Sinop Üniversitesi Fen Bilimleri Dergisi Sinop Uni J Nat Sci 5 (1): 64-76(2020)
ISSN: 2536-4383

Research Article **https://doi.org/10.33484/sinopfbd.724720**

Production of Ferromolybdenum from Mill Scale via Aluminothermic Process

Levent ÖNCEL*

Sinop University, Faculty of Engineering and Architecture, Metallurgical and Materials Engineering Department, Sinop, Turkey

Abstract

In this study, the production of ferromolybdenum (FeMo), which is an iron-based alloy, was carried out through the metallothermic reaction. This method was chosen due to its low cost, short process time and minimum energy need. Before the experiments, FactSage and HSC software were used for thermochemical modeling. Mill scale was used as a starting material in the experimental studies. Mill scale is waste material and it contains 70% iron by mass. MoO_3 was used as the molybdenum source and aluminum was used as the reducing agent. Produced samples were characterized by Atomic Adsorption Spectrometry (AAS), X-Ray Fluorescence (XRF) and hardness tests (micro-Vickers). Initially, the effect of aluminum stoichiometry, which was used as a reductant, on FeMo efficiency was investigated. The closest result to the target alloy was achieved with the sample having 105% aluminum stoichiometry. Fe and Mo efficiencies were 95.16% and 97.21%, respectively. The effects of weight change on Fe and Mo efficiencies were investigated by using samples having 105% aluminum stoichiometry. It was observed that the closest result to the target alloy was achieved with a 75 g charge. Fe and Mo efficiencies were 99.10% and 97.98%, respectively. These were the highest efficiency values obtained in all experiments. The hardness values of samples were between 678 HV10 and 767 HV10. The highest hardness value was obtained in the alloy containing 100% stoichiometric aluminum. It was concluded that there was no significant difference in the hardness values of the samples due to the similarity in their chemical structures.

Keywords: Mill Scale, Ferromolybdenum, FeMo, Aluminothermic Reduction, Recycling

Alüminotermik Yöntem Yoluyla Tufalden Ferromolibden Üretimi

Öz

Bu çalışmada, bir demir bazlı alaşım olan ferromolibdenin (FeMo) üretimi metalotermik reaksiyon ile gerçekleştirilmiştir. Bu metodun seçilme nedenleri maliyetinin düşük olması, prosesin kısa süre içinde tamamlanması ve enerji ihtiyacının çok düşük olmasıdır. Deneysel çalışmalar öncesinde FactSage ve HSC yazılımları kullanılarak termokimyasal simülasyonlar gerçekleştirilmiştir. Deneylerde başlangıç malzemesi olarak bir atık malzeme olan ve kütlece %70 demir içeren hadde tufali kullanılmıştır. MoO_3 molibden kaynağı olarak, alüminyum ise indirgeyici olarak kullanılmıştır. Deneyler sonucunda üretilmiş olan numuneler Atomik Absorbsiyon Spektrometresi (AAS), X-Işını Floresans Spektrometresi (XRF) ve sertlik testleri (micro-Vickers) ile karakterize edilmiştir. Deneysel çalışmalarda öncelikle indirgeyici olarak kullanılan alüminyumun stokiyometrisinin FeMo

* Corresponding Author: ORCID ID: orcid.org/0000-0002-6018-8741
e-mail: loncel@sinop.edu.tr
Received: 21.04.2020
Accepted: 12.05.2020

verimi üzerindeki etkisi araştırılmıştır. XRF sonuçlarına göre, %105 alüminyum stokiyometrisine sahip olan numune hedef alaşıma en yakın sonucu vermiştir. Bu numunede elde edilen Fe verimi %95,16, Mo verimi ise %97,21 olmuştur. Ağırlık değişiminin Fe ve Mo verimleri üzerindeki etkisi %105 alüminyum stokiyometrisine sahip olan numuneler kullanılarak araştırılmıştır. Hedef alaşıma en yakın sonucun 75 gram ağırlığındaki şarj ile elde edildiği görülmüştür. Bu numunedeki Fe verimi %99,10, Mo verimi ise 97,98 olmuştur. Bu numunede elde edilen Fe ve Mo verimleri bütün deneylerde elde edilen en yüksek verim değerleridir. Numunelere yapılan sertlik testlerinde 678 HV10 ve 767 HV10 arasında değerler elde edilmiştir. En yüksek sertlik değeri %100 stokiyometrik alüminyum içeren numune ile elde edilmiştir. Numunelerin kimyasal yapılarının birbirine yakın olması sebebiyle birbirine yakın sertlik değerlerinin elde edildiği sonucuna varılmıştır.

Anahtar Kelimeler: Hadde Tufali, Ferromolibden, FeMo, Alüminotermik Redüksiyon, Geri Dönüşüm.

Introduction

Mill scale is a waste material that occurs during annealing of steel slabs and billets in annealing furnaces, continuous casting plants and rolling mills. Mill scale is an oxide layer that forms on the surface, and it contains 70% iron by mass [1]. Every year, 13.5 million metric tons of mill scale is formed [2].

Recycling of the mill scale is an important issue since it is waste material and is formed in a very high amount. There are many applications where the mill scale is used as an additive. One of the most common use of mill scale as an additive is the Portland cement. It is added to the Portland cement's structure with casting sand and slag [3]. Mill scale is used as an additive in electromagnetic interference shielding [4] and stabilization of expansive soil [5]. Also, it is employed in the adsorbing of lead ions in aqueous solutions [6]. Besides, it is used as an iron oxide source in sintering applications [7]. Furthermore, mill scale is used in hydrogen fuel cells, medical imaging and improving of water quality when it is processed into nano-scale particles [8].

Molybdenum was discovered by Carl Wilhelm Scheele in 1778. Swedish chemist was working on a mineral which is now known as molybdenite (MoS_2). The molybdenite mineral was confused with graphite and lead at that time. However, studies showed that this mineral contains a new element. This element was called as molybdenum by Scheele [9]. MoS_2 is the main mineral used in the production of ferroalloys today.

Molybdenum is in the subgroup of VI b of the periodic table. Its atomic weight is 95.94, the melting point is 2622 °C and the boiling point is 4840 °C. Molybdenum's stable phase is body-

centered cubic (a=314 nm), and its external electron shell configuration is $4d^5 5s^1$ [10]. Molybdenum is one of the common elements used in the alloying of stainless steels. It is also used in alloyed cast irons and superalloys. Molybdenum provides hardenability in some of the heat-treatable alloys. It is also used in tool steels and hard metals. Besides, molybdenum is used for improving the corrosion resistance of stainless steels [11].

When the ancient artifacts are examined, it is seen that they were made of nearly pure iron. The only alloying element found in the structure of these ancient artifacts is carbon. It has been understood over time that the rate of carbon in iron can be controlled. The amount of carbon in the steel was adjusted to a certain extent by carburization and decarburization throughout the Iron Age. Over time, higher temperatures were reached in the steel production process and as a result, the carbon content of the steels was increased. Some major alloying elements of modern steels were found as natural impurities in the steels which were produced in ancient times [10].

Today, alloying elements are added to the steel in form of ferroalloys. There are many reasons why alloying elements are added as ferroalloys. The difficulty of obtaining alloying elements in pure form is one of the most important reasons. Also, in cases where the alloying elements have high oxygen and nitrogen affinities, it is possible that reactions such as oxidation and nitration can occur before the alloying operation. Besides, it is needless to remove the iron components in the structure of the alloying elements since these elements will be used in the alloying of steel. Furthermore, there is a risk that these elements can't maintain their stability at steel production temperatures. Moreover, price of the alloying elements in the ferroalloy form is cheaper compared to their pure forms [10].

Ferroalloys are formed by combining iron with at least one element. Production of ferroalloys started around the 1860s. Ferrochrome, ferromanganese, ferrosilicon productions were achieved around these years [12]. Electric furnaces were developed at the end of the 19th century. Then, the electric smelting of the ferroalloys has begun at the beginning of the 20th century. Today, electric furnaces are used in the production ferroalloys which require furnace technology [10].

Ferromolybdenum generally contains molybdenum between 50% and 60%. According to Voronov et al.'s study, ferromolybdenum with high silicon content

(up to 20% Si) has been produced [11]. Other impurities in ferromolybdenum are tungsten (0.3%-0.8%), silicon (up to 3%), copper (up to 2%), phosphorus (<0.05%) and sulfur (<0.15%) [10].

Today, the main method used in the production of ferroalloys is carbothermic reduction. In carbothermic reduction, the metal content of metal oxide is reduced by carbon. The metallothermic reduction is an alternative method for carbothermic reduction. The main principle of metallothermic reduction is to reduce the metal content of metal oxide by using a reductant with a higher oxygen affinity.

Various metals and alloys are produced by using metallothermic processes. In metallothermic reactions, the reaction is started by using external heat, then it self-propagates in the reactant mixture [13]. The exothermic characteristic of metallothermic processes ensures that lower energy is required compared to carbothermic processes. Therefore, the costs of metallothermic processes are lower compared to carbothermic processes. The completion of the process in a short time and the production of high-purity products without carbon are other important advantages of metallothermic processes. However, metallothermic processes also have some disadvantages. In these processes, the homogeneity problem may arise from time to time and reactants may not react completely. These potential problems can be eliminated by using additives or changing parameters such as particle size, ignition temperature and reaction temperature.

In this study, it was aimed to produce ferromolybdenum by metallothermic reduction using mill scale, which occurs during continuous casting. Aluminum was used as a reductant and ferromolybdenum meeting ASTM A132-04 standard was chosen as the target alloy. According to ASTM A132-04, the chemical composition of ferromolybdenum must be as follows; 60% Mo (minimum), 0.1% C (maximum), 0.05% P (maximum), 0.15% S (maximum), 1% Si (maximum) and 0.2-1% Cu (maximum) [14].

Material and Method

Theoretical Background

The main principle of metallothermic reduction is to reduce the metal content of metal oxide by using a reductant with a higher oxygen affinity. Two important thermodynamic parameters that show whether metallothermic reactions can proceed spontaneously are specific heat and adiabatic temperature (T_{ad}). Specific heat is calculated by dividing the enthalpy of the reaction at 25

°C by the sum of the molecular weights of the reaction products. When the specific heat of the reaction is less than 2250 J/g, heat is not enough to melt the charge and separate the metal and slag according to the density difference. The reaction will occur violently when the specific heat is greater than 4500 J/g, there is a possibility of explosion during the reaction, and that explosion can lead to loss of reaction products by scattering. When the specific heat is between 2250 J/g and 4500 J/g, a self-propagating and controlled metallothermic reaction occurs. The adiabatic temperature must be above 1527 °C for the reaction to start and then propagate spontaneously [15]. The mill scale used in this study mostly consists of hematite (Fe_2O_3) and wustite (FeO).

While determining the reduction parameters for FeMo production, FactSage 6.4 software was used to calculate the specific heat values for the reactions between aluminum and the reactants. The results of the calculations are given in Equations 1, 2 and 3.

$3FeO + 2Al \rightarrow 3Fe + Al_2O_3$
Specific Heat = 3243 J/g (1)

$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$
Specific Heat = 3988 J/g (2)

$MoO_3 + 2\ Al \rightarrow Mo + Al_2O_3$
Specific Heat = 4622 J/g (3)

When equations were examined, it was seen that specific heat values of Equation 1 and 2 were between 2250 J/g and 4500 J/g and specific heat value of Equation 3 was slightly over 4500 J/g. However, since the total charge consists of iron oxides and molybdenum oxide, the specific heat value of the reaction will be below 4500 J/g. The adiabatic temperature value of the reaction was calculated as 2700 ºC by FactSage 6.4. The reaction will proceed spontaneously because the adiabatic temperature of the reaction is higher than 1527 ºC.

Material

In the experiments carried out to produce FeMo, mill scale was used as the iron source, MoO_3 was used as the molybdenum source and aluminum was used as the reducing agent. The chemical content of the mill scale was determined by the titration method, and it consists of 42.8% Fe 3+ (Fe_2O_3), 24.59% Fe 2+ (FeO) and 3.56% Fe 0 (Fe). Total iron content of the mill scale is 70.95%. Chemical analyses of MoO_3 and aluminum are given in Table 1. Material characterizations of MoO_3 and aluminum were carried out by using Perkin Elmer Aanalyst 800 AAS (Atomic Absorption Spectrometer). Mill

scale, MoO_3 and aluminum were supplied from Colakoglu Metalurji, Nanokar Nanoteknoloji and Metkim Kimyevi Maddeler, respectively.

Table 1. *Chemical analyses of MoO_3 and Al.*

Material	Fe, %	Cr, %	Ni, %	Zn, %	Mn, %	Mg, %	Al, %	Mo, %	Si, %
MoO_3	0.008	2.59	0.004	0.036	0.01	0.12	0.07	Bal.	0.18
Al	0.028	0.29	0.004	0.56	0.45	4.65	Bal.	Trace	0.12

Method

In the first stage of the experimental studies, mixtures with different aluminum stoichiometries were prepared. Aluminum stoichiometries of the prepared charges were 100%, 105% and 110%. Then, the effect of weight on the efficiency was examined by preparing 50 g, 75 g and 100 g charges having 105% aluminum stoichiometry. Optimum production parameters were determined.

The samples were weighed and dried in the oven at 105 °C for two hours. The dried samples were mixed for thirty minutes in the WAB Turbula mixer and homogeneous powder mixtures were obtained. Then, prepared mixtures were charged into a copper crucible. The copper crucible used in the experiments consists of two parts. The first part is a cylinder. Its height is 140 millimeters, its inner diameter is 40 millimeters and outer diameter is 50 millimeters. The second part is used as a base for this cylinder. The outer diameter of the second part is 50 millimeters and the inner diameter is 40 millimeters. There is a 10-millimeter elevation along the inner diameter. Tungsten (W) resistance wire was placed on the upper part of the powder mixture in the crucible. The electrical conduction between the resistance wire and Varsan Variac VRK (0.5-50) power supply was carried out by using a copper cable connected in series. The current was supplied to the tungsten wire from the power supply, the tungsten wire warmed up because of this current, and metallothermic reactions were triggered in the reactant mixture because of the hot wire. After the reaction was completed and the crucible cooled down, the bottom of the copper crucible was removed, then the metal and slag phases were taken out of the crucible. The experimental setup of the reduction experiments is given in Figure 1 and the workflow diagram of the system is given in Figure 2.

ISSN: 2536-4383

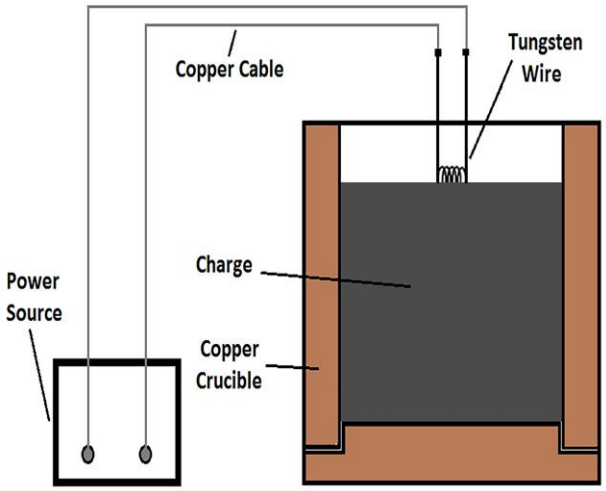

Figure 1. *Metallothermic experiment setup.*

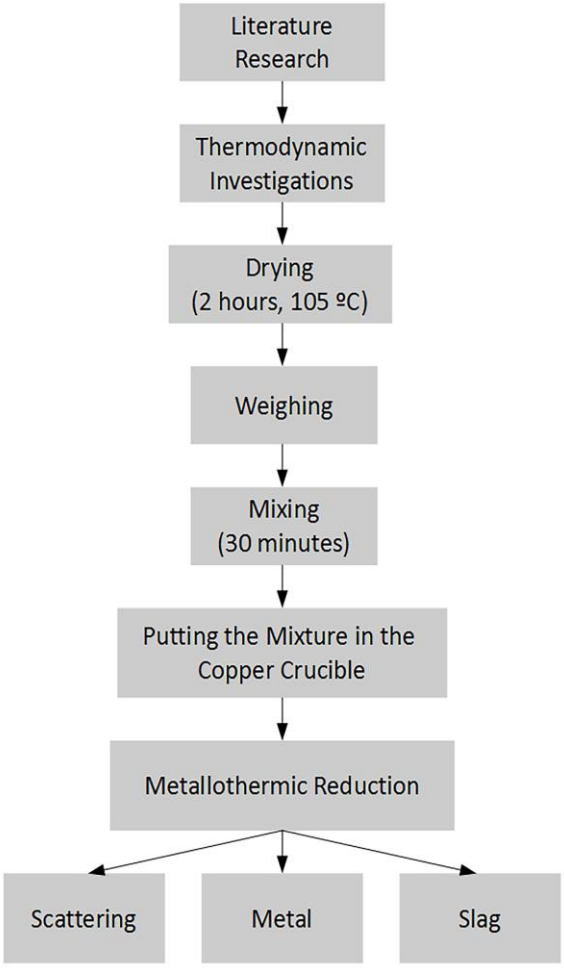

Figure 2. *Workflow diagram of the experimental studies.*

Characterization Techniques

Perkin Elmer Aanalyst 800 AAS (Atomic Absorption Spectrometer) was used for liquid chemical analyses of raw materials. Thermo Scientific Qualitative XL2 Plus XRF (X-Ray Fluorescence) was employed for determining the chemical compositions of the alloys and slags. Qness Q250C (HV 10) was used for measuring the hardness values of the produced alloys by micro-Vickers method.

Results and Discussion

The main principle of the metallothermic reduction process which is used in the experimental studies is the conversion of metal oxide to metal. For the reaction to take place and produce M_1, the metal oxide (M_1O) must react with a metal (M_2) with higher oxygen affinity. For the evaluation, the Ellingham Diagram of oxides is used. In the Ellingham Diagram, the materials at the bottom can reduce the ones at the top. Mill scale used in this study consists of iron (Fe), wustite (FeO) and hematite (Fe_2O_3). MoO_3 was used in addition to the mill scale to produce ferromolybdenum (FeMo). The Ellingham diagram which is containing these materials was modeled with the FactSage 6.4 software and the modeling is presented in Figure 3.

ISSN: 2536-4383

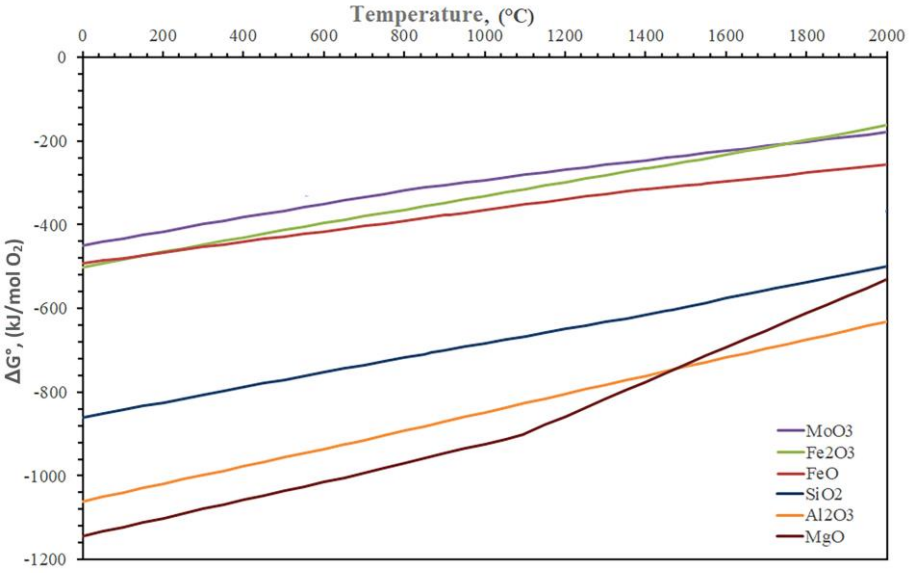

Figure 3. *Ellingham Diagram of reactants and probable reductants.*

It is seen in the Figure 3 that iron oxides and MoO_3 are at the top of the diagram, Al, Mg and Si are at the bottom of the diagram. So, aluminum can reduce all the reactants under these experimental conditions. Since molybdenum oxide (MoO_3) is at the top in the diagram, the heat that will be produced by the reaction of molybdenum will be higher than the reactions of other reactants. That is the reason of high specific heat value in the Equation 3 (4622 J/g).

In the second stage of thermodynamic modeling, possible phases that will occur with increasing Al stoichiometry are modeled using HSC 6.12 software. Figure 4 shows the result of the modeling. According to Figure 4, Fe and Mo to be produced will increase until the amount of Al reaches six moles. The amount of aluminum exceeding six moles has no effect on the amount of Fe and Mo produced. This data indicates that FeMo can be produced with the highest efficiency by using aluminum in amounts of six moles and above. For this reason, aluminum stoichiometry containing six moles of aluminum has been determined as 100% stoichiometric ratio. The amount of aluminum used in the experiments was determined based on this data.

ISSN: 2536-4383

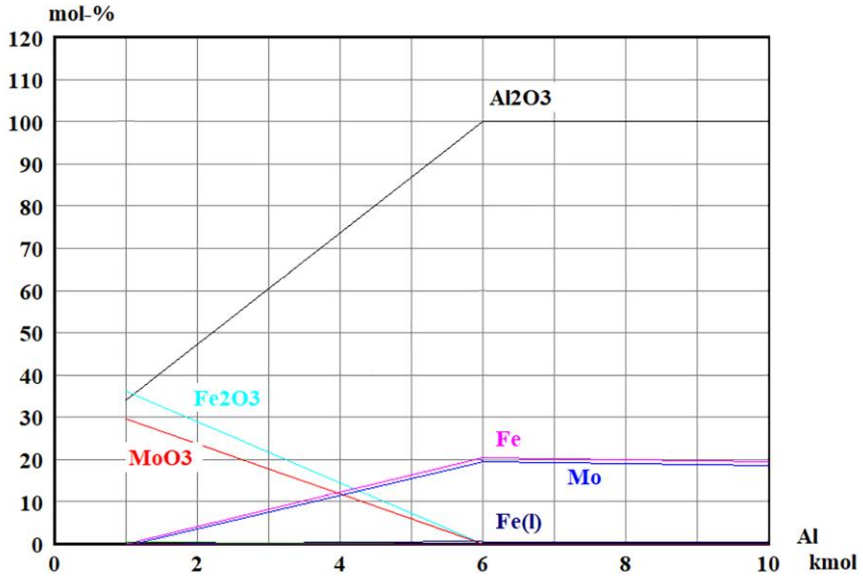

Figure 4. *Possible phases that will occur with increasing Al stoichiometry in aluminothermic FeMo production.*

In the studies carried out to produce FeMo, charges weighing 50 grams were prepared initially. These charges have aluminum stoichiometries ranging from %100 to 110% (100%, 105% and 110%). After determining the effect of aluminum stoichiometry on FeMo efficiency, the effects of weight change were examined. Experiments were carried out with samples having 105% aluminum stoichiometry, weighing 75 and 100 grams. The chemical compositions of the metallic materials obtained as a result of the experiments were analyzed with the XRF technique and the results are given in Table 2.

Table 2. *XRF analyses of metallic products.*

Al Stoc. %	Charge Weight, g	Fe	Mo	Al	Cr	Ni
100	50	43.11	56.19	0.11	0.12	0.39
105	50	40.31	58.33	0.11	0.29	0.91
110	50	41.59	56.58	0.12	0.25	0.66
105	75	40.54	58.79	0.11	0.15	0.39
105	100	41.47	57.97	0.09	0.16	0.26

According to the XRF results, the sample with 105% aluminum stoichiometry gave the closest result to the target alloy. Therefore, the effect of weight change on FeMo efficiency was investigated by using samples with 105% aluminum stoichiometry. When Table 2 is examined, it is seen that aluminum, which is used as a reductant, did not pass to metal. Considering the working principle

of the metallothermic reduction, this was an expected result. The results of the experiments in which the effects of weight change on FeMo efficiency were investigated were also given in Table 2. It is seen in the table that the closest result to the target alloy was achieved with 75 g charge. Then, Fe and Mo efficiencies were calculated according to Equation 4. Efficiencies that were calculated according to this equation are illustrated in Figure 5.

$$\text{Metal Recovery} = 100 \times \frac{\text{The weight of metal after metallothermic process (g)}}{\text{The weight of aspect metal after metallothermic process (g)}} \quad (4)$$

Figure 5. *Effect of aluminum stoichiometry and charge weight on Fe and Mo efficiencies.*

Figure 5 shows that very high Fe and Mo efficiency values are obtained in the experiments. Fe efficiency is 99.1% and Mo efficiency is 97.98% in 75 grams of charge containing 105% stoichiometric aluminum. The efficiency values obtained for both Fe and Mo in this experiment were the highest efficiency values obtained in all experiments. Also, according to the chemical analysis values shared in Table 2, the closest result to the target alloy was achieved in this experiment.

After calculating the Fe and Mo efficiencies, samples were cut and subjected to hardness test. The values obtained in the hardness tests are given in Figure 6.

As seen in Figure 6, the hardness values of samples were between 678 HV 10 and 767 HV 10. The highest hardness value was obtained in the alloy containing 100% stoichiometric aluminum. It was concluded that there was no significant difference in the hardness values of the

samples due to the similarity in their chemical structures.

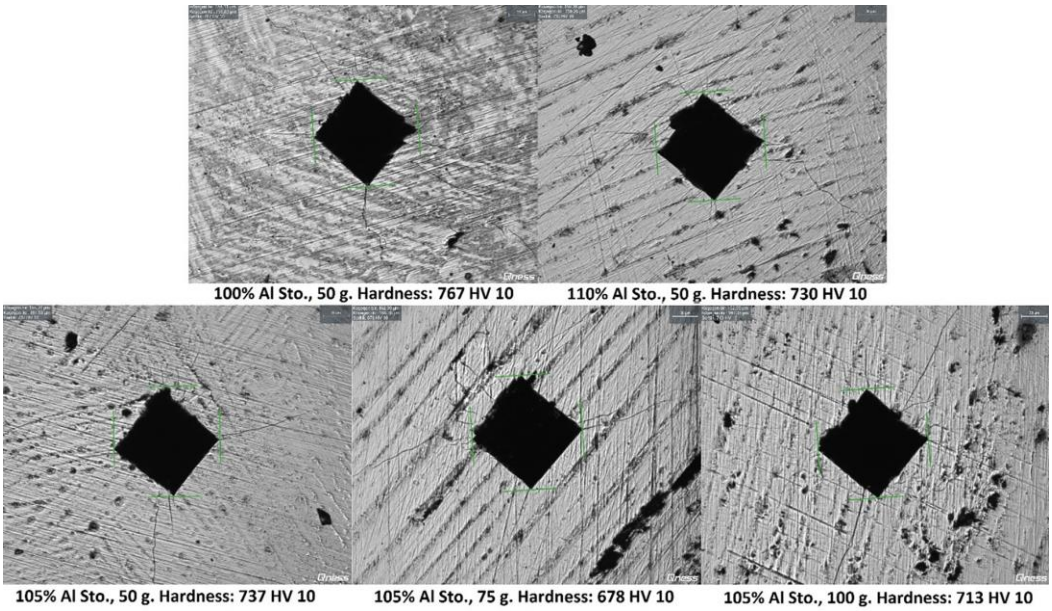

Figure 6. *Micro-Vickers hardness values of FeMo samples.*

Conclusion

In this study, it was aimed to produce ferromolybdenum (FeMo) by utilizing the mill scale, which is a waste material. In the production of ferromolybdenum, the metallothermic reduction method was chosen due to its advantages. Mill scale and MoO_3 were used as raw materials and aluminum was used to reduce the metal contents of the raw materials. The effects of aluminum stoichiometry and charge weight on Fe and Mo efficiencies were investigated. FactSage 6.4 and HSC 6.12 databases were used in the thermodynamic modeling. When data obtained from models were evaluated, it was seen that the total reaction will proceed in a controlled manner. Initially, mixtures having aluminum stoichiometries in the range of 100% to 110% were prepared, and the effect of aluminum stoichiometry on FeMo efficiency was investigated. Closest result to the target alloy was obtained with the alloy containing 105% aluminum stoichiometry. Fe and Mo efficiencies for this sample were 95.16% and 97.21%, respectively. Then, the effects of weight change on Fe and Mo efficiencies were investigated by preparing 50 g, 75 g and 100 g charges having 105% aluminum stoichiometry. It was observed that the closest result to the target alloy was achieved with a 75 g charge. Fe and Mo efficiencies for this sample is 99.10% and 97.98%, respectively. The efficiency

values obtained for both Fe and Mo in this experiment were the highest efficiency values obtained in all experiments.

Also, it was seen that highest hardness value in the experiments was obtained as 767 HV 10 with the alloy containing %100 stoichiometric aluminum, and there was no significant difference in the hardness values of the samples due to the similarity in their chemical structures.

References

[1] Martin MI, Lopez FA, Torralba JM, 2012. Production of Sponge Iron Powder by Reduction of Rolling Mill Scale, Ironmak Steelmak, 39 (3): 155-162.

[2] Cho S, Lee J, 2008. Metal Recovery from Stainless Steel Mill Scale by Microwave Heating, Met Mater Int, 14 (2): 193-196.

[3] Turkiye Celik Ureticileri Dernegi, 2015. Demir Celik Curuf Raporu, Ankara.

[4] Bantsis G, Sikalidis C, Betsiou M, Yioultsis T, Xenos T, 2011. Electromagnetic Absorption, Reflection and Interference Shielding in X-band Frequency Range of Low Cost Ceramic Building Bricks and Sandwich Type Ceramic Tiles Using Mill Scale Waste as an Admixture, Ceram Int, 37 (8): 3535-3545.

[5] Murthy YI, 2012. Stabilization of Expansive Soil Using Mill Scale, Int J Eng Sci Technol, 4 (2): 629-632.

[6] Martin MI, Lopez FA, Alguacil FJ, 2009. Use of By-Products of the Steelmaking Industry for Removing Pb+2 Ions from Aqueous Effluents, 1st Spanish National Conference on Advances in Materials Recycling and Eco-Energy, Madrid, Spain, 34-37.

[7] Wang Z, Pinson D, Chew S, Monaghan BJ, Pownceby MI, Webster NAS, Rogers H, Zhang G, 2016. Effect of Addition of Mill Scale on Sintering of Iron Ores, Metall Mater Trans B, 47 (5): 2848-2860.

[8] Azad AM, Kesavan S, Al-Batty S, 2008. Redemption of Microscale Mill Waste into Commercial Nano Scale Asset, Key Eng Mater, 380: 229-255.

[9] Cardarelli, F, 2000. Materials Handbook: A Concise Desktop Reference. 2nd ed. London: Springer.

[10] Gasik M, 2013. Handbook of Ferroalloys: Theory and Technology. Oxford: Butterworth Heinemann.

[11] Voronov YI, Zaiko VP, Zhuchkov VI, 2000. Technology of molybdenum ferroalloys, IMET Euro RAS, Ekaterinburg, Russia, 267.

[12] Volkert G, Frank KD, 1972. Metallurgie der Ferrolegierungen, 2nd ed. Berlin: Springer-Verlag.

[13] Gungor MN, Benzesik K, Bugdayci M, Yucel O, 2015. Production of Molybdenum, Nickel, Chromium Containing Iron Based Alloys Via Metallothermic Process, XIV. Infacon: International Ferro-Alloys Congress, Kiev, Ukraine.

[14] ASTM Standard A132, 2004. "Standard Specification for Ferromolybdenum", West Conshohocken: ASTM International.

[15] Bugdayci M, Alkan M, Turan A, Yucel O, 2014. Production of Iron Based Alloys from Mill Scale through Metallothermic Reduction, High Temp Mat Pr-Isr, 37(9-10): 889-898.