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Kinetics of oxidation of boron powder

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ABSTRACT

The kinetics of the oxidation of electrodeposited boron powder and the boron powder produced by the reduction process were studied using thermogravimetry (TG). The oxidation was carried out by heating boron powder in a stream of oxygen. Both isothermal and non-isothermal methods were used to study the kinetics. Model-free isoconversional method was used to derive the kinetics parameters. A two step oxidation reaction (exothermic) was observed. The oxidation reaction could not be completed due to the formation of glassy layer of boric oxide on the surface of boron powder which acts as a barrier for further diffusion of oxygen into the particle. The activation energy obtained using model-free method for electrodeposited boron is 122 ± 7 kJ mol^{-1} whereas a value of 205 ± 9 kJ mol^{-1} was obtained for boron produced by the reduction process (commercially procured boron). Mechanistic interpretation of the oxidation reaction was done using model based method. The activation energy was found to depend on the size distribution of the particles and specific surface area of the powder.

1. Introduction

Boron carbide, containing boron enriched in ^{10}B isotope (^{10}B ~ 65 at %) will be used as control rod material in India's first proto type fast breeder reactor (PFBR) [1]. High density pellets of boron carbide containing enriched ^{10}B are produced by a high temperature reaction between the enriched elemental boron and carbon. A pilot plant was established in our laboratory for the production of enriched elemental boron. In this facility boron is electrodeposited on mild steel cathode by molten salt electrolysis of a mixture of potassium chloride, potassium fluoride and potassium tetra fluoroborate. The details of the production of elemental boron and boron carbide are described elsewhere [2,3].

Information on the mechanism and kinetics of the oxidation of elemental boron are required for establishing a procedure for the safe handling of elemental boron in air. Boron undergoes oxidation to form boric oxide by the following reaction: $4B + 3O_2 = 2B_2O_3$. B_2O_3 is a thermodynamically stable compound as it has large negative Gibbs energy of formation (for example, −1139.18 kJ mol^{-1} at 500 K).

Rizzo [4] has studied the oxidation of boron powder compacts (crystalline and amorphous) at temperature between 673 K and 1573 K and reported the formation of a protective coating of boric oxide which broke beyond 1273 K. They have also observed that the oxidation of boron followed a parabolic rate law during the initial stages of the oxidation. However, these authors did not study the mechanistic aspects and kinetics parameters of the oxidation process.

Talley [5] has studied the oxidation of boron in 1 atm pressure of oxygen at 1500–2300 K and observed two rate-limiting processes. They obtained an activation energy of 50 kJ mol^{-1} for the lower temperature region (700–800 K), where the flow of molten B_2O_3 (melting point 723.15 K, formed during the oxidation of boron) is the rate-limiting process, and an activation energy of 321 kJ mol^{-1} for the high temperature region (~2300 K), where evaporation of B_2O_3 is the rate controlling mechanism.

DiGiuseppe and Davidovits [6] have studied the gas phase reactions of boron atoms with O_2, SO_2, CO_2 and N_2O in a flow tube apparatus. They obtained a bimolecular rate constant for the oxidation of boron in oxygen at 300 K by measuring the density of boron in the downstream of flow tube as a function of gas reactant concentration.

In order to explain the reaction of oxygen with the boron beneath the oxide layer Glassman et al. [7] have presented a theoretical explanation and showed that the first stage combustion of the boron takes place by the diffusion of boron through the oxide layer to the B_2O_3–gas interface. Yeh and Kuo [8] observed using environment scanning electron microscopy (ESEM) that at elevated temperatures (>1200 K) the diffusion of boron into molten B_2O_3 (l) dominates over the diffusion of gaseous O_2 through the B_2O_3 (l) layer.

King et al. [9–12] have developed models to describe the mechanism of boron oxidation and combustion. They have assumed that oxygen diffuses through the oxide layer to reach the B–B_2O_3 inter-

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Table 1
The physicochemical characteristics of the boron samples.

Nature of the sample	Chemical purity (wt%)	Specific surface area (m^2/g)	Particles size (μm)	Bulk density ($g\,cm^{-3}$)
Electrodeposited boron	~96	4.2	<10	0.41
Boron-commercial	~99	3.8	<100	0.45

face. The heterogeneous reaction between oxygen and boron can provide heat for vaporization of the oxide layer. The particle temperature will continue to rise if the heat input is greater than the energy loss associated with vaporization of B_2O_3. If it continues to the point at which the remaining oxide layer is sufficiently thin, an abrupt increase in temperature would take place.

Macek and Semple [13] have observed that the burning time of the boron powder was inversely proportional to the mole fraction of oxygen and ambient gas temperature. This implies that both chemical kinetics and oxidizer diffusion play important role in the bare boron combustion.

Most of the studies reported in the literature describe the high temperature oxidation of boron powder as it is used as combustible in aerospace applications [14]. The information on the quantitative treatment of the data to obtain kinetic parameters (rate constant and activation energy) and mechanistic aspects is scarce. In view of the above it was decided to carry out studies on the oxidation of boron powder. This paper describes isothermal and non isothermal kinetics of the oxidation of elemental boron powder. Oxidation behavior of the electrodeposited boron and boron powder procured commercially (which was synthesized by the reduction of boron halide in the presence of hot tantalum filament henceforth called 'boron-commercial') was studied and kinetic parameters such as activation energy were calculated using isoconversional method. The mechanism of oxidation process is proposed based on the analysis of thermogravimetric data using reported models of the solid state reactions.

2. Experimental

2.1. Chemicals

Boron-commercial (purity >99.999 wt%) was procured from M/s. Aldrich Chemical Company, Inc., USA. Electrodeposited elemental boron (purity >96 wt%) was obtained from the Boron Chemistry Laboratory, Indira Gandhi Centre for Atomic Research, Kalpakkam.

2.2. Experimental procedure

The boron powders were characterized for their chemical composition, impurity content, bulk density, specific surface area, particle size distribution and X-ray diffraction. The boron samples were analyzed for their impurity content by inductively coupled plasma mass spectrometry (ICPMS, Model: Elan 250, M/s. Sciex, Toronto, Canada). The carbon content was determined by oxidizing the sample in a stream of oxygen in an induction furnace and measuring the carbon dioxide evolved by an infrared detector. The X-ray powder patterns were obtained using an X-ray diffractometer (XPERT MPD system obtained from M/s. Philips, The Netherlands), employing filtered Cu Kα radiation. BET surface area of the powder was measured using a continuous flow Nelson Eggersten type surface area analyzer, M/s. Quantasorb Jr. system obtained from Quantachrome, USA. The particle size analysis was carried out with a Mastersizer Particle size analyzer obtained from M/s. Malvern, Worcestershire, UK. The simultaneous thermogravimetry and differential thermal analyses were carried out using a TGA/SDTA851e thermogravimetric analyzer supplied by M/s. Mettler Toledo, Switzerland.

The temperature calibration of thermogravimetric analyzer was carried out by the method of fixed melting points employing International Confederation for Thermal Analysis and Calorimetry (ICTAC) recommended standards such as indium, tin and gold. This equipment has a weight sensitivity of 0.1 μg and a temperature sensitivity of 0.01 K. A Platinum crucible of 70 μl capacity was used as the sample container. For each experiment 5 mg of the boron powder was used as sample. The temperature was measured using a Pt–Pt–10% Rh thermocouple which was in firm contact with the sample holder on which the Pt sample container was placed. The inner muffle of the furnace was constantly purged with oxygen, the flow of which was controlled by a mass flow controller. A constant gas flow of $0.33\,l\,s^{-1}$ and a predetermined rate of heating were used to carry out dynamic experiments. A program with three segments was used for this study. In the first segment the sample was heated from 303 K to 393 K at a heating rate of $10\,K\,min^{-1}$. In the second segment, in order to remove the moisture absorbed on the surface of fine powder, the sample was heated at 393 K for 30 min. In the third segment dynamic experiments were carried out. In this segment sample was heated from 393 K to 1073 K at various heating rates viz. 1, 3, 5, 10 and $15\,K\,min^{-1}$. A fresh sample was taken for each experiment. Reproducibility of the results obtained from different measurements was verified by carrying out measurements in duplicate or triplicate. The results were found to be in excellent agreement with each other. Isothermal experiments were carried out by heating the sample at pre-determined temperatures viz. 713 K, 733 K, 753 K, 773 K, 793 K and 813 K for 420 min. The furnace was preheated to the desired temperature and sample was introduced at that temperature.

3. Results and discussion

The physicochemical properties of the boron powder samples (electrodeposited boron and boron-commercial used in the present study) such as chemical purity, specific surface area, particle size and bulk density are given in Table 1. The total metallic impurities present in the sample were less than 1% (by weight). The detailed chemical assay of electrodeposited boron is described elsewhere [15]. Hence, the influence of metallic impurities on the oxidation behavior of boron is expected to be insignificant. The X-ray diffraction pattern of the electrodeposited boron and boron-commercial is shown in Fig. 1. The X-ray diffraction pattern shows the crystalline nature of boron-commercial. It was observed that the peak positions of the diffraction pattern of boron-commercial match with the standard pattern of rhombohedral boron (JCPDS file no. 80-0322). The X-ray diffraction pattern of electrodeposited boron is also shown in the same figure. The absence of sharp peaks in the diffraction pattern shows the amorphous nature of the electrodeposited boron. This was further confirmed by transmission electron microscopy analysis of the electrodeposited boron where nano crystallites of boron (rhombohedral) were seen embedded in an amorphous mass of boron [16]. The product of oxidation reaction was found to be boric oxide as confirmed by taking X-ray diffraction pattern of the reaction product. The X-ray diffraction pattern matches with the reported pattern for cubic boric oxide JCPDS file no. 06 0297. This X-ray diffraction pattern was recorded after heat treating the oxidized product at 700 K for 150 h in air to convert amorphous boric oxide to crystalline form.