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Processing of enriched elemental boron (^{10}B ~ 65 at. %)

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HIGHLIGHTS

- Purification of enriched electrodeposited boron.
- Water leaching to remove anionic impurities.
- Acid leaching to remove cationic impurities.
- Optimization of processing parameters.
- Flowsheet for the purification of boron.

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ABSTRACT

Procedures were developed for purification and processing of electrodeposited enriched boron powder for control rod application in India's first commercial Proto Type Fast Breeder Reactor (PFBR). Methodology for removal of anionic (F^-, Cl^-, $BF_4{}^-$) and cationic (Fe^{2+}, Fe^{3+}, Ni^{2+}) impurities was developed. Parameters for grinding boron flakes obtained after electrodeposition were optimized to obtain the boron powder having particle size less than 100 μm. The rate of removal of impurities was studied with respect to time and concentration of the reagents used for purification. Process parameters for grinding and removal of impurities were optimized. A flowsheet was proposed which helps in minimizing the purification time and concentration of the reagent used for the effective removal of impurities. The purification methodology developed in this work could produce boron that meets the technical specifications for control rod application in a fast reactor.

1. Introduction

Boron (natural or enriched in ^{10}B isotope) finds numerous applications in nuclear and non-nuclear industries. Its remarkable properties such as low density, high melting point and hardness make it suitable to work in areas requiring high hardness [1]. Boron in the form of boron carbide is used in nuclear reactors, armor plating, nozzles, bearing, dies and cutting tools [2].

Boron carbide, containing enriched elemental boron (^{10}B ~ 65 at. %), is the control rod material in India's first commercial fast breeder reactor. It is being fabricated by the reaction of isotopically enriched boron with carbon at high temperature. The methodology for the production of boron and boron carbide is described elsewhere [3,4]. To establish a technology for large scale production of elemental boron suitable for fabrication of reactor-grade boron carbide, a pilot plant facility was established at the Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, India. In this facility, elemental boron is produced by electrolysis of potassium tetrafluoroborate (KBF_4) dissolved in molten mixture of KCl and KF. The container for the molten salt mixture, which acts as anode, is high density graphite ($\rho = 1.84$ g cc^{-1}) crucible. The mild steel in cruci-form is used as cathode. The electrolysis is carried out at 1073 K. During the electrolysis, elemental boron is deposited on mild steel cathode and chlorine is evolved at the anode. The KBF_4 containing ^{10}B is obtained by dissolving boric acid ($H_3^{10}BO_3$) in hydrofluoric acid followed by precipitation using KOH at pH 7. Boric acid is enriched in ^{10}B isotope by using ion exchange method.

During the electrolysis, electrodeposited boron gets contaminated with impurities. These impurities arise due to the erosion of cathode and anode materials and the corrosive environment of salt and salt vapours which prevail in the electrowinning cell. The complete assay of electrodeposited elemental boron shows the presence of fluoride, chloride, tetrafluoroborate, iron, nickel, carbon and oxygen as impurities [3]. Boron to be used for the synthesis of boron carbide for control rod application in fast reactors must meet

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the stipulated technical specifications. Hence, impurities in boron need to be controlled. Boron carbide can react with metallic species such as iron and nickel to form low melting intermetallic compounds such as metal borides, the melting point of which is lower than that of boron and boron carbide. This makes boron carbide, containing impurities such as Fe, Ni etc. unsuitable for application at high temperatures prevailing in the nuclear reactor. Hence, it is essential to remove all the cationic and anionic impurities to the minimum acceptable level before synthesizing the boron carbide from boron [4].

The literature on the purification of elemental boron is scarce. Istratov et al. [5] have described leaching methods for the purification of silicon used for solar cells. These methods were used by Istratov et al. to remove iron, nickel and oxygen impurities from silicon.

In order to remove surface impurities such as moisture and oxygen (adsorbed moisture, oxygen and B_2O_3) present in the boron powder, Jiang et al. [6] heat treated the pellets of amorphous boron (pressed into pellets using cold isostatic pressing, CIP) at 1223 K for 48 h in flowing Ar-4% hydrogen mixture.

Chen et al. [7] described acid leaching using HCl to purify boron nitride nano tubes. They found hydrochloric acid (HCl) to be effective in leaching out both Fe and Cr from boron nitride nano tubes, BNNT. BNNT samples were leached using HCl solution (3 M) at 363 K for 3 h. The leaching process remarkably reduced the Fe content from 4.5 to <0.1 at. %, and Cr from 0.7 to 0.2 at. %.

Ozarkar et al. [8] used a mixture of acetone and HCl to remove the catalyst particles such as iron and nickel present in single walled carbon nano tubes. They have postulated that the compound produced due to the reaction of acetone and HCl is able to form a complex with the metal catalyst particles that are subsequently removed from the single walled carbon nano tubes.

Koi et al. [9] have described purification of BNNT using HCl, HNO_3 and pyridine. They have used 4 M HCl solution to remove excess iron catalyst and 1 M HNO_3 to remove unreacted boron.

Wang et al. [10] have described removal of iron impurities in single walled carbon nano tubes (SWNT) using an aqueous mixture of H_2O_2 and HCl at 313–343 K. Carbon shell over the catalytic iron particles was destroyed/removed by oxidizing it with H_2O_2 and subsequently iron was removed by HCl. These two reactions were typically carried out sequentially. They could reduce the iron content from 35 wt. % to 5 wt. %.

Chiang et al. [11] have described a low temperature wet Ar/O_2 (or wet air) oxidation step to remove carbon shell over the catalyst particles. This process appears to break the carbon shell and convert the metal particles to an oxide and/or hydroxide. The expansion (densities for Fe and Fe_2O_3 are respectively 7.86 and 5.18 g cm^{-3}) of the metal particle, due to the lower density of the oxide, breaks the carbon shells open and exposes the metal which is removed by HCl.

Although these methods are reported for the removal of iron and nickel impurities in various products, specific methods for the removal of these impurities from electrodeposited boron are not reported so far. Hence, in this study, methods were developed to remove impurities present in electrodeposited boron. The methods developed are based on the requirement that the loss of precious enriched boron during the purification process should be minimum and hence most of the solvents and reagents employed for the purification process are chemically inert towards elemental boron. It is also important that the reaction products of the purification process should not react with boron and should easily be separable from it.

KF, KCl and KBF_4 salts used for the electrodeposition of elemental boron are water soluble. The solubilities of KCl, KF and KBF_4 in water are 56.7 g/100 cc, 92.3 g/100 cc [12] and 4.4 g L^{-1} (293 K) respectively [13]. Electrodeposited boron remains in contact with the molten salt during electrolysis. Molten salt adheres to the electrodeposited boron and remains there even after quenching in water. The property of extensive solubility of these salts in water was exploited for the development of methodology for removing these impurities. As the solubility of these salts in water increases with temperature, the rate of removal of these water soluble impurities from the electrodeposited boron was studied as a function of temperature.

In electrodeposited boron, iron and nickel impurities are present either in the form of their halides (MX_n, where $n = 2–3$) or borides (M_xB_y where x and $y = 1–3$) [3]. It is reported that iron, nickel and their borides react with HCl to form Fe/Ni chlorides which are soluble in water. The product of dissolution reaction viz. chlorides of iron and nickel can easily be removed by leaching with water. The other advantage of using HCl is that boron does not react with hydrochloric acid in aqueous medium as the reaction is kinetically hindered. Other acids such as sulphuric and nitric acids are not suitable for the purification process because of their ability to oxidize boron to form boric oxide and boric acid.

This paper reports the purification methodology established to remove anionic impurities (F^-, Cl^-, BF_4^-) and cationic impurities (iron, nickel and other metallic impurities) present in the electrodeposited elemental boron. The rate of removal of cationic impurities with respect to the concentration of hydrochloric acid and temperature was studied. Purification process was optimized to remove the metallic impurities in minimum time and concentration of hydrochloric acid.

2. Experimental

2.1. Chemicals

Electrodeposited elemental boron was prepared by high temperature molten salt electrolysis method. Analytical reagent grade hydrochloric acid (11.3 N) and acetone were procured from M/s. Rankem Pvt. Ltd., Chennai, India.

2.2. Filteration of quenched electrodeposited elemental boron

Electrodeposited boron was stored in acidified water (pH < 4) after quenching. This slurry was then filtered through G-4 glass frit under suction. Large pieces/flakes of boron were crushed into small pieces using a mallet.

2.3. Water leaching of electrodeposited boron

100 g of the quenched electrodeposited boron powder (wet weight after removing water completely from the deposit) was taken in a polypropylene (PP) beaker. 1 L of distilled water was poured into the beaker. A flange fitted with a heating coil and a stirrer assembly was lowered and fixed on to the beaker. Temperature of water was controlled within ±5 K. The contents of the beaker were stirred at 400 ± 20 rpm using a stirrer with a speed regulator. During the stirring process the flakes of elemental boron got de-agglomerated into fine powder. The salt adhered on to the surface of boron particles got dissolved in water. After half an hour of water leaching, the stirring was stopped, slurry allowed to settle and supernatant water sample taken for chemical analysis. This process was continued for 3 h.

In another set of experiments the supernatant water was removed after taking out the sample and fresh water was charged. The water sample was analyzed for fluoride, chloride and tetrafluoroborate ions. This process was repeated till the concentration of fluoride, chloride and tetrafluoroborate decreased below