



The Effect of Mechanical Activation Process on the Production of Elemental Boron

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In this study, the mechanical alloying-metallurgical reduction-the leach process was carried out one after the other and the elemental boron was produced from the B₂O₃ powders with the metallurgical method. Magnesium metal powders were used as a reducing agent for the production of elemental boron by metallurgical method. In the first stage of the studies, B₂O₃ powders mixed with metallic magnesium powders in different ratios (Mg/B₂O₃) were activated in a high energy mill for various times. In the mill, it was chosen to the weight ratio of the balls to the mixture was 20:1. These activated samples were subjected to reduction in a box-type oven at 1000 °C for 1 hour. Samples taken from the oven were subjected to the leach process in 6 M HCl solution for 6 hours. SEM and EDX analysis of the filter cake obtained after the leaching process were examined. In the EDX analysis, it was seen that the samples contained 97% of the elementary boron.

Keywords: Elementary Boron, Mechanical Alloying, Magnesiothermic Reduction, Leach.

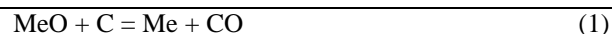
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1. Introduction

The elementary boron, which is one of the high technology products, can be used in many places due to its superior properties. The elementary boron produced by various methods in the world is a strategically important product. The first academic publication on elementary boron production was made in 1808 [1]. After that, the works were carried out intensively between 1900-1960 [2-9]. The most widely used area of elemental boron is as a reinforcement material for metals and plastics. Besides, it is used as a dopant in semiconductors, as a neutron inhibitor in nuclear reactors and as a target material for the beam sputtering and physical vapor deposition processes. It may be used in abrasers thanks to its property of being the second hardest element after diamond. Reduction of metal oxides is divided into two parts: carbothermic reduction and metallurgical reduction. Carbothermic reduction is the reduction of metal oxides by carbon (C) and carbon derivatives. During carbothermic reduction, it is possible to examine the reactions in two separate groups as direct reduction and indirect reduction. Direct reduction is the reduction form of metal oxides, which is produced by direct reaction of carbon (C) and indicated by the reaction (1) [10].



In the case of the reduction of the metal oxides by carbon monoxide (CO) caused by the gasification of carbon (C), the indirect reduction shown by the reaction (2) occurs.



Metallurgical reduction is the process of reducing the metal oxides by using another metal with higher affinity to oxygen. Metallurgical reduction is a displacement reaction occurring between the metal oxide and another metal and is expressed as follows;



This reaction is due to the greater affinity of (Me_{II}) metal to oxygen than the (Me_I) metal. Its thermodynamic expression is given in (4) [11].

$$\Delta G_R = \Delta G_{\text{Me}_{II}\text{O}} - \Delta G_{\text{Me}_I\text{O}} < 0 \quad (4)$$

Elementary boron production is carried out by means of metallurgical reduction, mechanochemical synthesis, molten salt electrolysis and gas phase reduction depending on

the equipment and process used. The traditional method used in elementary boron production is the method of metallothermic reduction. In the first step of this method, boron-containing compounds (B_2O_3 , H_3BO_3 , HBO_2 , $NaBO_3 \cdot 4H_2O$, $Na_2B_4O_7$, etc.) are reduced in a high temperature environment with a reducing agent to form elementary boron containing too much contaminant. The reaction temperature used is between 300-1200 °C and some processes are carried out under pressure. After this step, in general, by making hot acid leaching, the product is removed from impurities. However, the elementary boron produced by this method is not obtained in high purity and crystal structure. The intermediate product obtained as a result of metallothermic reduction contains 85-95% boron and it is amorphous. The most preferred reducing agent in the production with metallothermic reduction is magnesium and this method is called as “magnesiothermic reduction”. When the oxide formation tendencies of boron and magnesium are examined (Figure 1), it is seen that magnesium has a greater tendency to form an oxide. When B_2O_3 is used as the boron source, a reduction reaction (5) occurs according to the Ellingham diagram.

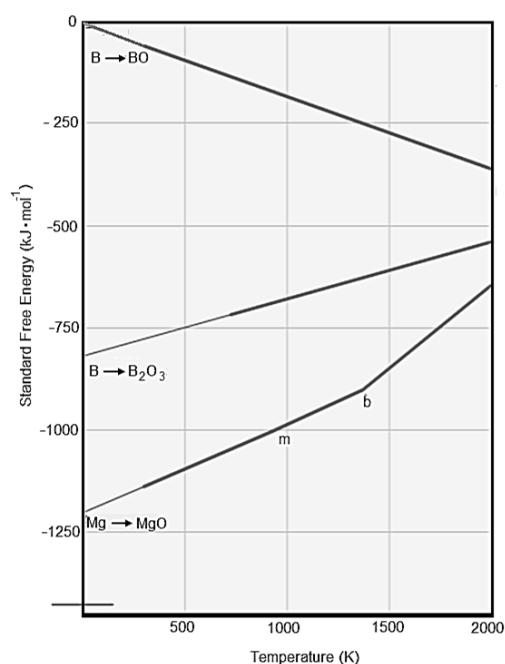
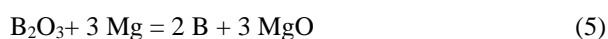


Figure 1. The standard free energy of formation of boron and magnesium oxides [12].



There are also production studies of elementary boron by high temperature reduction of B_2O_3 with alkali metals, alkaline earth metals or Ti, Zr, Hf and Al metals. After the heating of these elements, HCl leaching is applied and the product is removed from its impurities. Another method used to remove impurity is the passage of chlorine gas through the product at temperatures between 650-900 °C. Thus, metal impurities can be removed as metal chlorides. With this method it is possible to produce elementary boron with high purity [13-20]. A common aspect of these methods is the reduction of boron-

containing compounds by an element, and obtaining boron elementally.

2. Experimental details

Boron oxide (B_2O_3) powder used; 98% pure purity (SO_4 : 500 ppm max, Cl: 10 ppm max, Fe: 15 ppm max) and +315 μm (75%) in particle size (granulated) was supplied from Eti Maden Operations. Magnesium metal powders of 99.95% purity and 100 μm grain size were used for the metallothermic reduction of boron oxide (B_2O_3) powders. 37% purity hydrochloric acid (Merck) was used for the leaching operations. For the mechanical activation process, a spex type, high energy mill was used (fig. 2 (a)). The spex chamber (fig. 2 (b)) in which mechanical activation is carried out is a receptacle specially manufactured from tungsten carbide (WC) material. The steel balls of 4.75 mm diameter were used in the spex mill for the mechanical activation experiments.

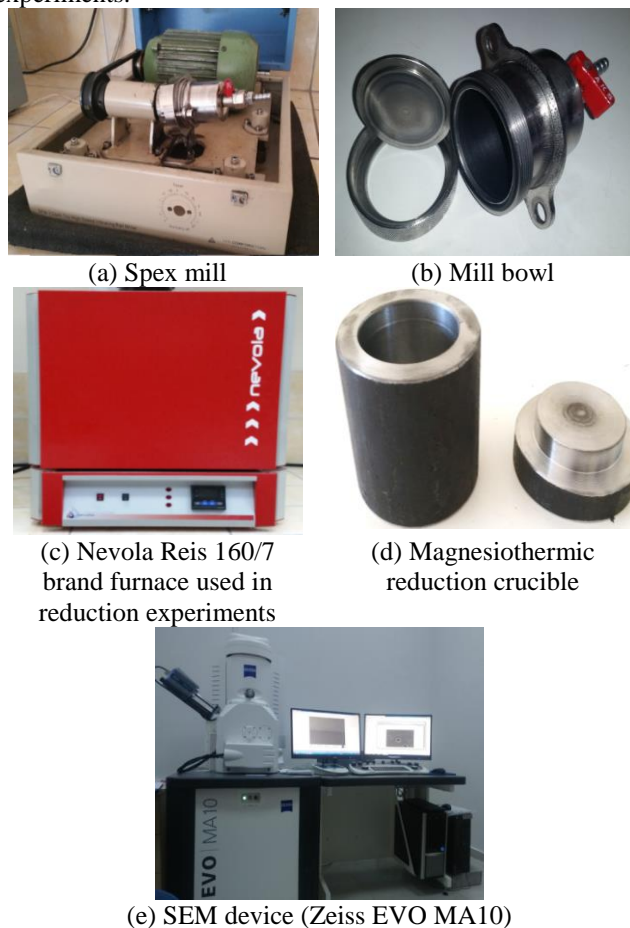


Figure 2. Devices used in experiments

In this study, the mechanical alloying-metallothermic reduction-the leach process was carried out one after the other and the elemental boron was produced from the B_2O_3 powders with the metallothermic method.

Magnesium metal powders and B_2O_3 powders were mixed into a spex mill according to the stoichiometric calculations made according to $B_2O_3 + 3Mg = 2B + 3MgO$ reaction. After adjusting the ball/mixture ratio to 20/1, the grinding time was

selected for 60 minutes. After milling, the mill's chamber was opened in a glove box under the nitrogen gas atmosphere, and the milled powders were taken into sample containers containing 25 ml of alcohol. The sample containers were then kept in an inert environment at a temperature of 40 °C for a certain period of time (until caking) in order to evaporate the alcohol. The cakes were placed into a special pot seen in Figure 2 (d), and left in the furnace (fig. 2 (c)) at room temperature. The argon gas was blown into the furnace at a rate of 6 l/min for 5 minutes before the furnace was started to run. While the argon gas supply was in progress, the furnace temperature was arranged that it would rise to 1000 °C in 45 minutes and wait at this temperature for 60 minutes and then cool down spontaneously. When the furnace temperature decreased to room temperature, the pot was got out from the furnace and the powders in the pot were removed by using a spatula and a clean brush and then they placed in the beaker containing 6M HCl solution. The powders in the beaker were subjected to leaching process on a hotplate at 300 °C for 6 hours. After leaching, the solution consisting of liquid and solid was filtered. The solid particles remaining on the filter paper were dried in an oven for 12 hours at 60 °C. At the beginning of the milling process, samples were coded as N1, N2, N3, N4, N5 and N6 according to their stoichiometric ratios. SEM and EDX analyzes of the samples were performed on the Zeiss EVO MA10 device as shown in Figure 2 (e). SEM and EDX images were examined for the samples which were only subjected to milling process and coded as N1 (2 times of stoichiometric ratio), N2 (3 times of stoichiometric ratio), N3 (4 times of stoichiometric ratio) and N5 (6 times of stoichiometric ratio). The samples coded as N4 and N6 were subjected to metallothermic reduction process after milling. Then, these powders were leached in the HCl solution.

The experimental conditions carried out with magnesium metal powders are summarized in Table 1.

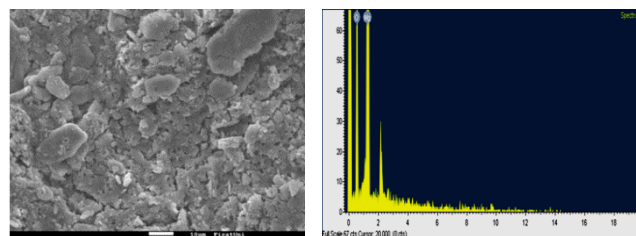
Table 1. The experimental conditions carried out with magnesium metal powders

Sample Name	St.	Milling Time (min.)	Ball/Mix.	Red. Temp. (°C)	Red. Time (min.)	HCl Conc. (mol/l)	Leach Time (min.)	Leach Temp. (°C)
N1	2	60	20/1	-	-	-	-	-
N2	3	60	20/1	-	-	-	-	-
N3	4	60	20/1	-	-	-	-	-
N4	4	60	20/1	1000	60	6	360	300
N5	6	60	20/1	-	-	-	-	-
N6	6	60	20/1	1000	60	6	360	300

3. Results and discussion

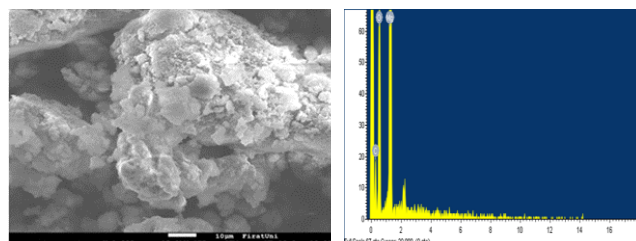
After 60 minutes milling, SEM and EDX images of samples coded as N1, N2, N3 and N5 were given in Figure 3. In the SEM images of these samples and in the EDX analyses taken from certain regions of these images, it was seen that the

crystal structure of the material was deteriorated because of the partial alloying during mechanical activation carried out in the mill. It was seen that metallic magnesium particles were partially integrated into the structure. Furthermore, in the EDX analysis, it was observed that the amount of magnesium decreased below the initially added stoichiometric ratio. This analysis is important in terms of giving an idea even though it does not represent the whole structure.



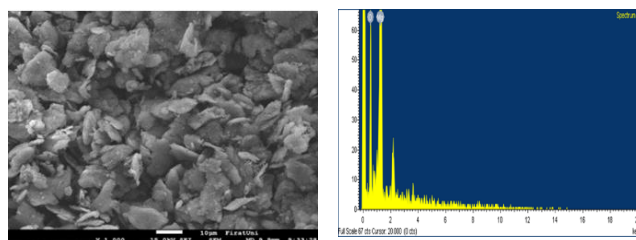
Element	Weight (%)	Atomic (%)
B K	30,20	32,6
O K	12,40	15,10
Mg K	57,40	52,30
Totals	100,00	

(a) N1 (St:2, M.T=60', B/M=20/1, No Reduction and Leaching.)



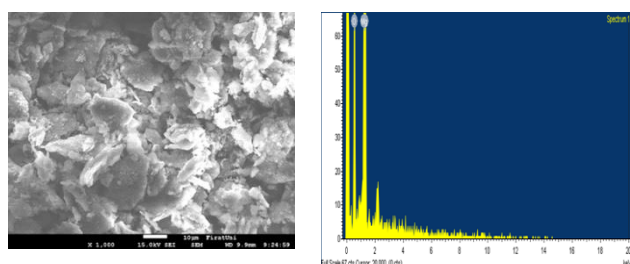
Element	Weight (%)	Atomic (%)
B K	12,30	13,20
C K	3,31	4,40
O K	31,36	32,15
Mg K	53,03	50,25
Totals	100,00	

(b) N2 (St:3, M.T=60', B/M=20/1, No Reduction and Leaching.)



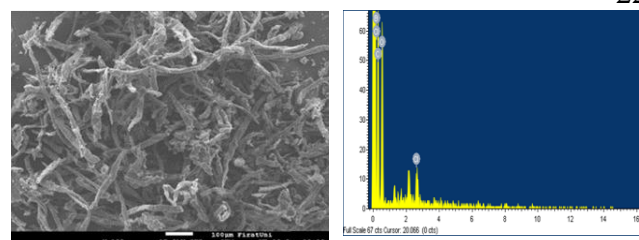
Element	Weight (%)	Atomic (%)
B K	21,10	23,20
O K	12,40	17,70
Mg K	66,50	59,10
Totals	100,00	

(c) N3 (St:4, M.T=60', B/M=20/1, No Reduction and Leaching.)



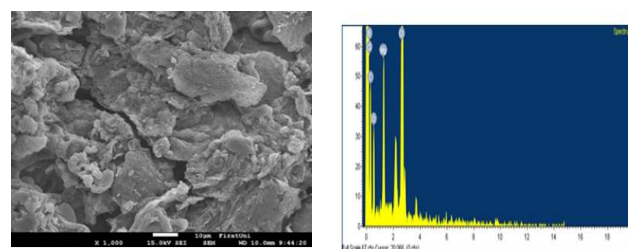
Element	Weight (%)	Atomic (%)
B K	15,30	20,30
O K	11,10	12,60
Mg K	73,60	67,10
Totals	100,00	

(d) N5 (St:6, M.T=60', B/M=20/1, No Reduction and Leaching.)



Element	Weight (%)	Atomic (%)
B K	97,89	97,90
C K	1,77	1,92
O K	0,23	0,16
Cl K	0,01	0,00
Mg K	0,10	0,02
Totals	100,00	

(a) N4, St:4, M.T=60', B/M=20/1, R_T:1000 °C, R_t=60', L_t= 360', C_{HCl}:6 M, L_T=300 °C, P:1 atm



Element	Weight (%)	Atomic (%)
B K	97,18	97,95
C K	2,51	1,91
O K	0,12	0,08
Cl K	0,17	0,05
Mg K	0,03	0,01
Totals	100,00	

(b) N6, St:6, M.T=60', B/M=20/1, R_T:1000 °C, R_t=60', L_t= 360', C_{HCl}:6 M, L_T=300 °C, P:1 atm

Figure 3. SEM and EDX images of samples with 60 minutes mechanical activation, (a) N1, (b) N2, (c) N3 and (d) N5 (St=Stoichiometry, M.T.=Milling time, B/M=Ball/Mixture)

Considering the EDX analysis of N4 and N6 samples, it was seen that the rate of metallic magnesium was very low (fig. 4). It was understood that almost all of magnesium was taken into solution in the leaching process after reduction. In EDX analysis, the chlorine and oxygen ratios are almost zero. This means that the leaching process has been successful.

It had been stated by some researchers that local temperatures were able to reach 10000 °C during the grinding process in the high energy mills such as the spex mill, attritor mill etc. [21]. It was understood from the EDX analyzes given figure 3 (a), (b), (c) and (d) that the ratio of Mg/B₂O₃ decreased as a result of partial reduction occurred due to grinding in the spex mill for 60 minutes. In a study in the literature, although reduced powders were subjected to the leaching process for 96 hours in the HCl solution without mechanical activation [22], the values obtained in present study could not be reached. During the leaching process, some studies have reported the presence of a hydroxide layer on the surface of MgO reacting with HCl [23-25]. In some studies, it has been emphasized that the effect of grain size and temperature on MgO's dissolution is very important [26].

Figure 4. SEM and EDX images of (a) N4 and (b) N6 samples (R_T: Reduction Temperature, R_t = Reduction Time, L_t = Leaching Time, C_{HCl} = HCl Concentration, L_T = Leaching Temperature, P = Pressure value of leaching)

4. Conclusion

In this study, mechanical alloying-metallothermic reduction-the leach process was carried out one after the other and the elemental boron production was carried out by magnesiothermic method. As a result of experimental studies, the following results were achieved.

-After 60 minutes of milling, the SEM and EDX images of some samples showed that the crystal structures were damaged after mechanical activation, and due to the partial alloying within the mill during activation, the metallic magnesium particles were partially integrated in the structure.

-In the EDX analysis, it was found that the amount of magnesium fell below the initially added stoichiometric ratio.

-In the EDX analysis of the samples subjected to reduction and leaching processes, it was seen that the amount of metallic magnesium was nearly zero due to the fact that almost all of the magnesium oxide was dissolved in the leaching process.

-Besides, EDX analysis revealed that these samples contained more than 97% elemental boron.

5. Acknowledgement

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