 2001.

[5] Absolute, A.B. "Bonding of aluminum plates with joint season reinforced by hard nanoparticles with Using combustion synthesis phenomenon", Master's degree, Ferdowsi University of Mashhad, 2019.
[6] Radev, D.D. and M. Marinov, "Properties of titanium and zirconium diborides obtained by self-propagated high-temperature synthesis", Journal of Alloys and Compounds, 244, 51-48, 1996.
[7] Yeh, C.L. and W.H. Chen, "Preparation of niobium borides NbB and NbB 2by self-propagating combustion synthesis", Journal of Alloys and Compounds, 420, -111 116, 2006.
[8] Novikov, V., "A new concept of pulsed MHD power generation with application of Self-Propagating High-Temperature Synthesis", MHD Electrical Power Generation, Moscow, Rossia, 1996.
[9] Ivleva, T.P. and A.G. Merzhanov, "Three-dimensional spinning waves in the case of gas-free combustion", Doklady Physics, 45, 141-136, 2000.
[10] Mukasyan, A.S. and J.D.E. White, "Combustion joining of refractory materials", International Journal of Self-Propagating High-Temperature Synthesis, 16, -154 168, 2007.
[11] Cao, G. and R. Orrù, "Self-propagating reactions for environmental protection: state of the art and future directions", Chemical Engineering Journal, 87, 249-239, 2002.
[12] Department of Metallurgy, Jihad University, Iran University of Science and Technology, "Preparation of FERROMOLYBDENUM using Sarcheshme copper molybdenite concentrate and recovery of its secondary elements", research project, Tehran, Iran University of Science and Technology, 1988.
[13] Habashi, F., "Handbook of extractive metallurgy", Canada, Wiley-VCH, 1997.