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Electroextraction of boron from boron carbide scrap

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ABSTRACT

Studies were carried out to extract elemental boron from boron carbide scrap. The physicochemical nature of boron obtained through this process was examined by characterizing its chemical purity, specific surface area, size distribution of particles and X-ray crystallite size. The microstructural characteristics of the extracted boron powder were analyzed by using scanning electron microscopy and transmission electron microscopy. Raman spectroscopic examination of boron powder was also carried out to determine its crystalline form. Oxygen and carbon were found to be the major impurities in boron. Boron powder of purity ~92 wt. % could be produced by the electroextraction process developed in this study. Optimized method could be used for the recovery of enriched boron ($^{10}B > 20$ at. %) from boron carbide scrap generated during the production of boron carbide.

1. Introduction

High-density pellets of boron carbide, containing boron enriched in ^{10}B isotope (~67 at. %), are the control rod material for India's first prototype fast breeder reactor (PFBR) [1]. Boron carbide is synthesized by a high temperature reaction between boron and carbon. Boron carbide thus obtained is subsequently powdered and hot pressed to produce high-density boron carbide pellets. The methodology to synthesize high-density boron carbide pellet is described elsewhere [2–4]. An exhaustive physicochemical characterization of boron carbide pellets is carried out to ascertain the suitability of these pellets for control rod applications in fast reactors. Those pellets which do not meet the technical specifications are rejected (~10%) during quality control. Synthesis of isotopically enriched boron ($^{10}B > 20$ at. %) is a time consuming and energy intensive process. It is advantageous to recover enriched elemental boron from those boron carbide pellets which were rejected based on chemical specifications. Hence, there is a need to develop a methodology to recover isotopically enriched elemental boron ($^{10}B > 20$ at. %) from these rejected pellets.

Information on the recovery of boron from boron carbide is scarce. Boron carbide is chemically inert, hard and refractory in nature [5]. Hence, only electrolytic method had been used for the recovery of boron from boron carbide in the past. The electroextraction process can be used to recover enriched boron from boron carbide scrap.

Stern [6] has described an electrolytic method for the extraction of boron from boron carbide on laboratory scale. He has carried out electrolysis of a molten mixture of pre-dried sodium chloride (40 wt. %), potassium chloride (40 wt. %) and potassium fluoborate (20 wt. %). The anode compartment was filled with boron carbide. During electrolysis, the electrolyte was maintained at 1073 K. Pre-electrolysis was carried out at 2.5 V for 30 to 60 min. The electrolysis was carried out at 1 V. Boron was deposited on mild steel cathode. Though the

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purity of this boron was claimed to be 99.8 wt. %, the results of chemical analysis of electroextracted boron were not reported. The electrolysis was described as anode transfer reaction by using material balance calculations.

Stern et al. [7] have described in their patent that the elemental boron from boron carbide passed into the melt if boron carbide was made anode and submerged in a fused salt (mixture of alkali chloride or a mixture of alkali chlorides and potassium fluoborate). Under the influence of direct current boron was deposited on the cathode as elemental boron.

Nair et al. [8] have described the electrochemistry of electroextraction of boron from boron carbide. They have suggested that until and unless the electrodes get polarized to a great extent electrolysis cannot be conducted. It was expected that boron carbide dissolved anodically to supply B^{3+} ions which got discharged at the cathode without change in soluble boron concentration in the electrolyte and evolution of any gas at the anode.

Although laboratory scale electroextraction of boron from boron carbide through molten salt electrolysis is reported in the literature, no information is available on its large scale extraction. It is of interest to study the viability of this process for the large scale extraction of boron from boron carbide. This will also serve as a method to recover enriched boron from boron carbide scrap generated during its synthesis. In order to study the electroextraction process for the synthesis of boron from boron carbide on large scale, a pilot plant facility was established at Chemistry Group, Indira Gandhi Centre for Atomic Research (IGCAR). This paper describes the methodology developed for the extraction of boron from boron carbide scrap and the physicochemical properties of boron thus obtained from the process. The data generated through characterization could be used for further optimization of process parameters for the electroextraction.

2. Experimental

2.1. Chemicals

Analytical reagent grade KCl, NaCl and KBF_4 having purity greater than 99 wt. % were procured from M/s. Rankem Laboratory Chemicals Pvt. Ltd., Chennai. Analytical reagent grade HCl and acetone were procured from M/s. ILE & Co. Chennai, India.

2.2. Electrolytic Cell for the Electroextraction

The electrolytic cell used for the electroextraction of boron is shown in Fig. 1. This cell is similar to the one used for the synthesis of boron by electrowinning method [4,9]. The electrolytic cell essentially consisted of a cylindrical vessel (height: 710 mm, OD: 273 mm) made of inconel-600. A liner made of nickel (purity ~99%) was placed inside this vessel. A high-density ($\rho = 1.84$ g cm^{-3}) graphite crucible (height: 300 mm, OD: 240 mm) was used as the container for molten salt mixture. It was placed inside the nickel liner. A graphite sleeve (having same height as that of graphite crucible) was placed over the graphite crucible to prevent corrosion of the nickel liner by salt vapors. A perforated graphite sleeve (OD: 150 mm) was placed inside the graphite crucible. The annular space thus created between the graphite crucible and the perforated graphite sleeve was filled with granules of boron carbide which acted as the consumable anode. In addition to this, a 50 mm thick layer of boron carbide granules was placed at the bottom of the graphite crucible.

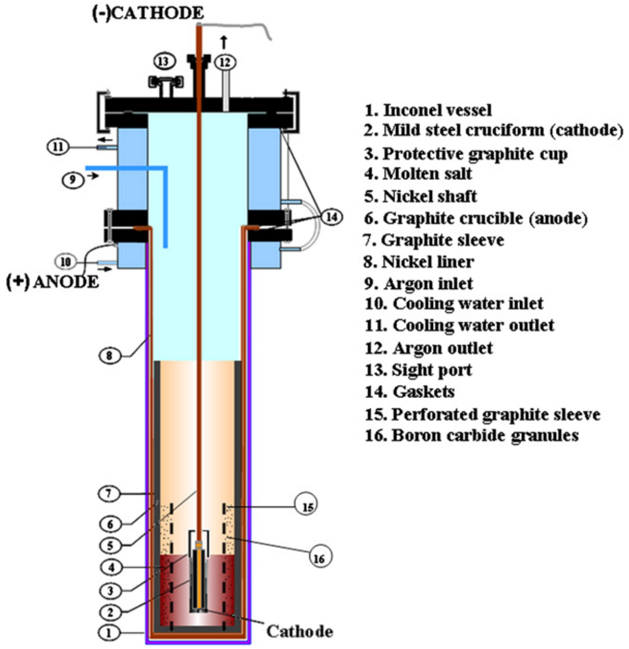

Fig. 1 – Electrolytic cell for the electroextraction of boron from boron carbide granules.

A water-cooled stainless steel collar was placed over the inconel vessel. A water-cooled top flange having provision for an inlet for the mild steel cathode, connection for the positive terminal of the DC power supply, argon inlet and an outlet for gaseous products was placed on the cooling collar. This top flange also had sight and evacuation ports. The circulation of chilled water (296 K) through the collar and flange was essential to maintain the skin temperature of the same below 313 K.

Boron was electroextracted from boron carbide and deposited on a mild steel cathode (cruciform). In order to facilitate its immersion into the molten salt and subsequent withdrawal, it was connected to a long nickel shaft. This shaft was introduced into the retort through a hermetically sealed feed-through provided on the top flange. To start the electrolysis, cathode was lowered and dipped into the molten salt. In order to prevent corrosion at the junction of dissimilar joint between mild steel cathode and nickel shaft, they were connected using a graphite union. The electrolytic cell (portion up to water collar) was placed inside a pit type resistively heated cylindrical furnace. The temperature of this furnace was controlled by a PID (Proportional, Integral and Derivative) temperature controller. The temperature of the upper and lower chambers of the furnace was monitored and displayed on the panel of a temperature controller.