

THE EFFECT OF TEMPERATURE AND MAGNESIUM SIZE ON LOW TEMPERATURE MAGNESIOTHERMIC SYNTHESIS OF NANO STRUCTURES BORON CARBIDE BY MESOPOROUS CARBON (CMK-1)

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Abstract: In this study, Boron carbide was synthesized using Mesoporous Carbon CMK-1, Boron oxide, and magnesiothermic reduction process. The Effects of temperature and magnesium grain size on the formation of boron carbide were studied using nano composite precursor containing mesoporous carbon. Samples were leached in 2M Hydrochloric acid to separate Mg, MgO and magnesium-borate phases. SEM, XRD and X-ray map analysis were carried out on the leached samples to characterize the boron carbide. Results showed that the reaction efficiency developed in samples with weight ratio of B₂O₃:C:Mg = 11:1.5:12, by increasing the temperature from 550 to 650 °C and magnesium powder size from 0.3 μm to 3 μm.

Keywords: Boron Carbide; CMK-1, Magnesiothermic, Temperature, Magnesium Grain Size.

1. INTRODUCTION

Nowadays, porous materials have been taken into consideration in various fields. Molecular sieve materials with template are a new classification of compounds with high surface area and massive pores that enjoy great importance in absorption and catalytic applications [1]. For the first time in 1992, Ryoo et al presented a new approach, using ordered silicate as a template in carbon based molecular sieve compositions synthesis according to nano casting method, after the successful silicate based molecular sieve patterns synthesis, along with its scientific and consequent developments in various fields [2].

In this method, ordered materials like: zeolites, SBA-15, KIT-5 and MCM-48 are used as templates in carbon molecular sieve material production. A member of mesoporous carbon, named CMK-1, is synthesized by sucrose as carbon source inside and the silicate mesoporous template MCM-48 as the pattern. Nano templates have had great impacts on non-oxide material synthesis over the last decade [3].

Boron carbide is an interesting compound among non-metallic and inorganic materials, in other words, ceramics. Boron carbide is a suitable material in many applications due to its high

toughness (29.1 GPa), low density (2.52 gr/cm³), high melting point (2450 °C), high elastic modulus (448 GPa), being chemically neutral, high neutron absorption and excellent thermoelectric properties. Boron carbide has high refractory characteristic and because of its covalent bond, it is chemically neutral and normally demonstrates tendency to decompose during melting; therefore, heating processes at high temperatures for the synthesis of this material is not recommended [4].

Currently, various methods have been used for boron carbide synthesis which could be used as an advanced ceramic. Carbo-thermal method is one of the synthesis methods that are produced from direct reaction between boron oxide and carbon. This reaction is highly endothermic and the boron carbide production temperature is about 1500 °C. Therefore, it is limited to nano-sized boron carbide powder preparation due to sintering. B₄C crystals have more tendencies to grow because of the high temperature, and will eventually form into different morphologies and structures. Furthermore, providing a high temperature costs a small fortune and is energy consuming [5].

Researchers have used reducing metal powders, also known as magnesiothermic process in references, such as magnesium to

decrease carbon thermal process temperature and synthesize different type of carbides.

In present study Boron carbide powders are produced by boron oxide magnesiothermic reduction in the presence of carbon. This reaction is highly exothermic and happens by self-propagating high-temperature synthesis (SHS) [6].

Using mesoporous carbon CMK-1, B₂O₃ and two type of magnesium, weight ratio of B₂O₃:C:Mg = 11:1.5:12, under argon atmosphere at 550 °C and 650 °C, boron carbide synthesis

was studied in this report. Results confirmed that temperature and magnesium size played an important role in the amount of boron carbide synthesis production.

2. EXPERIMENTAL

2. 1. Synthesis MCM-48, CMK-1 and Boroncarbide

MCM-48, CMK-1 [7, 8] and Boroncarbide synthesized by following process are shown in

Table 1. the specifications of the processed powder specimens

Spec. no.	The chemical composition B ₂ O ₃ :CMK-1:Mg	Temp. °C	Magnesium grain size (μm)	Acid leaching
1	11:1.5:12	550	300	✓
2	11:1.5:12	650	300	✓
3	11:1.5:12	650	3000	-
4	11:1.5:12	550	3000	-

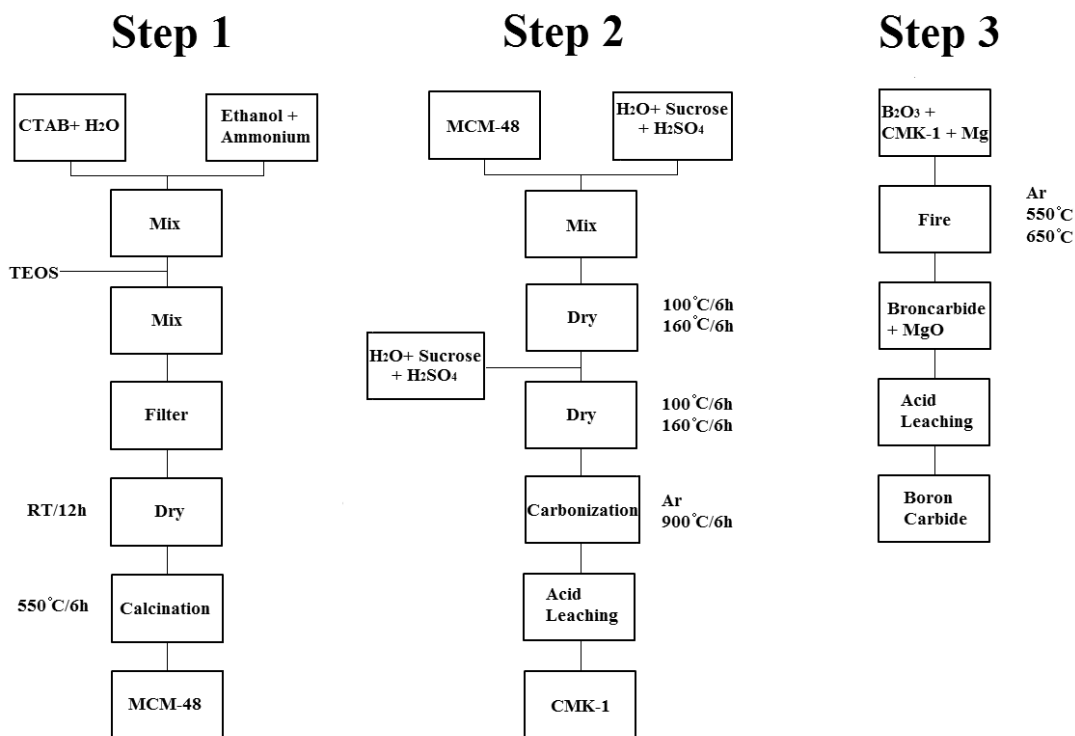


Fig. 1. Schematic of MCM-48, CMK-1 and Boron carbide synthesis procedures.

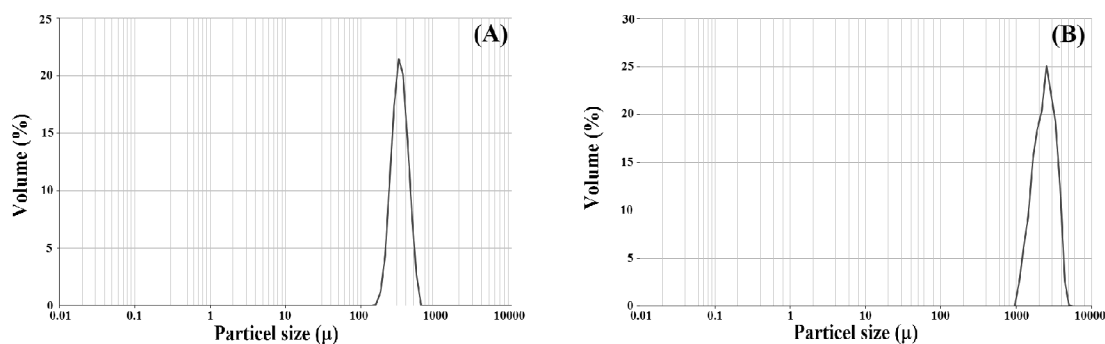
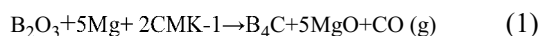


Fig. 2. Particle size of magnesium (A) fine Mg (B) coarse Mg

Fig. 1. According to the results which published previously the optimum weight ratio B_2O_3 :CMK-1:Mg = 11:1.5:12 for synthesis of boroncarbide was considered [9] by using mesoporous carbon (CMK-1). In this research 4 samples were prepared according to table 1. samples were fired at two temperature 550 °C - 650 °C under Ar atmosphere with two particle sizes of magnesium, therefore, the product was washed with hot water to remove B_2O_3 and then leached in 2M HCl to obtain boron carbide phase.

To synthesis boron carbide we used boron oxide, CMK-1 and different sizes of magnesium which is shown in Fig. 2.



2. 2. Characterization of the Reactants and Products

The synthesized powders' phase structures were studied by XRD technique at low and high angles after heat treatment. XRD patterns were

drawn by Bruker XRD (40 Kv, 20 mA, Cu $K\alpha$, wl 1.5015). Scanning electron microscope (SEM) was used to study the microstructures (LEO.435VP model). The specific surface areas of the carbon starting materials were measured using a micromeritics flow 2300 apparatus, transmission electron microscopy (TEM, Zeiss EM10C, Germany)

3. RESULTS AND DISCUSSION

3.1. Characterization of MCM-48 and CMK-1

Low angle XRD analysis (Fig. 3) showed the MCM-48 and CMK-1 structures have been formed correctly. Also TEM (Fig. 4) and BET (table 2) analysis approved that mesoporous structure formed for MCM-48 and CMK-1.

Table 2. BET data for MCM-48 and CMK-1 template

Sample	Total pore volume (p/p0=0.99) (g/cm^3)	BET surface area, as, BET (m^2/g)	Average pore diameter (nm)
MCM-48	0.4	658	3
CMK-1	0.6	759	4

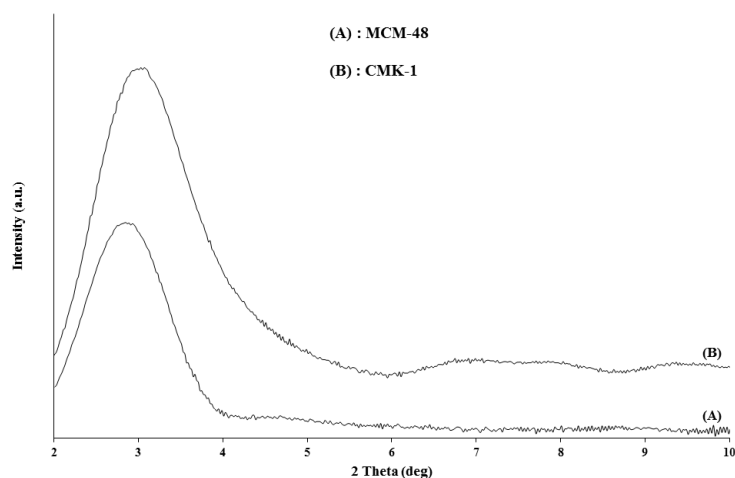


Fig. 3. Low-angle XRD patterns of (A) MCM-48 and (B) CMK-1. [9]

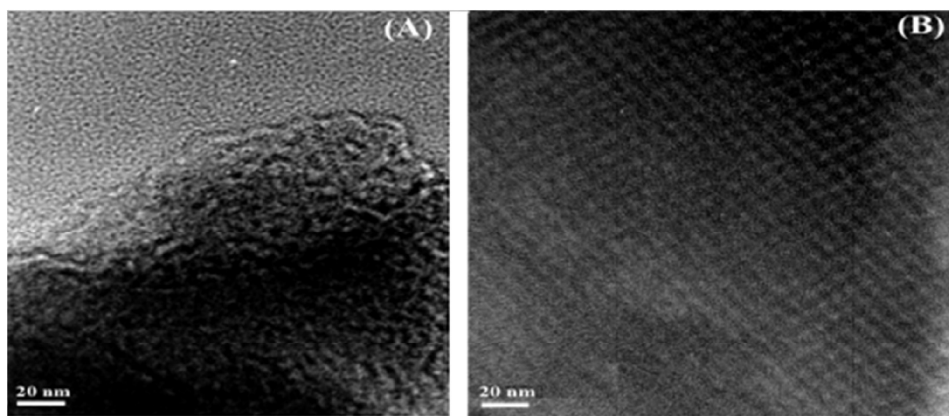


Fig. 4. TEM images of (A) MCM-48 and (B) CMK-1

3. 2. Effects of Temperature and Particle Size of Magnesium on Boron Carbide Synthesis

3. 2. 1. Effect of Temperature with Magnesium Fine Powder

XRD patterns of samples 1 and 2 before leaching process is shown in Fig. 5. This pattern approved that boron carbide formed in sample 2, meanwhile in sample 1 boron carbide didn't form and only MgO and small amount of $Mg_3B_2O_6$ could be seen.

This phenomena could be observed in XRD pattern of leached samples more than unleached, that shown in Fig. 6.

This is because of vapor pressure of magnesium powder which increases with temperature change from 550 °C to 650 °C. Vapor pressure of solids increases when temperature rises, Therefore vapor pressure of magnesium at 650 °C is much more than magnesium at 550 °C. Due to the vapor pressure increment, magnesium easily transfers to boron oxide surface and consequently reduction happens quickly.

$$\text{Log}(p/\text{atm}) = 8.489 - 7813/T - 0.8253 \cdot \log(T) \quad [10] \quad (2)$$

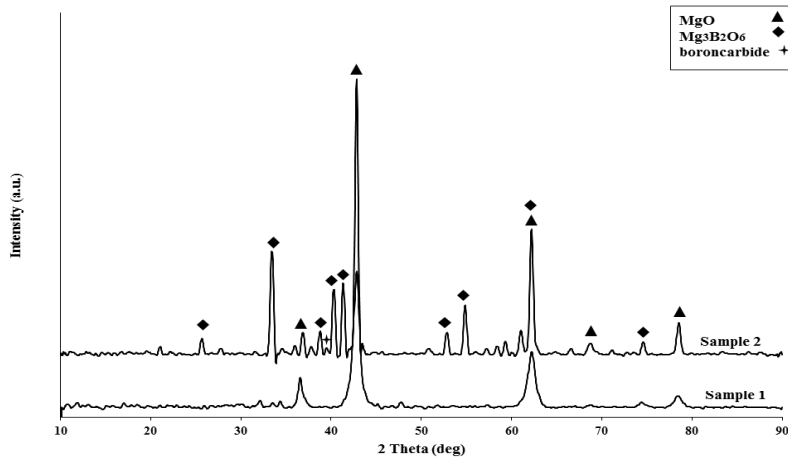


Fig. 5. XRD patterns of sample 1 and sample 2 prior to acid leaching

3. 2. 2. Effect of Temperature with Magnesium Course Powder

From XRD patterns of samples 3 and 4 shown in Fig. 7 It could be concluded that by using coarse powder of magnesium we didn't get any suitable results to obtain boron carbide, even when we applied 650 °C for firing of samples. This phenomenon is related to the decreased of vapor pressure by decreasing of surface area of magnesium.

X-ray map analysis of samples before firing is shown in Fig .8. Fine magnesium powder could be distributed better than coarse and from kinetic studies the effect on magnesiothermic reaction is evident.

Regarding to above results the sample 2 was selected as an optimum sample.

3. 3. SEM/EDS Analysis of Optimum Sample 2

According to SEM/EDS analysis of sample 2

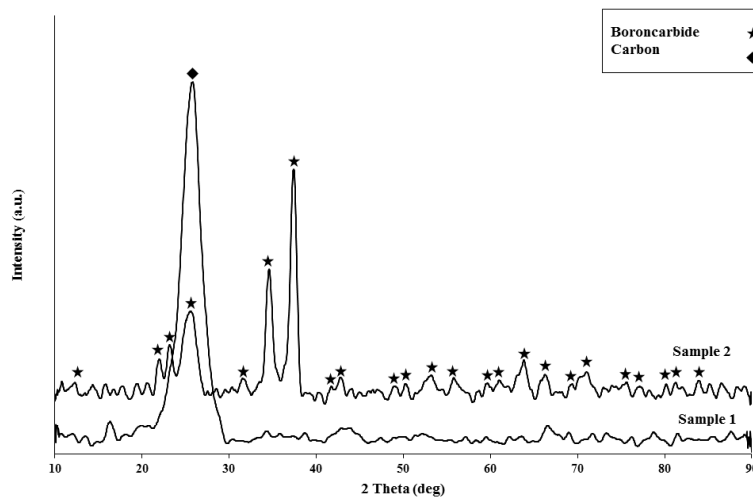


Fig. 6. XRD patterns after leaching of sample 1 and sample 2

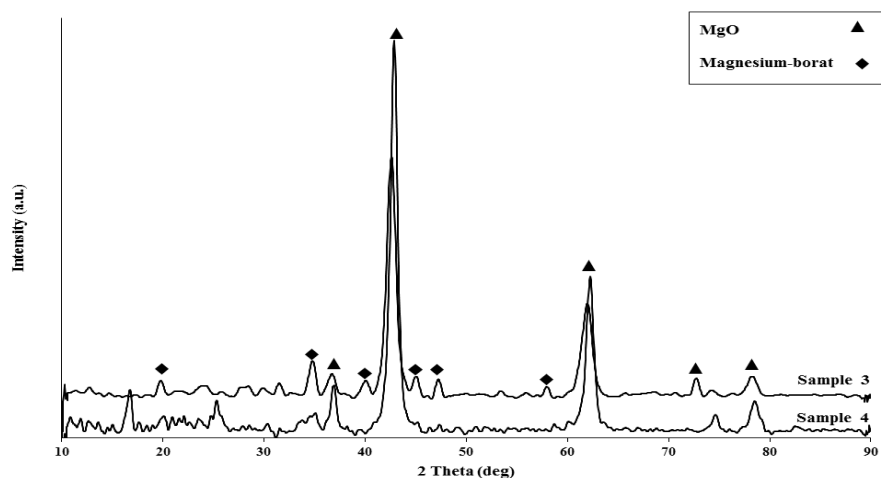


Fig. 7. XRD patterns of sample 3 and sample 4 prior to acid leaching

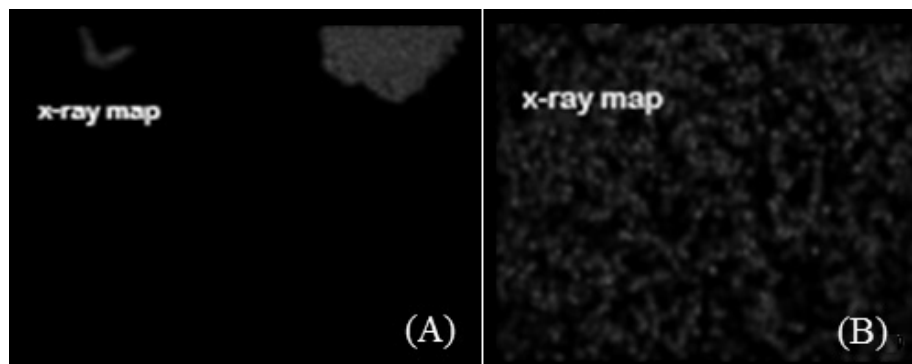


Fig. 8. Different size of magnesium Xray map (A) coarse Mg and (B) fine Mg

after leaching, the boron carbide is the main phase manual and in sample 1 after leaching the carbon is main phase. Micro structure of figure.9.(B) is a fine particle hexagonal compact that implies the boron carbide formation. Layered Micro structure of figure 9.(A) signifies carbon presence.

Crystal size of boron carbide was calculated by following Scherrer equation

$$t = 0.9\lambda / \beta \cos\theta \quad (3)$$

where t , β , λ , θ were denoted to particle size, peak

width at half maximum intensity, X-ray wavelength, Bragg angle of the diffraction peak respectively. Particle size of the synthesized boron carbide was calculated using each of θ and its β . The β was measured by X'Pert software. Crystal size of synthesized boron carbide was calculated to be about 24 nanometer at 650 °C using the CMK-1 mesoporous carbon.

4. CONCLUSION

Investigation of temperature and particle size distribution of magnesium as a reduction agent in magnesiothermic process approved that not only

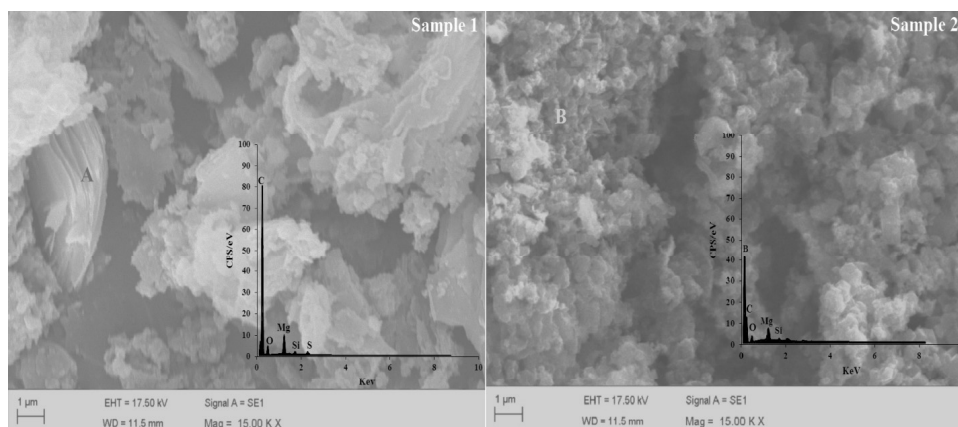


Fig. 9. SEM and EDS images (A) sample 1 (B) sample 2

temperature range is important, but also size of magnesium could effect on boron carbide formation during magnesiothermic reduction process.

Result showed that to obtain suitable amount of boron carbide stoichiometric weight ratio of $B_2O_3:C:Mg = 11:1.5:12$, temperature and size of magnesium are important. According to result, it could be concluded that the reaction efficiency developed in samples with weight ratio of $B_2O_3:C:Mg = 11:1.5:12$, by increasing of temperature from 550 to 650 °C and magnesium size powder from 0.3 μm to 3 μm.

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