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ZrB_2 POWDER PRODUCTION FROM ZrO_2 BY CARBOTHERMIC REDUCTION

Emrullahoglu Omer Faruk, Emrullahoglu Abi Cemile Betul, Saral Ufuk

Afyon Kocatepe University
Engineering Faculty
Department of Materials Science and Engineering
Afyonkarahisar, Turkey
E-mail: cbetul@aku.edu.tr

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ABSTRACT

Turkey has the largest boron (B) deposits in the world. But, it can get insufficient share/income from these natural resources because of non-production of high technology end-products. This article describes the procedures and results of a laboratory scale production of zirconium diboride (ZrB_2) powder using carbothermic reduction method in the tube furnace. Experimental studies consist of three steps. In the first step the mixtures containing zirconia (ZrO_2), boron oxide and two different proportions of carbon were shaped using uniaxial dry presssing. Boric acid was calcinated for transformation to boron oxide (B_2O_3) before addition to the mixtures. In the second step, carbothermic reduction was applied to the shaped samples in the argon gas atmosphere for three hours at 1350, 1450 and 1500°C. In the third step, XRD (X Ray Diffraction) analysis was applied to the samples. Carbon amount of the mixtures and the reaction temperatures were changed to observe the effects on the zirconium diboride productions. Carbon amount increased the peak intensities of zirconium diboride. XRD analysis results showed that major phase is zirconium diboride and minor phases are monoclinic and tetragonal zirconia. Minor phases are decreased with the increasing reduction temperature.

Keywords: zirconium diboride, zirconia, boron oxide, carbothermic reduction.

INTRODUCTION

ZrB_2 referred to as ultra high temperature ceramics is characterized by high melting temperature, high hardness, good electrical and thermal conductivity, high thermal shock resistance, strength, and chemical stability. These excellent properties present a wide range of high temperature applications including melting crucible for nonferrous alloys (Al, Cu, Mg, Zn, etc.), electrode, furnace elements, and antioxidant for carbon bonded refractories [1]. Ultra-high temperature ceramics (UHTCs) include borides, carbides and nitrides with melting temperatures above 2700°C [2]. Recently, numerous researches have been focused on UHTCs, with the mushroom development of hypersonic vehicles and re-usable atmospheric re-entry vehicles [3, 4]. ZrB_2 is one of the candidates for thermal protection materials in both re-entry and hypersonic vehicles because of its high melting point and good oxidation resistance [5 - 9].

The self-propagating-high temperature synthesis (SHS) process is one advanced method which has been used extensively for preparing refractory materials such as carbides, silicides, nitrides and various composite materials [10, 11]. Mishra et al. synthesised a zirconium diboride–alumina composite by SHS process of a milled and pelletised mixture of zirconium oxide, aluminum and boron oxide [12]. Radev and Klissurski used pure elemental zirconium and boron to synthesis ZrB_2 by SHS [13]. However, the use of elemental Zr and B is much more expensive than using the oxides due to the high

cost of extracting metals from the minerals. A similar argument regarding costs can be made for recent processes which use complex polymeric metal alkoxides or air and moisture sensitive materials, such as borazine, as the precursors [14, 15]. These preparations also require pyrolysis before the required phases are formed.

ZrB_2 powders can be synthesized by solid-state reaction. The most common process is the solid-state reduction involving a metal oxide, boron oxide and a reducing agent such as carbon, aluminum, or magnesium [16] at temperatures above 1500°C.

This paper focuses on the reaction sequence between ZrO_2, B_2O_3 and carbon black and the effect of carbon black quantity and carbothermic reduction temperature on the production of ZrB_2. XRD phase analysis results of samples are also discussed.

EXPERIMENTAL

Commercially available boric acid (H_3BO_3) (Etibank Bandırma/Turkey Boron cnd Acid Factory) was used to prepare the materials for this study. XRD patterns of boric acid and calcined boric acid were provided at Fig. 1a and 1b respectively. This powder had a reported purity of > 56.25 % B_2O_3. The ZrO_2 powder (DVS-Ukraine) was monoclinic zirconia. It had a reported purity of 99 % and a reported d_{90} particle size of 45µm. The carbon black powder (Tüpraş-Turkey) was Petkara PEF-N 550 coded carbon black. Reported ash content of the carbon black and specific surface area were 0.2 % and 40 $m^2 g^{-1}$. Polyvinil Alcohol (Merck) 1 % of solution was prepared and used as binder.

Boric acid was calcinated as following reaction;

$$H_3BO_3 \rightarrow 1/2\, B_2O_3 + 3/2\, H_2O \quad (1)$$

Calcination process was carried out at 900°C. The metal crucible containing boric acid powder was set into the furnace. At first, the temperature of the furnace was set to 110°C, after 4 hours the temperature was increased to 400°C, 1 hour later it was set to 900°C and after 1 hour the calcination process was finished. Finally, the furnace was turned off and the melt was poured on a metal plate before solidification.

Boron oxide in the glassy structure obtained by the calcination process was dry grinded for 1.5 hours in a ball mill after pre-crushing process. The powders were dry milled (Model ECeR Ceramic Mill, Afyon-Turkey) to reduce particle size and promote intimate mixing of the ZrO_2, B_2O_3 and carbon black. Dry milling was per-

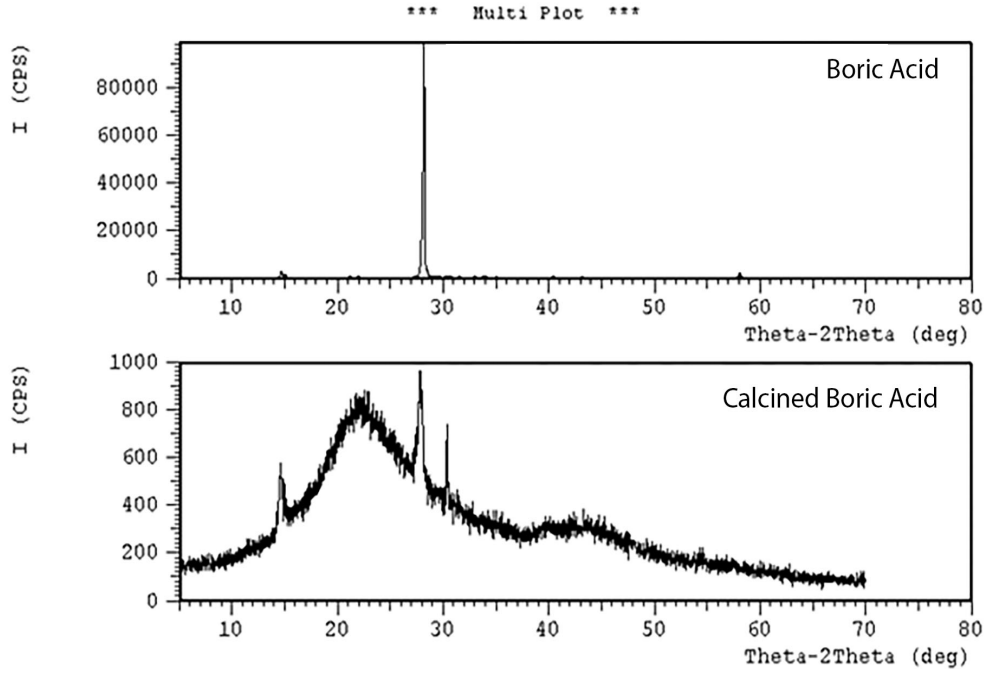

Fig. 1. XRD patterns of boric acid (a) and calcined boric acid (b).

formed for 2 h. Two different batches were prepared.

1th recipe: 29.52 gr ZrO_2 +16.68 gr B_2O_3 + 14.4 gr C
2th recipe: 29.52 gr ZrO_2 +16.68 gr B_2O_3 + 28.6 gr C

Powders were shaped by dress press (Model Hidroliksan Konya-Turkey, max. capacity 5 tonnes).

Tupe furnace (Model PLF 150, Protherm, Ankara-Turkey) was heated at a rate of 10° C min^{-1} under argon gas atmosphere up to the experiment temperature (1350, 1450 and 1500°C). The soaking time was 2 hours. During the carbothermic reduction process the following reaction occurs between zirconia, boron oxide, and carbon black:

$$ZrO_{2(s)} + B_2O_{3(s)} + 5C_{(s)} \rightarrow 2ZrB_{2(s)} + 5CO_{(g)} \quad (2)$$

Since the excessive amount of carbon not reacted with O_2 in the structure remains as unburned, the sintered samples were ground and then heated to 700°C in a normal atmosphere furnace, for 2 hours to remove the excessive amount of carbon.

The samples were washed using hydrocholoric acid solution following carbon removal. The aim of the washing process is to remove the free carbon, impurities and boron oxide in the powder obtained.

XRD technique (Shimadzu XRD 6000 model difractometer) was used for the characterization of the samples.

RESULTS AND DISCUSSION

It can be concluded from the investigation that the calcination of boric acid which will be used in the production of boron nitride is important, otherwise there may be overflows of melted boron oxide because of the foaming and this may damage the furnace refractory.

Figs. 2 and 3 show XRD of synthesized powders

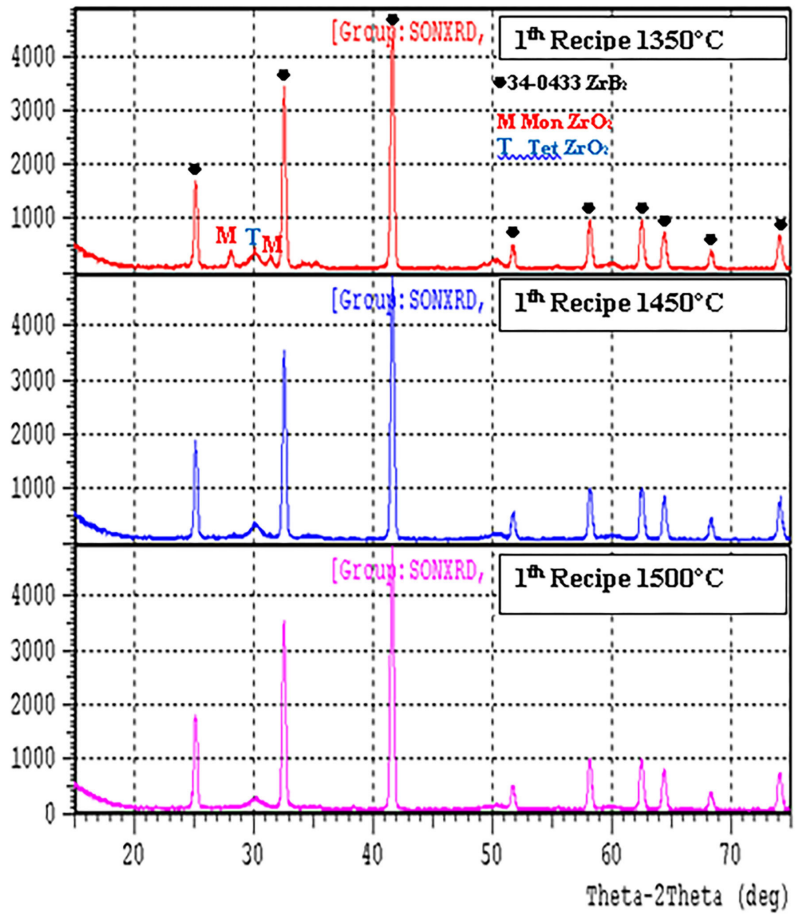

Fig. 2. XRD patterns of the 1th recipe heat treated at 1350-1500°C (•: ZrB_2, M: m-ZrO_2, T: t-ZrO_2).

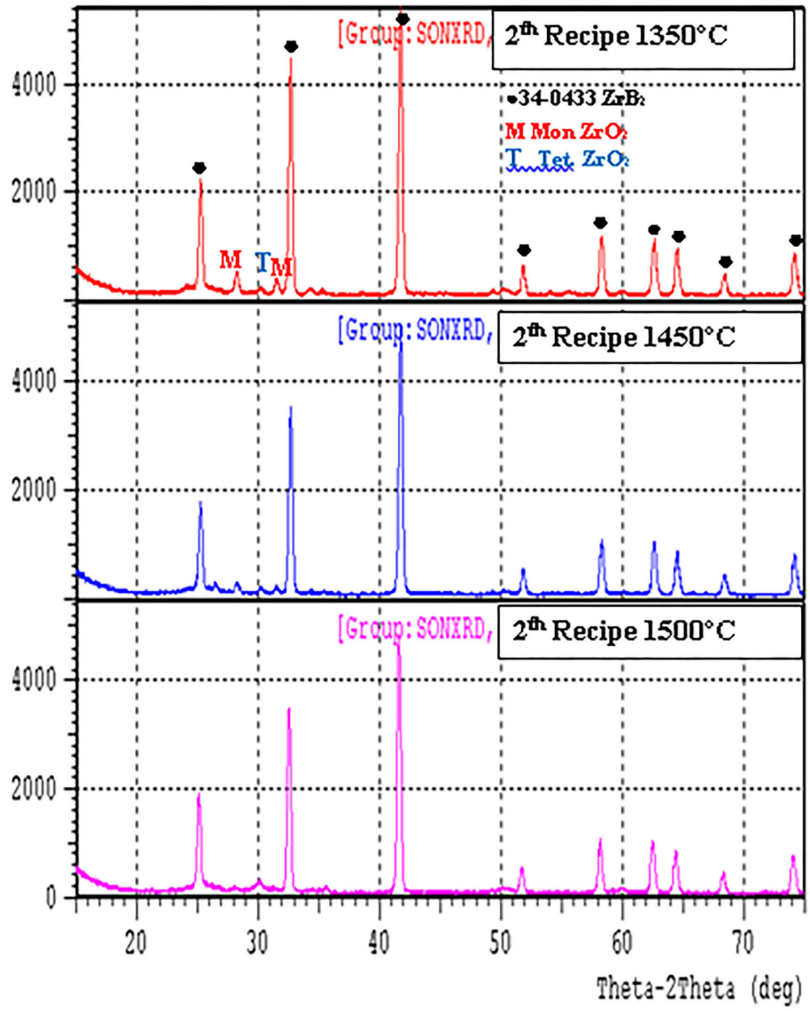

Fig. 3. XRD patterns of the 2th recipe samples heat treated at 1350-1500 °C (•: ZrB_2, M: m-ZrO_2, T: t-ZrO_2).

heat treated at different temperatures (1350, 1450 and 1500°C) to identify the formation of ZrB_2 (phase compositions). After heat treatment at 1350°C, t-ZrO_2 and m-ZrO_2 were detected. Formation of ZrB_2 was observed at all heating temperatures along with some tetragonal zirconia (t-ZrO_2).

As shown at Fig 2, the sample produced at 1350°C, was predominantly zirconium diboride phase. Monoclinic and tertragonal zirconia were minor phases. While monoclinic zirconia phase intensities decreased with the increasing process temperature, zirconium diboride phase intensities increased. The tetragonal zirconia intensity (shown at 2 theta 30) did not change.

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Well defined ZrB_2 peaks were observed in heat treated samples at 1500°C, which is lower than the temperature required for conventional solid state synthesis of ZrB_2 (~ 2000°C) generally employed to synthesize diborides [17].

Finally, at the end of this study, the production conditions of zirconium diboride using domestic carbon black and boric acid were determined and optimized.

CONCLUSIONS

The production conditions of zirconium diboride using domestic black carbon and boric acid were determined and optimized. Zirconium diboride as major phase and monoclinic and tetragonal zirconia as minor phases are obtained. Minor phases are decreased with the increasing reduction temperature. Increasing carbon amount increases the peak intensities of zirconium diboride. The best results for zirconium diboride production were obtained at 1500°C.

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