Determination of Magnesium Production Parameters by Metalothermic Reduction Method

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Abstract

In magnesium production via metallothermic reduction; silicon (Si) or ferro-silicon (Fe-Si) is the first to come to mind as a reducing material. Beside this, aluminum (Al) and very rarely carbon (C) are used. Furthermore, even if calcium carbide (CaC2) is present as another reducing agent in the literature, commercial use of it is not feasible because the purity of the produced metal is lower than the others. In this study, reduction of magnesium oxide (MgO) was carried out using aluminum metal chips as the reducing agent. A mixture of MgO and Al was prepared by stoichiometry ratio of Al/Mg equals to 1/1, and CaO-containing slag was also added as a fluxing agent. This mixture was pressed into a mold under constant force (100Bar). Reduction experiments were carried out in an electric arc furnace under an argon atmosphere. Reduction process was carried out in 1, and 1.5 minutes by applying currents of 400, 500 and 600 Amperes. The chemical properties of the obtained magnesium wase characterized by XRF and XRD analysis.

Keywords: Magnesium oxide 1, Metallic magnesium 2, Reduction 3, Magnetherm process 4.

1. Introduction

Magnesium has a dense hexagonal crystal structure and it has two valance electrons. Its melting and boiling point are 650 ± 2 ºC and 1107 ± 10 ºC respectively. Magnesium has a very low density (1.738 g/cm^3) when it is compared to other structural metals (Andreassen ve ark., 1997).

Due to its features, magnesium has a several applications in lots of fields such as aircraft, rockets, the desulphurisation and nodularization of iron and steel, corrosion applications, production of Al-Mg alloys, some chemical applications and replace to denser materials, not only steels, cast irons, and copper-based alloys in automobile industry (Emley,1966; Ding-Fei ve ark., 2011; Rong-Ti ve ark., 2003).

Magnesium (Mg) and its alloys will become more popular because of their favorable combination of tensile strength, elastic modulus, low density, high strength-to-weight ratios, high damping capacity (Brown,2009), high specific strength, good thermoformability, and high performance of electromagnetic shielding (Brown, 2009; Rongtı, 2003).

There are two major process routes for magnesium production in industry. One is to recover magnesium chloride from the raw materials and converts it to metal through molten salt electrolysis; the other is to reduce magnesium oxide at high temperature using reducing agents, such as ferrosilicon, aluminum or carbon. The raw materials for production of magnesium used in these process are sea water, lake brines, camallite, dolomite, serpentine and magnesite (Li ve ark., 2009; Tıan ve ark., 2014; Morsi ve Ali, 2014).

Although the silicotermic reduction method in pidgeon process is widely used over the world, we have used the aluminatermic reduction method in the Magnetherm process.

The main characteristic technology of magnetherm process is the heating and production furnace in which the heating takes place with electrodes using alternating current. Flax, dolomite or magnesite and reduction agents such as silicon or aluminum, is added in furnace for producing magnesium. The process operates within a temperature range of 1,300–1,700°C (Friedrich, Mordike; 2006).

In aluminatermic reduction process, aluminum is used as the reduction material for the production of magnesium. In the main reaction is shown in Eq. (1) (Friedrich, Mordike; 2006).

$$3MgO_{(s)} + 2CaO_{(s)} + 2Al_{(l)} \rightarrow 3Mg_{(g)} + 2CaO * Al_2O_{3(S)} \quad (1)$$

P = 1 atm ; T = 1,300°C or P = 10 mm Hg ; T = 900°C

The process is based on the use of Dolomite and magnesite that have undergone calcination, and aluminum scrap as reduction material. The furnace works according to the working principles of the DC transferred arc plasma furnace. This process is supposed to work at atmospheric pressure and under argon atmosphere at temperatures of about 1,500°C (Friedrich, Mordike; 2006).

In this study, it was aimed to determine optimum experimental conditions for magnesium production. For this purpose, the current values and the experiment period have been changed and the conditions have been examined.

2. Experimental Procedure

MgO, CaO and Al2O3 powders were purchased from MERCK and used as received. As reducing agent, Aluminum shavings were used with the chemical composition given in the Table 1. The composition of the aluminum shavings was obtained from S1 TITAN 600 BRUKER XRF analyzer

Table 1. Chemical composition of the aluminum shavings.

Al	Mg	Fe	Si	Cu	Zn	Mn	Ti
98,71	0,48	0,43	0,22	0,05	0,04	0,04	0,01

Initially, CaO-Al2O3-MgO mixture was prepared as a flux. The stoichiometric ratios of the flux mixture were set to be 60-35-5, respectively. Then the mixture was mixed for 30 minutes at 30rpm

MgO powder and the previously prepared flux were mixed with the ratio of 1:1 and aluminum shavings were add with the elemental ratio of Al/Mg 1:1 as well. All the blend was mixed in a plastic bowl for 30 minutes. After that, the mixture was moistened (15% H_2O) and pressed at 100 bar pressure for 30 seconds. Then, the pressed samples were dried for 8 hours at 105 ° C. The pressing mold and the sample are given in Figure 1.



Figure 1. presleme kalıbı ve preslenmiş numune örneği.

Experiments were carried out in an atmosphere controlled electric arc furnace and the schematic appearance of the furnace is given in Figure 2. Experiments were carried out at three different current values of 400-500-600 amperes and two different times of 1-1.5 min. Experiments were also carried out in an argon atmosphere.

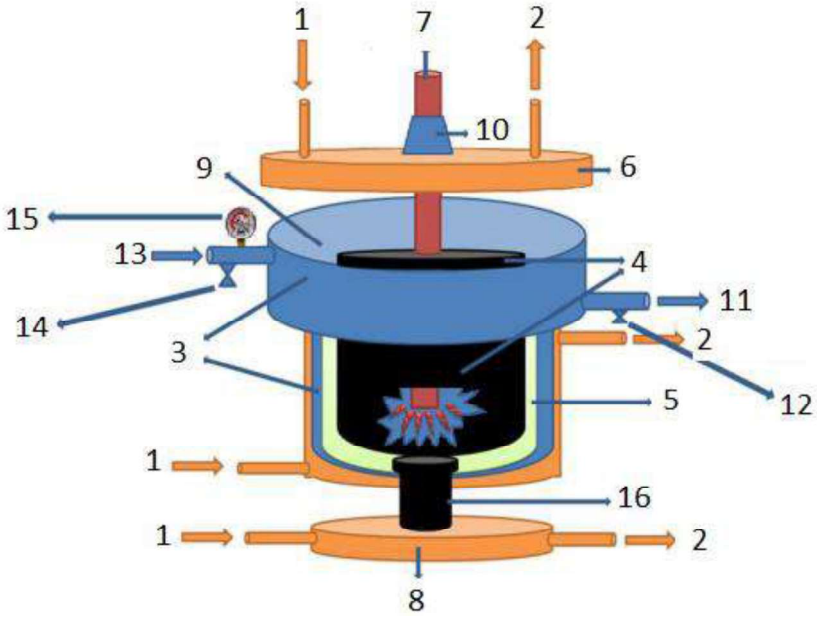


Figure 2. Schematic appearance of the electric arc furnace. Parts of the experimental setting; 1 water entrance, 2 water exist, 3 stainless steel body, 4 graphite pot, 5 alumina refractory, 6 upper cover, 7 graphite electrode, 8 conductive table(Cu), 9 Mg(steam) condensation zone, 10 metal sealing, 11 vacuum 10^{-1}atm, 12 vacuum valve, 13 argon gas enter, 14 argon shut off valve, 15 vacuum gage, 16 graphite conductor.

As can be seen in Figure 2, the experiments were carried out in a stainless steel chamber (3) with stainless steel cover (6). Graphite electrode (7) and graphite crucible (4) were used as

electrode and pot material to applied an electric arc. First, the graphite electrode was connected to the water-cooled copper electrode holder and then the electrode holder was fixed to the top cover by a metal bellows (10). Plastic sealing was also used for vacuum sealing. The graphite crucible was fixed by screwing it to the conductive table (8) with a molybdenum reinforced graphite conductivity provider (16). Also, a refractor (5) is placed between the stainless steel body and the graphite crucible for both electrical and thermal insulation. To protect the system from high temperatures, the electrode holder, the top cover, the conductive plate and a part of the stainless steel body were cooled with water (1-2).

The pressed and dried samples were adjusted to be 36 grams and it was put into the graphite crucible. Vacuum operation (13) was performed after the cover and electrode were placed. The cover and electrode were fixed to the body with screws after vacuuming. When the vacuum indicator showed 680 mmHg pressures, the vacuum valve was turned off and argon gas was vented to the system. This process was repeated 3 times to evacuate the oxygen. As a final step, the system was fixed at 740 mmHg pressure and the experiment was started.

Magnesium oxide was reduced by aluminum and then magnesium was evaporated at about 1550°C. Magnesium in the vapor phase was condensed by hitting multiplying to the condensation zone as it moves upward in the system. After the test, magnesium powder in the condensation zone was removed and weighed after the system was completely cooled. Amount of the unreduced MgO and slag was weighed to calculate the efficiency of the reduction process.

Then, to determine the degree of purity of the powders, XRD analysis was performed by using PANalytical X'Pert Pro XRD device and to analyze the amount of carbon coming from the graphite crucible and the electrode, Carbon analysis was performed with Behr CS50 HT.

3. Results and Discussion

XRD analyzes were performed to determine the degree of purity of the magnesium powder and the chemical composition of the slag, and the results are given in Figure 3.

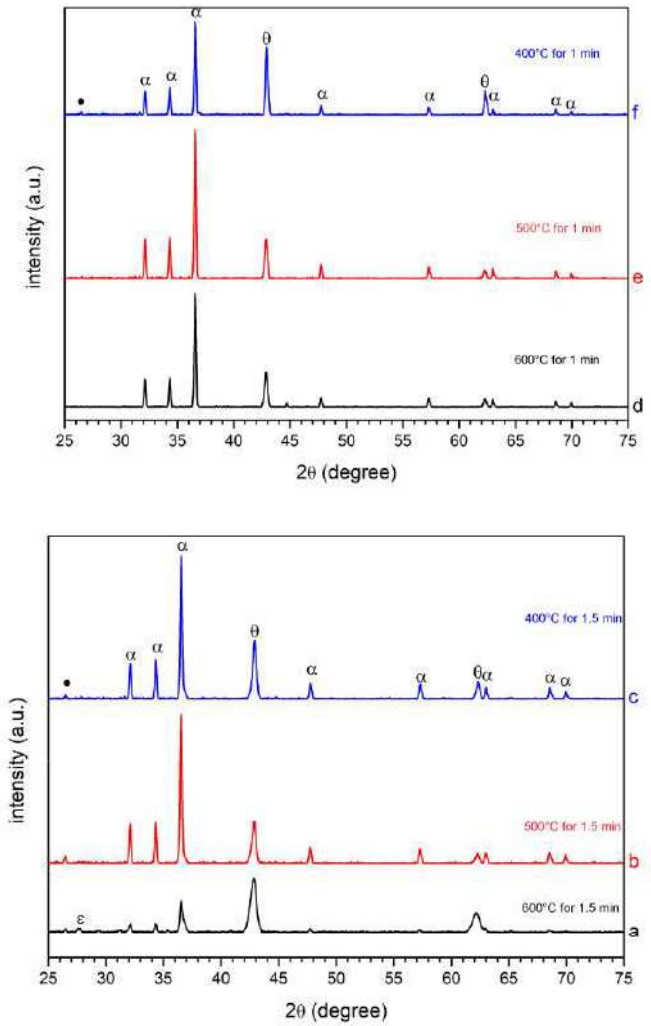


Figure 3. Analysis results of magnesium powders.

From the phases shown in Figure 3, α phase represents the metallic magnesium phase, θ phase represents the MgO phase, ε phase represents the $MgCl_2$ phase and • phase represents graphite phase.

The XRD analysis results showed; it was appeared that nearly all of the powders produced were close to pure magnesium and a small fraction of it is oxidized. It was observed that the degree of oxidation was close to each other in all of the test results, whereas in the test No. A (600 Amperes and 1.5 minutes), it was observed that magnesium was oxidized more than the others. This situation is thought to be due to oxygen leaks in the system during cooling process after arc, rather than changes in experimental conditions. In addition, reducing agent (aluminum) did not evaporate, instead it oxidize by reducing MgO to Mg because of increasing the temperatures during arc processing,. In addition, XRD results show that magnesium powder

contains trace of carbon or graphite powders. Apart from that, no other impurities were found in the Mg powder.

Since the XRD analysis does not reveal the amount of carbon completely, additional carbon analysis was carried out to determine the carbon content and degree of purity of the powders as shown the results in Table 3. These results were plotted for a better comparison in Figure 4.

Table 3. % Carbon content of magnesium powders.

Time(mins)	1,5			1		
Current (A)	600	500	400	600	500	400
Expt. No	a	b	c	d	e	f
Carbon (%)	13.82	7.16	5.21	7.28	4.92	4.21

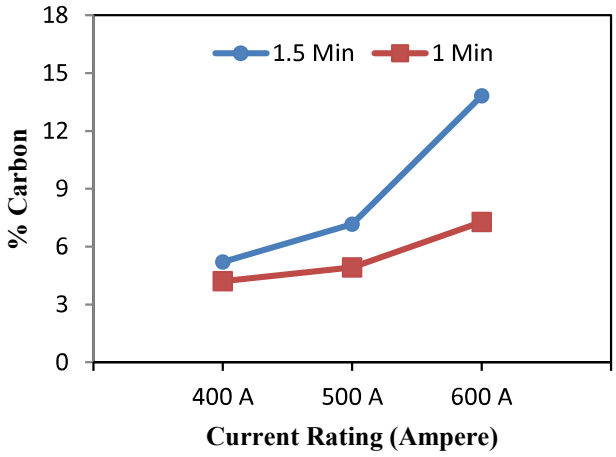


Figure 4. % Carbon amount graph of magnesium

As can be seen in Figure 4, the amount of carbon in the products increased with increasing the applied current rates. This situation was similar in both experiments at 1 and 1.5 minutes. It was observed that the amount of carbon measured was too high at high current rates, especially for the 600 Amperes and the 1.5 minute test. The reason for this situation is that the crucible and electrodes are graphite, and their interaction with the blend at high arc current rates might causes disintegration of the graphite itself.

Table 4. % Efficiency values of magnesium powders.

Time(mins)		1,5			1	
Current (A)	600	500	400	600	500	400
Expt. No	a	b	c	d	e	f
Efficiency %	73	54,78	39,16	61,73	7	29,79

The efficiency values of the magnesium powders were given in Table 4. These values were graphically shown in Figure 5 as well.

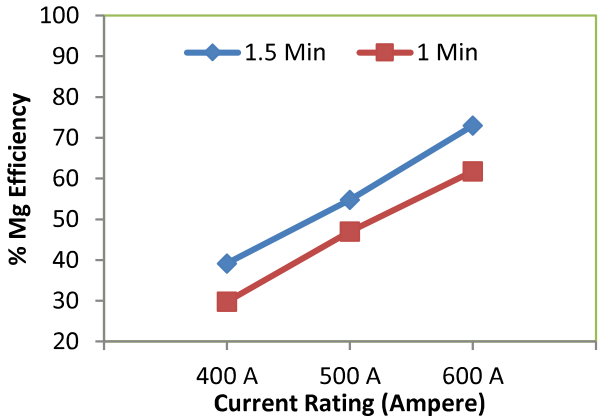


Figure 5. % Efficiency value graph of produced magnesium.

As can be seen in Figure 5, , the efficiency of magnesium also increases with increasing the current rate. This value reached its highest value in 1.5 minutes and 600 amperes. Nevertheless, the maximum efficiency value remained below 80%. Experiments at 600 amperes, when the duration increased from 1 minute to 1.5 minutes, the efficiency were increased for 18.26%. These ratios were reached 16.55% at 500A and 31.45% at 400A. In addition, for the experiments at 1.5 minutes, when the current rate increased from 400 A to 600 A, the efficiency increased by 86.4%, this rate has been 107,2% for 1 minute. In addition, for the experiments at 1.5 minutes, when the current rate increased from 400 A to 600 A, the efficiency increased by 86.4%, which was 107.2% for 1 minute.

4. Conclusion

It was observed that the efficiency increases with increasing the current rates in the experiments performed. Applying longer arc current also increased the reduction efficiency. However, as the applied current rates increased, the carbon contamination lowered the quality of product, Mg.. While the highest efficiency values were obtained at 600 amperes, the amount of carbon contained in the powder was also the highest. Considering the energy consumption