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Oxidation of boron carbide particles at low temperatures

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ABSTRACT

In the present work, the partial oxidation of boron carbide particles having average sizes of 10, 32 and 93 μm was studied in air. Prior to the oxidation process, the oxidation reactions were investigated by differential thermal analysis (DTA) studies. The values of the enthalpy of oxidation reaction of B_4C particles have been determined approximately −4216.35 J/g, −1941.36 J/g and −817.65 J/g respectively. According to the DTA analysis results, B_4C particles have been oxidized at selective temperatures 600, 650 and 700 °C in the range between 10 and 120 min. Results showed that temperature, time, particle size, and specific surface area of B_4C particles influenced oxidation process, intensely.

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1. Introduction

B_4C is one of the super-hard materials with its hardness (2900–3900 kg/mm^2) just below that of diamond [1,2]. Furthermore, it has excellent wear and chemical resistance, high melting point (2350 °C), low density (2.52 g/cm^3) and very high neutron absorption cross-section, which makes it extremely suitable for both room and high temperature applications such as lightweight ceramic armour, wear-resistant components such as blasting nozzles, grinding wheels, and control rods in nuclear reactors [3–6]. However, oxidation resistance of B_4C is low at high temperatures [7].

It has been reported that oxidation of boron carbide is not significant at temperatures below 500 °C and it becomes remarkable after 700 °C [8,9]. The oxidation reactions of boron carbide with oxygen and water are given below [7]

$$B_4C + 4O_{2(g)} \rightarrow 2B_2O_{3(l)} + CO_{2(g)} \quad (1)$$

$$B_4C + 7/2O_{2(g)} \rightarrow 2B_2O_{3(l)} + CO_{(g)} \quad (2)$$

$$B_4C + 8H_2O_{(g)} \rightarrow 2B_2O_{3(l)} + CO_{2(g)} + 8H_{2(g)} \quad (3)$$

$$B_4C + 7H_2O_{(g)} \rightarrow 2B_2O_{3(l)} + CO_{(g)} + 7H_{2(g)} \quad (4)$$

$$B_4C + 6H_2O_{(g)} \rightarrow 2B_2O_{3(l)} + C_{(s)} + 6H_{2(g)} \quad (5)$$

$$B_4C + 6H_2O_{(g)} \rightarrow 2B_2O_{3(l)} + CH_{4(g)} + 4H_{2(g)} \quad (6)$$

It has been reported that all reactions are thermodynamically favourable ($\Delta G < 0$) and reaction (1) has the lowest ΔG value [7].

The present work aims to investigate the partial oxidation of boron carbide particles at low temperatures based on DTA studies.

2. Experimental work

Angular shape B_4C particles with average particle sizes of 10, 32 and 93 μm and specific surface areas of 0.705, 0.253 and 0.176, m^2/g, respectively were used. The thermal behaviour of the powders was investigated by a PerkinElmer Pyris Diamond thermal analysis equipment at a heating rate of 10 °C/min under oxygen atmosphere. Oxidation studies were performed in a muffle furnace having an open atmosphere at the selective temperatures of 600, 650, and 700 °C within the time range of 10–120 min. 500 ± 1 mg of B_4C particles were spread homogenously on porcelain crucibles. The particles were weighted before and after the oxidation using a precision balance, with an accuracy of 0.1 mg. Oxidation degrees are calculated by using the following formula:

$$OD = \frac{\Delta W_0}{\Delta W_{th(\infty)}} \quad (7)$$

where OD is the oxidation degree (%), ΔW_0 is the weight change in time t, and $\Delta W_{th(\infty)}$ is the weight change corresponding to the complete oxidation by considering that all B_4C particles are transformed into B_2O_3 according to reaction (7) [7]. Before and after oxidation studies, structural analysis of particles was carried out by XRD using a Rigaku MiniFlex diffractometer equipped with a Cu Kα radiation source.

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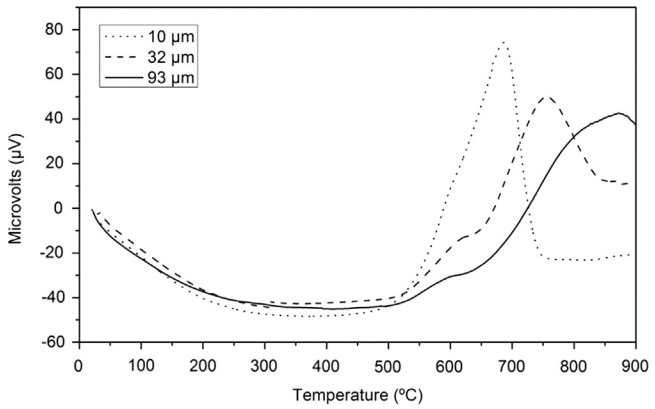


Fig. 1. DTA curves of the B_4C particles at a heating rate of 10 °C/min under O_2 atmosphere.

3. Results and discussion

DTA curves showed that oxidation reactions started at similar temperatures for all powders, however finished at different temperatures (Fig. 1). Within the studied range, oxidation reaction of the fine particles occurred in a single step whereas three and two exothermic reactions were observed for middle-sized and coarse particles, respectively.

DTA analyses were performed from room temperature to 900 °C at 10 °C/min under oxidative atmosphere. As can be seen from the DTA curves, particle sizes were affected by the oxidation temperatures of the reaction. The exothermic reactions of 10 and 32 μm particles were completed at 750.02 °C and 875.13 °C, respectively. Reaction enthalpy values were calculated from the peak areas of the exothermic reactions as −4216.35 and −1941.36 J/g.

For the coarse particles, the oxidative reaction was not completed up to 900 °C so that the peak area between 643.92 °C and 900.00 °C was calculated considering the maximum working temperature of the DTA instrument. Reaction enthalpy was determined from the peak area, which occurred between 643.92 °C and 900.00 °C, as −817.65 J/g.

Results showed that oxidation behaviour of B_4C particles was influenced by the particle size i.e. as the particle size increased, the reactions were completed at higher temperatures.

Fig. 2 presents the variation of oxidation degree with time at 600, 650, and 700 °C for three different particle sizes. Results showed that oxidation degree increased with increasing temperature and decreasing particle size. The greatest increase of the oxidation degree was observed for the fine particles at 600 °C where the oxidation degree increased from 1.8% to 15.2% between 10 and 120 min. Regarding the coarse particles, the oxidation degree was under 5% after 120 min of oxidation time for 600 and 650 °C whereas the oxidation degree increased almost linearly with time at 700 °C. The results are in agreement with the previous works [7].

Fig. 3 presents the XRD spectrum of B_4C particles with average particle size of 32 μm before and after oxidation at 650 °C for 30 min. For the oxidized powders, the co-existence of B_4C and B_2O_3 can be seen indicating the uncompleted oxidation.

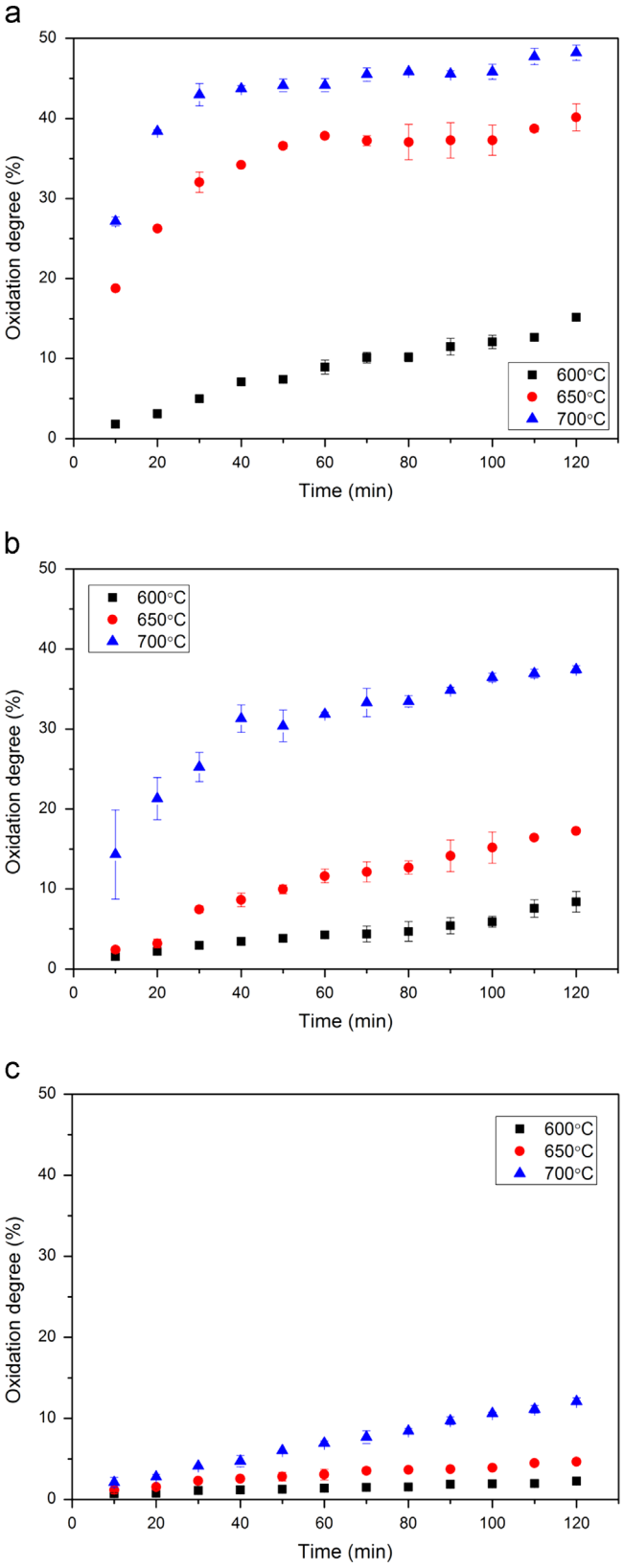


Fig. 2. Oxidation degree of a) 10 μm, b) 32 μm and c) 93 μm B_4C particles.

4. Conclusions

Partial oxidation behaviour of B_4C particles with average sizes of 10, 32 and 93 μm is investigated at low temperatures together with DTA studies. The enthalpy values of oxidation reactions of B_4C particles were calculated from the DTA curves to be approximately −4216.35 J/g, −1941.36 J/g and −817.65 J/g for fine, middle-sized and coarse particles, respectively. It is observed from DTA curves that the initial temperatures of the oxidation reactions are similar whereas the reactions end at higher temperatures for the coarse particles. The oxidation degree of B_4C particles increased with increasing temperature and decreasing particle size.

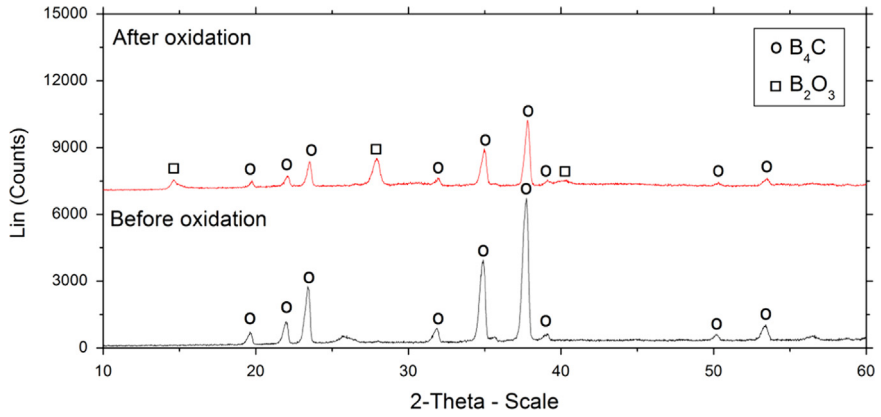


Fig. 3. XRD spectrum of 32 μm B_4C particles both in as-received conditions and after oxidation at 60 °C for 120 min.

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