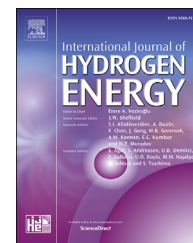


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A new approach to the manufacturing of elemental boron from boron oxide by carbon monoxide

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ABSTRACT

Elemental boron is one of the most valuable high-tech boron products and it has highest energy density 14 kcal/g in the world for this type of product. With the rapid advancements in technology in recent years, a demand has grown for a light materials with functionality and excellent properties such as high hardness, high melting point, high strength, high chemical resistance and nuclear characteristics that can be used in the fields of aerospace, aviation, automotive and solar cells. In this study boron oxide was reduced using carbon monoxide via a batch system to produce elemental boron. To determine the most suitable conditions for the reduction reaction different temperatures and different CO/B₂O₃ mol ratio parameters were studied. As a result of thermodynamic calculations for the most efficient parameters for reaction temperature was 140–210 °C and the CO/B₂O₃ mol ratio being studied was 3/1 and 2/1 for the batch system. Boron oxide reduction was performed by carbon monoxide gas with the pressure set at 10 bar. Characterization of the product was carried out by using X-Ray Diffractometer (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) at optimum temperature and mol ratio (140 °C and 3/1). Boron phase was seen in both XRD and FT-IR analysis. Also, SEM analysis was performed in order to observe morphological structure of elemental boron.

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Introduction

Although Turkey's boron reserves are very high the technology and facilities to process crude boron are insufficient. However, elemental boron is a very valuable for high-tech boron products as mentioned earlier both for its different uses and chemical properties [1]. Elemental boron production methods and equipment used for the process are examined in four groups: Methalothermic reduction, mechanochemical synthesis, production by electrolysis of a molten salt and the

reduction in gas phase. Each method of production, leads to formation of different structures and different purity of elemental boron [2].

Recently several studies were conducted in order to show how to produce elemental boron. The study done by Harold et al. includes the development of a process by where a magnesium reduction occurs, so as to produce high purity amorphous elemental boron. In this study the removal of impurities and the creation of the molten boron oxide was done by leaching the boron to achieve a higher purity product. End product was that it increased the purities up to 95% [3].

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Tilekar et al. was able to achieved high purity of elemental boron using two methods; oxidative annealing of boron and annealing of boron with zinc. Roasting boron with zinc in the ratio 1:1 at 600° C for 30 min in an inert atmosphere of argon could yield a purity of 93–94 percent, whereas by oxidative roasting method, 92% boron purity could be obtained [4]. Vignolo et al. has developed a new method for obtaining elemental boron by synthesizing magnesium diboride superconductors. Unlike other studies this experiment made boron oxide a nano-sized structure and achieved amorphous nano-sized elemental boron [5]. In a study by Stern and McKenna, molten salt electrolysis system was used to produce elemental boron by using boron carbide [6]. Jain et al. has produced elemental boron with electrowinning by dissolving potassium fluoroborate in molten potassium fluoride and potassium chloride [7].

Reduction in gas phase method is known as thermal decomposition of boron-containing compounds and at an elevated temperature of 900 °C the conversion of diborane to decaborane and reduction of boron chloride via hydrogen occurs which transforms the crystal structure and creates high purity elemental boron [2]. This method mixes a boron-containing gaseous compound with a reducing gas and then it is sent through an electrically heated surface. Principle of this method is based on thermal dissociation. This process offers many advantages the high yield, and the ability of obtained the product in single step is suitable for both semi-batch and continuous systems. Additionally the process does not contain mechanical handling which can affect the purity and the absence of corrosion in the produced gas. Kuehl produced elemental boron by reducing boron trichloride with hydrogen gas. This was carried out by having hydrogen gas pass through the reactor together with boron trichloride gas in a liquid state. Afterwards elemental boron powder was obtained [8]. Bean and Okla's study involves depositing elemental boron powder on tantalum filament. Where, dendritic, an amorphous-like low temperature alpha rhombohedral form of boron is deposited very quickly on a filament, which is protected by a tantalum diboride film [9]. Diborane and decaborane are used as a feed material at high temperature in the study done bt Allen and Ibrahim. Decomposition is formed in the fluidized bed reactor at 500–600 °C. Purity of the product reached 99.5% [10].

Carbon monoxide is an alternative reducing agent to hydrogen. It is a waste gas from iron-steel factories; it is cheap and reusable for many applications. Carbon monoxide is generally used as a reducing agent for iron oxide [11–13]. There have been several research papers on this subject. Bonalde et al. studied the kinetic analysis of the iron oxide reduction using hydrogen–carbon monoxide mixture as reductant. They formulated a successful kinetic model to describe the reduction process with carbon monoxide. Iron oxide pellets are reduced using carbon monoxide which is a mixed controlled type of system during the first 20 min of the process. Last step of the process is controlled by internal gas diffusion [14]. The study Zhang et al. a catalyst of type Pd/Co/Ba/Al was studied in a non-thermal plasma NOx trap (LNT) applications, and it was compared with Pd/Ba/Al and Pt/Ba/Al as reference catalysts for NOx storage and reduction using H₂ and/or CO as reductants. Because of the strong poisoning

effect of carbon monoxide on Pt when CO was used as the reducing agent at low temperatures the activity of Pt/Ba/Al was widely decreased [15].

The purpose of this study was to investigate if it is possible to achieve elemental boron from boron oxide by means of carbon monoxide as the reducing agent in a batch reactor. The conclusion reached is that this study will help to shed light on how productions of expensive boron end products can occur in subsequent studies.

The batch system is given in Fig. 1 and is used in order to determine the appropriate conditions for the reduction of elemental boron production by the method of gas reduction.

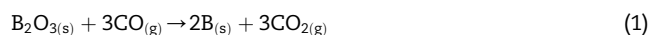
Materials and methods

Materials

In this study carbon monoxide has been used as a reducing agent with a purity of 99% to form elemental boron. Boron oxide has been used as a raw material supplied by Eti Maden (0.315 mm particle size, min 98% purity).

Elemental boron manufacturing process

Autoclave-type high pressure reactor was used in the system. The reduction process was carried out at 10 bar pressure in a carbon monoxide atmosphere. The highest amount of carbon monoxide gas that can be used at 10 bar boron oxide (solid) was calculated to be 4 g considering the amount of reaction stoichiometry. The reaction that is occurring in the batch system is as follows;



In this reaction both reduction and oxidation occur together. While boron oxide becomes elemental boron, carbon monoxide has been oxidized to carbon dioxide. Since boron oxide powder is very sensitive to air and moisture, the powder processing operations are carried out in an argon atmosphere in a glove box. 4 g of a solid powder was placed in the reactor

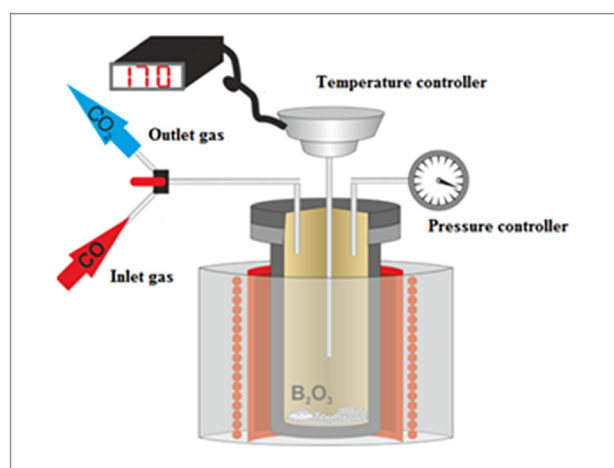


Fig. 1 – Batch system used for reduction of boron oxide.

with magnetic stirrer. After the reactor was closed, it was filled with argon gas in order to eliminate the presence of oxygen. Reactor was placed into the magnetic stirrer heater and a fume hood was wrapped in glass wool with the aim of providing thermal insulation. After this step, the jacket temperature was adjusted to the desired value and a certain CO/B₂O₃ molar ratio was expected after the completion of the reaction. This was repeated using different temperatures and CO/B₂O₃ molar ratio. The measurements taken for the trials are given in Table 1.

The sample codes shown in the table are temperatures and mole ratios used. The numbers mean as follows; “12” represents that reaction occurred with 3/1 M ratio, “9” represents that reaction took place with 2/1 M ratio. The most important parameter is temperature for solid–gas reactions firstly this parameter was investigated. Molar ratio of 3/1 was kept constant and reduction was performed at 140, 150, 170, 190 and 210 °C respectively. After determination was made of most suitable temperature, reduction was also carried out at a molar ratio of 2/1. Reaction time was 3 h for each of reaction. In order to remove the carbon dioxide formed by the reaction from the system, it was degassed then given a new carbon monoxide at amount preset by the experiment.

Characterization of elemental boron

Structural analysis of elemental boron was determined by using XRD (Panalytical, Empyrean) in order to obtain the impurities in the resulting product and the phases in the structure. XRD analysis was performed between 5 and 60 theta and 0.05 magnitude of steps. FT-IR (Perkin Elmer, Spectrum 100) analysis was used to observe the bond of compounds after the completion of reduction. It was realized in the range of 300–4000 cm⁻¹ wavelength. SEM (Zeiss Supra 40VP) analysis was performed to investigate the morphological structure of the products. Magnification of the images were 3000 and 10,000 respectively.

Results and discussions

Thermodynamic analysis

Carbon monoxide has effective reducing properties and is used as a reductant in iron production in the fuel and iron ore industry. In this study carbon monoxide has been used as a reducing agent so as to ensure the creation of conditions

Table 1 – Experimental study conditions.

Sample code	CO/B ₂ O ₃ molar ratio	Reaction temperature (°C)	Amount of B ₂ O ₃ (g)	Analysis
140–12	3/1	140	4	XRD, FT-IR, SEM
150–12	3/1	150	4	XRD
170–12	3/1	170	4	XRD
190–12	3/1	190	4	XRD, FT-IR
210–12	3/1	210	4	XRD
140–9	2/1	140	4	XRD

necessary to obtain elemental boron. Thermodynamic calculations were performed in order to determine the operating temperature prior to the experiments. Fig. 2 shows the change in Gibbs free energy versus the temperature which belongs to the above reaction.

After examining the graphic, it can be seen that a negative value for the Gibbs free energy exists even at low temperatures and that the reaction tends towards the products. Therefore keeping the reaction temperature low is both economical and applicable. For this reason reaction temperature was kept between 140 and 210 °C.

Temperatures used in the reduction method are 140, 150, 170, 190 and 210 °C. The XRD pattern of the products is shown in Fig. 3.

Effect of temperature on manufacturing of elemental boron

Temperatures used in the reduction method are 140, 150, 170, 190 and 210 °C. The XRD pattern of the obtained products is shown in Fig. 3.

When examined the XRD patterns of materials produced at different temperatures in each reaction their peak is at 28.6 with an intensity of 100 which belongs to unreacted boron oxide. For the solid and gas reactions in a closed and heated vessel the reaction continues until the equilibrium. If carbon dioxide which is occurring due to the reaction is removed from the system continuously boron oxide reduction will also continue. For most of the metal group elements reaction rate decreases with time because of the low permeability of the solid oxide layer that is formed at the surface of the particles and grows with time, therefore it limits the full conversion of the reactants to form pure metal [16]. Gas must penetrate further into the interior of the material so that reduction may occur. Reduction speed is also limited by the internal speed of the gas diffusing portion and diffusing speed of the product or rate of chemical reactions occurring at the interface. Thus, unreacted boron oxide is seen in graphics because carbon monoxide could not diffuse into the solid surface thoroughly [17]. The mean peak at 20.3 belongs to elemental boron was appeared in 140, 150 and 190 °C. When looking at XRD pattern

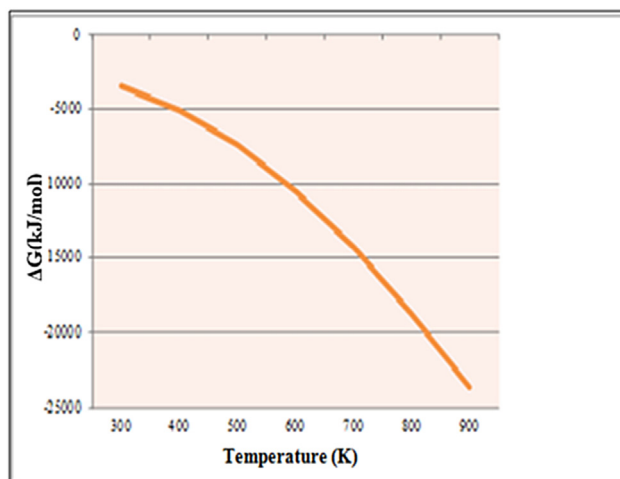


Fig. 2 – Gibbs free energy change in different temperatures.

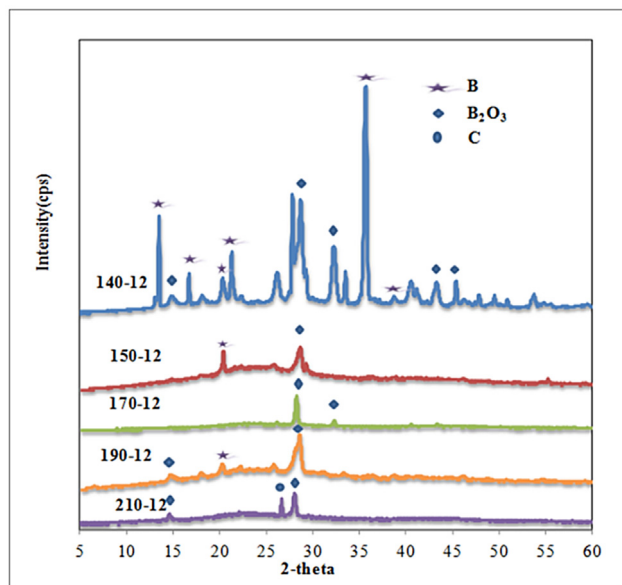


Fig. 3 – XRD pattern of the powder obtained at different temperatures with a 3/1 M ratio.

at 140 °C it has more boron phases than at other temperatures. XRD pattern of 140 °C with the main peak 17.62 and auxiliary peaks 20.26, 36.88 showing substantial concurrency with the elemental boron of tetragonal crystal phase. XRD pattern at 210 °C shows that elemental boron phase did not occur. The main peak at 26.6 belongs to carbon phase. This phase revealed that auto-reduction of carbon monoxide is used to form carbon. This situation shows that while carbon monoxide can reach high temperatures and carbon monoxide moves towards carbon by reducing itself [18]. When evaluation is done optimum temperature was obtained at 140 °C.

Effect of molar ratio on manufacturing of elemental boron

After determining optimal temperature for the gas reduction effect, the molar ratio for manufacturing elemental boron was studied. In order to determine whether the reaction can occur with less carbon monoxide molar ratio of $\text{CO}/\text{B}_2\text{O}_3 = 2/1$ was studied.

Fig. 4 shows the XRD pattern for the powder obtained at 140 °C with molar ratio of 2/1. In this pattern boron oxide was observed. According to this card number the most intense boron oxide peak was determined at 31.22 theta. The same card number belonging to boron oxide peak at 44.98 can also be seen in the chart. Elemental boron didn't occur in this reaction and the boron oxide powder was insufficient in reducing carbon monoxide. Feeding less carbon monoxide caused no reaction for boron oxide. Unreacted boron oxide phase is compatible with the study of Li and colleagues [17].

FT-IR characterization of boron products

FT-IR analysis was performed in order to see the B–B bond that occurred during the reduction process. When XRD results were evaluated elemental boron phase is shown most clearly at 140 °C, in addition elemental boron phase was seen at

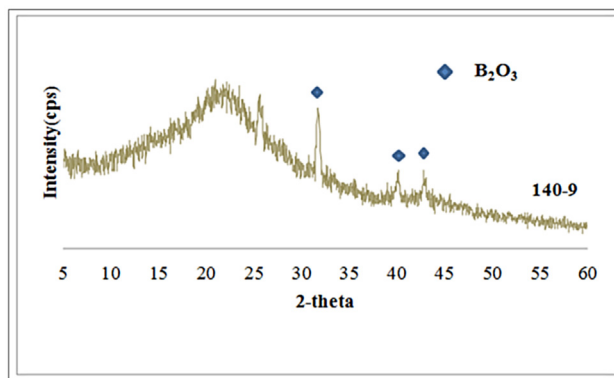


Fig. 4 – XRD pattern of the powder obtained at 140 °C with a molar ratio of 2/1.

190 °C $\text{CO}/\text{B}_2\text{O}_3 = 3/1$ M ratio of the powder therefore FT-IR analysis was performed for these two samples. Analysis of these samples is given in Fig. 5.

To decide at which wavelength B–B bonds occurred a FT-IR analysis of the commercial high purity boron was performed and compared with data from the literature.

According to FT-IR analysis results when both graphs are compared with the data in literature clear picture can be seen. The stress in the wavelength at 550 cm^{-1} belongs to B–B bond in form of B_5 [19]. It is also possible to determine that the stress at 636 cm^{-1} refers to B–B bond in form of B_4 [20]. The stress at 1460 cm^{-1} shows a B–O bond which usually occurs because of unreacted boron oxide. Due to the deformation of boron oxide there is stress at 1195 and 780 cm^{-1} wavelengths [21]. The stress which happens at 335 cm^{-1} in commercial boron was not observed in other products. In accordance with XRD and FT-IR analysis boron phase was observed in both characterization and the results are compatible with each other.

SEM characterization of boron products

Before the SEM analysis the powder was coated with platinum. The images in Fig. 6 were taken with magnification set to 3000 and 10,000 respectively.

It was observed that the structure appears to be dispersed uniformly. Stratification occurred in some places because the

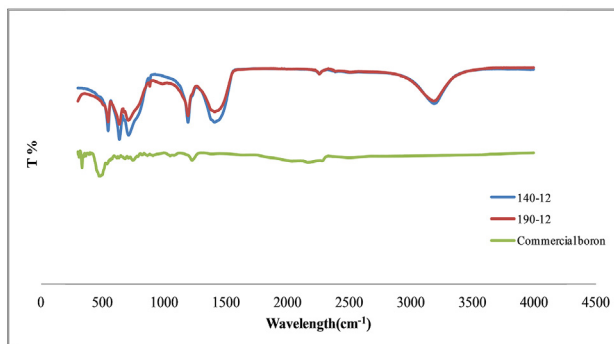


Fig. 5 – FT-IR analysis of the powders obtained at 140, 190 °C with a molar ratio of 3/1 and commercial high purity boron.

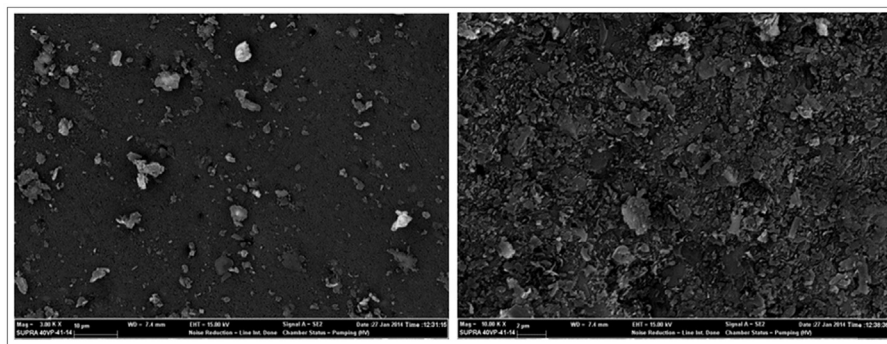


Fig. 6 – SEM images of powder obtained at 140 °C with a molar ratio of 3/1.

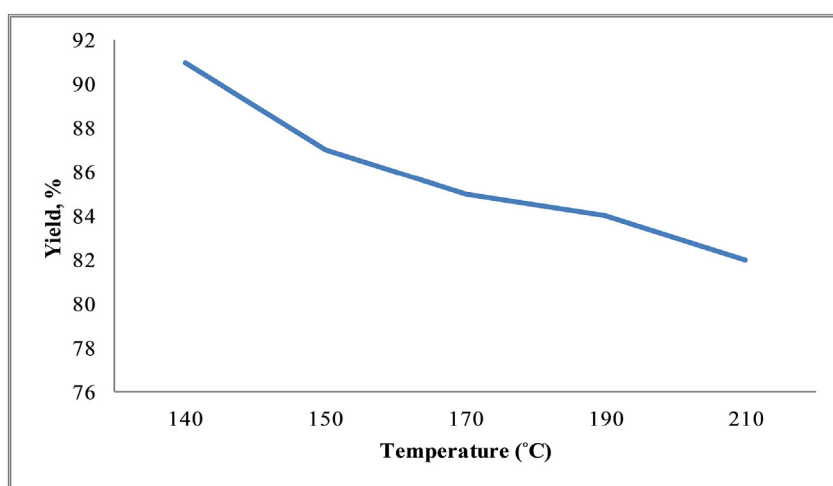


Fig. 7 – Yield analysis of boron products for different temperatures.

gas could not penetrate into the boron oxide sufficiently. While the bright parts of the image represent boron oxide non-glossy part representing elemental boron.

Yield analysis

Fig. 7 shows the yield analysis of boron products at different temperatures. The amount between the theoretically calculated product for the reactions and the actual obtained product are usually not the same. Chemical processes during synthesis such as drying, purification, etc. can lead to some loss of obtained product. For this reason boron yield was calculated using Equation (2).

$$\text{Yield \%} = (\text{Actual yield} / (\text{Theoretical yield}) \times 100) \quad (2)$$

It is not possible to achieve 100% efficiency in production due to chemical reactions. The reason for this is the above reaction (1) has two reactions competing with each other in the same conditions. If there are contested reactions, the reactants turn into different products, which mean that the actual yield is low. As indicated in XRD results at higher temperatures auto reduction of carbon monoxide occurs. It

can be clearly seen that from the figure for the highest temperature, 210 °C; less boron yield was achieved. Besides this, the unreacted boron oxide was also affected by the yield of reaction. As seen from the XRD figures the boron oxide could not be fully formed into elemental boron.

Conclusion

In this study the effect of temperature, which is the most important parameter, in manufacturing of elemental boron was observed. Molar ratio of $\text{CO}/\text{B}_2\text{O}_3 = 2/1$ was found to be insufficient in reducing boron oxide in batch system. Best results for reduction were obtained at 140 °C with a molar ratio of $\text{CO}/\text{B}_2\text{O}_3 = 3/1$. This method can be realized at low temperature and therefore make this method far superior to other ones. Because the method has not been tried before it needs to be developed. As a suggestion the reaction time can be reduced by using continuous reaction. In addition carbon monoxide which is a waste product that comes from iron and steel factories can be used in an economical manner to produce expensive boron end products. The production of other

boron end products such as boron carbide can be manufactured by using this method also.

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