Development of Boron-based materials for nuclear applications

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Abstract

Due to high neutron absorption cross section, boron and its compounds find extensive application in the nuclear industry. The former Metallurgy Division and the present Materials Processing Division have developed processes for the production of boron, its compounds and components for application as control/shutoff rods in nuclear reactors, sensors for neutron counting, shapes for neutron shielding etc. Some of the technologies have been transferred to other units, Ministry of Defense and private industries for regular production. This article traces the research and development activities, carried out on boron based neutron absorber materials.

Introduction

One of the basic requirements associated with the development and operation of nuclear reactors is control and containment of neutrons that sustain, and are also produced during fission reaction. Boron is one of the few elements to possess nuclear properties, which warrant its consideration as neutron absorber material. Boron and its compounds boric acid, boron carbide, rare-earth and refractory metal borides find extensive applications in the nuclear industry as neutron sensors, human and instrument shielding against neutrons, nuclear/neutron poison, control/shutoff rods and in nuclear material storage, due to their high neutron absorption cross section. Boron has two principal isotopes, $^{10}$B and $^{11}$B and the effectiveness of boron as neutron absorber is due to the high absorption cross sections of $^{10}$B isotope (thermal neutron absorption cross-section for $^{10}$B and $^{11}$B are 3837 barn and 0.005 barn respectively).

The neutron absorption of natural boron containing ~19% $^{10}$B is sufficiently high (752 barn) in the low neutron energy range to make it an excellent candidate for use in thermal reactors. At higher energies, the cross section of most other elements becomes very small, often abruptly as in the case of cadmium, whereas that of $^{10}$B decreases monotonically with energy and the absorption cross-section is sufficiently high at 1 barn for 1 MeV energy neutrons. Absolute values along the entire energy spectrum are of sufficient magnitudes to make it very effective in the intermediate and fast energy range also. In addition to a high absorption cross section, boron has another advantage over other potential neutron absorber materials. The reaction products, helium and lithium, are formed as stable, non-radioactive isotopes. As they do not emit nuclear radiation, decay heating problems during reactor shutdowns and transfer of depleted control rods are minimal.
The \((n, \alpha)\) reaction
\[ ^7\text{B} (n, \alpha)^4\text{He} + ^3\text{Li} + 2.4 \text{MeV} \]

however leads to release of helium, posing problems in the design of control rods. With fast neutrons \((E > 1.2 \text{MeV})\) there is a secondary reaction as given below
\[ ^7\text{B} (n, \alpha)^4\text{He} + ^1\text{H} \]

Though this reaction has a very less probability compared to \(n, \alpha\) reaction, it has great importance from the viewpoint of reactor waste, since it constitutes one of the major sources of tritium production in the reactor core.

Some of the actual applications of boron and its compounds in Indian nuclear industry are as follows:
Boric acid is used as poison in moderator/coolant of research reactors. Boric acid and boron carbide powder have been used in concrete while constructing reactor buildings. Natural as well as \(^{10}\text{B}\) enriched elemental boron are used as neutron detectors. Boral (boron carbide in aluminium matrix), Bocarsil (boron carbide in silicon rubber), Polyboron (boric acid in polyethylene) are used as neutron shields in reactors, nuclear materials storage and nuclear instrumentation. Boron carbide powder is used as control rod material in BWR (Boiling Water Reactor at Tarapur) and dense pellets of \(^{10}\text{B}\) enriched boron carbide in PFBR (Prototype Fast Breeder Reactor at Kalpakam). TiB\(_2\) and B\(_x\)C\(_x\)-ZrO\(_2\) composites are useful in control and shielding of packaged reactors.

Boron carbide and refractory metal borides in addition have an attractive combination of properties such as low density, high melting point and hardness, chemical inertness and excellent thermal and electrical characteristics making them potential materials for many advanced applications. In the recent past, the Materials Processing Division has been engaged on synthesis, consolidation and composite fabrication of various refractory/rare earth metal borides.

1. Boron powder

Due to its high reactivity, it is extremely difficult to prepare pure boron, which is further complicated by the fact, that the impurities are mainly present within the crystal lattice combined with boron or combined together. Due to its extreme hardness, pulverization of boron introduces impurities from the crushers and causes a superficial oxidation of the grains. In view of these difficulties, the electrolytic process was chosen for the extraction of pure boron where no reductant is used, the deposit is in fine form and the process itself is very selective to obtain boron of high purity. Two different methods 1) namely extraction of boron by fused salt electrowinning from KCl-KF-KBF\(_4\) electrolyte and 2) electroextraction from soluble B\(_2\)C anodes in NaCl-KF-KBF\(_4\) melt were developed.

In the electrowinning of boron, the following overall reaction can be assumed to take place.

\[ 4\text{KBF}_4 + 2\text{KCl} \rightarrow 4\text{B} + 6\text{KF} + 5\text{F}_2 + \text{Cl}_2 \]

Under optimum electrowinning conditions, a current efficiency of about 84% and a boron yield of \(>90\%\) were obtained. The purity of boron was high at \(\text{B} - 96.8\%; \text{Fe} - 0.52\%; \text{SiO}_2 - 1.25\%; \text{C} - 0.26\%; \text{Mg} - 0.62\%; \text{N}_2 + \text{O}_2 - 0.55\%\).

In the other process, B\(_2\)C is used as a soluble anode; the following two reactions take place during electrodeposition at the electrodes.

At the anode: \(\text{B}_2\text{C} \rightarrow x\text{B}^{3+} + \text{B}_x\text{C} + 3\text{ne}^-\)

At the cathode: \(x\text{B}^{3+} + 3\text{ne}^- \rightarrow x\text{B} \text{ where } x = 4\).

Hence, this deposition is conducted at sufficiently low voltage of just above 1 V. In this process, the current efficiency is high at 98% and boron yield about 82% under the optimum conditions. Boron of much higher purity \((\text{B} - 99.8\%; \text{Fe} - 0.06\%; \text{Si} - 0.08\%; \text{C} - 0.06\%; \text{Na} - 0.04\%; \text{N}_2 + \text{O}_2 - 0.03\%\) is obtained. A sketch of the electrolytic cell used for
These studies is shown in Fig. 1 and electro deposit of boron in Fig. 2. For preparation of $^{10}$B enriched boron, electrowinning from KBF$_4$ is the most suitable process.

The technology for production of enriched boron was transferred to IGCAR, Kalpakkam. A few electrolytic cells were operated at IGCAR to produce $^{10}$B enriched boron in kilogram scale. Regular production of enriched boron has recently started at HWB, Manuguru by this method. Technology for production of natural boron from boron carbide was transferred to the Ministry of defense (for use in pyrochemical formulations in a wide range of military explosives) and a plant with a capacity of 200 kg/year of boron was set up at Jabalpur.

Coating of natural and enriched boron on aluminium as well as stainless steel material have been carried out by dip coating method from fine suspension of boron in an organic medium. These coated elements have been used as sensors in neutron counters for measurement of neutron flux in various reactors at different locations.

2. Boron carbide

Boron carbide is usually prepared from its oxide by carbothermic or magnesiothermic reduction in the presence of carbon. Carbothermic reduction route was developed in our laboratory using commercially available boric acid in place of boron trioxide as per the following reaction.

$$4H_3BO_3 + 7C \rightarrow B_4C + 6H_2O + 6CO$$

This process requires a temperature of $>1500^\circ$C to start the formation of boron carbide and is generally carried out at temperatures in the range of 1900°C - 2500°C. A photograph of the furnace used in our laboratory for the production of B$_4$C is shown in Fig. 3.
The boron carbide lumps, as obtained from the furnace, varying in size upto 80-100mm, are further crushed to small pieces in a jaw crusher and then to a fine powder in a pulveriser using multiple hammer heads lined with hardened manganese steel. This powder needs further purification to remove the small amounts of unreacted / partially reduced charge and the contaminants picked during the process of size reduction. The aqueous processing of boron carbide powder to remove the impurities is carried out in polypropylene lined fiber reinforced plastic tanks using hydrochloric acid for the dissolution of impurities and silica lined heaters for heating the solution. Agitation of the solid liquid mixture is effected by passing air under pressure through the bed. The flow sheet for the production of boron carbide powder from boric acid is given in Fig. 4. Graded powder mix filled in stainless steel tubes is used as control rods in TAPS.

3. Boral sheets

Boral is a composite made up of boron carbide and aluminium where aluminium provides the bonding between the particles. This material is fabricated by powder metallurgy route. Powders of boron carbide and aluminium in the required ratio are mixed thoroughly and hot pressed at temperatures close to the melting point of aluminium. The sintered compact is sandwiched between aluminium sheets and picture framed all around, using aluminium sheet. This block is then hot rolled to produce boral sheets of required thickness. Boral sheets with a maximum boron carbide content of 50-60 wt% could be produced with good adhesion. Boral sheets produced in our laboratory were used in the construction of Dhruva reactor for neutron shielding in beam hole inner gate and other locations.

4. Bocarsil sheets

Bocarsil is a composite of silicon rubber, using boron carbide as the filler material. Silicon rubber was specially chosen for its longer shelf life. Fine boron carbide powder of median particle size in the range of 10-20μm is thoroughly mixed with silicon rubber in a sigma kneader. The mixed dough is rolled into sheets of required thickness and then cured at a temperature of 150°C. Some of the properties of these composite sheets (Boral and Bocarsil) are given in Table 1. Bocarsil sheets are used as neutron shield in online fuelling machines of power reactors, for storage of nuclear materials and also in nuclear instrumentation.
5. Poly boron blocks

Poly boron is a composite, made up of boron compound in High Density Polyethylene (HDPE) matrix. For neutron shielding surrounding instruments using various radioactive isotopes, composites with boron content of less than 10% are also useful. The procedure for fabrication of Polyboron shapes consists of mixing of the polymer with the chosen compound of boron, melting the mixture and casting into moulds of requisite shapes. These cast blocks can be easily cut, drilled, worked in lathes etc. to form complex final shapes. Hydrogen content of the polymer also acts as a good moderator for neutrons.

6. Enriched boron carbide

The second generation nuclear reactors in India are proposed to be fuelled by Plutonium containing materials and the energy of neutrons in such reactors is much higher than the present reactor systems. Boron enriched in 10B is the only available suitable material for control rod application in such systems. As the enriched boron material is prohibitively costly, the extraction processes should consider the recovery of boron to a very high extent and also suitable techniques to be developed for in house scrap reclamation, recovery from effluent and reprocessing of used materials. Keeping this in view, investigations have been carried out for the development of suitable processing schemes for the extraction of enriched boron and fabrication of dense pellets of enriched boron carbide to be used as control rod materials.

Boric acid containing enriched boron is the raw material available for extraction of enriched boron. Carbothermic reduction of boric acid or boron trioxide, as they are carried out commercially, gives a very poor yield of 60-65% only in boron terms. Hence a different route for the preparation of enriched boron carbide was adopted. In the new scheme, enriched boric acid is first chemically converted to potassium fluoroborate and extraction of boron from this potassium compound is carried out by fused salt electrolysis. Enriched boron prepared by this method is further converted to its carbide by reacting with carbon.

Synthesis of boron carbide by solid - solid reaction between its elements was studied, which can be represented by the following equation:

\[ 4B + C \rightarrow B_4C \]

Since B₄C is in equilibrium with free carbon and is only boundary between BₙC and BₙC+C (where 4<n<10), synthesis of B₄C without free carbon is extremely difficult. With the view to produce pure B₄C without graphite, experiments were carried out by varying BoronyCarbon ratio from 4.0 (stoichiometric) to 4.6. XRD of the products revealed the presence of B₄C only when B/C ratio is 4.0 but boron rich B₃C and B₂C with higher B/C ratios. In all the experiments, the product in addition to boron carbide contained graphite. These clearly show that

<table>
<thead>
<tr>
<th>Table 1: Properties of Boral and Bocarsil sheets</th>
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<tbody>
<tr>
<td><strong>Boral</strong></td>
</tr>
<tr>
<td>Boron carbide content</td>
</tr>
<tr>
<td>Density</td>
</tr>
<tr>
<td>Thickness</td>
</tr>
<tr>
<td>Absorption cross section, ( \Sigma a )</td>
</tr>
<tr>
<td>Sp.heat</td>
</tr>
<tr>
<td>Working temperature</td>
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<tr>
<td>max.Absorption cross section, ( \Sigma a )</td>
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</tbody>
</table>

ISSUE NO 313 • MAR. - APR. 2010
by simply increasing the boron content of the charge, one cannot avoid the presence of carbon in the product as shown in Table 2.

6.1 Densification

6.1.1 Pressureless sintering

Though boron carbide in powder form is used for control rod application in BWR, Fast breeder reactors need dense boron carbide pellets containing $^{10}$B enriched boron due to high neutron flux. Consolidation of $B_4C$ is complicated due to its high melting point, low self diffusion coefficient and high vapour pressure. Very high sintering temperatures are required for densification due to the presence of predominantly covalent bonds in $B_4C$. Boron carbide particles generally have a thin coating of surface oxide layer which also hinders the densification process. At temperatures $>2000^\circ C$, surface diffusion and evaporation condensation mechanism occur, which result in mass transfer without densification. Densification is achieved only at temperatures $>2000^\circ C$, by grain boundary and volume diffusion mechanisms. At higher temperature exaggerated grain growth also takes place, resulting in poor mechanical properties. One more observation at temperatures $>2150^\circ C$ is volatilization of non-stoichiometric boron carbide, leaving minute carbon behind at the grain boundaries. Densification of boron carbide powder was studied by pressureless sintering with and without additives and also by hot pressing. Particle size of boron carbide powder and the sintering temperature are two key parameters in densification. While pressureless sintering of $B_4C$ powder, though compaction can be done under an inert gas cover, the use of vacuum appears to have beneficial effects. By pressureless sintering up to $2300^\circ C$, a maximum density of $85\% \rho_{th}$ was obtained when the carbide starting particle size was in the range of $0.5-2.0 \mu m$. Compact densities of above $90\% \rho_{th}$ could be achieved by sintering at $2375^\circ C$ using finer particles of median diameter $0.5/0.8 \mu m$. SEM image of pressureless sintered boron carbide is presented in Fig. 5. Hardness of the samples sintered with $ZrO_2$ additive was higher at $30-31.5 \ GPa$, compared to $27 \ GPa$ of $B_4C$ obtained without additive. Variation of hardness with $ZrO_2$ addition and back scattered image of dense $B_4C+ZrO_2$ are presented in Figs. 6 and 7. Both carbon and zirconium are neutron transparent, hence could be used with boron carbide for nuclear applications.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>B/C</th>
<th>Phase present</th>
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<tbody>
<tr>
<td>1</td>
<td>4.0</td>
<td>$B_4C$ and Graphite</td>
</tr>
<tr>
<td>2</td>
<td>4.2</td>
<td>$B_4C$ and Graphite $B_8C$</td>
</tr>
<tr>
<td>3</td>
<td>4.4</td>
<td>$B_4C$ and Graphite $B_8C$</td>
</tr>
<tr>
<td>4</td>
<td>4.6</td>
<td>$B_4C$ and Graphite $B_8C$</td>
</tr>
</tbody>
</table>

Table 2: Effect of B/C ratio in the charge (Temperature: $1850^\circ C$, Duration: 3 hours)

6.1.2 Hot pressing

As the required density of $95\% \rho_{th}$ could not be obtained by pressureless sintering, hot pressing method was chosen for compaction of $^{10}$B enriched boron carbide. Density of pellets obtained by hot pressing method is a function of temperature,
pressure, particle size of powder and length to diameter ratio (L/D) of the pellet. Effect of these factors on densification process was studied. Hot pressing of boron carbide powder was carried out in a graphite resistance heated vacuum furnace using high density graphite dies. Effect of particle size on pellet density was studied by conducting experiments at 1850°C under 35 MPa pressure. It was observed that density (measured using Archimedes principle) improved from 83% to 95% \( \rho_{th} \) with the decrease in particle size from 12.73 \( \mu m \) to 2.98 \( \mu m \). Fig.8 presents the progress of densification with time while hot pressing. A high temperature high vacuum hot press was indigenously developed for this purpose. A photograph of the hot press and the products are shown in Fig.9 and Fig.10. Fractured surface of the high density boron carbide is presented in Fig.11. Density, mechanical (hardness, young’s modulus, shear modulus, bulk modulus, flexural strength, fracture toughness) and physical properties (coefficient of thermal expansion, electrical resistivity, thermal conductivity) of dense (95% TD) boron carbide pellets prepared by the above methods were measured and found to be comparable to the literature values and meets the requirement of intended application. This data is given in Table 3.
7. Summary

Research and development activities carried out in Materials Group, BARC have made a strong base for the production of boron based neutron absorber materials.

1. Technology for the production of natural boron carbide powder has been established and transferred to private industry. M/s. Boron carbide India have been successfully producing and marketing this material for the last 15 years. Major requirements of neutron shielding material for the proposed PFBR at Kalpakkam have been successfully met due to the pioneering work of the former Metallurgy Division.

2. Elemental boron production plant of 200 kg/annum has been set up at Jabalpur to meet the defense requirements.

3. A process for the production of $^{10}$B enriched elemental boron has been established. Based on this, a bench scale facility at IGCAR and a plant by Heavy Water Board at Manuguru have been set up.

4. Method for synthesis and densification of $^{10}$B enriched boron carbide has been established and a trial production run of PFBR control/shutoff rod material has been completed.

5. Process for boron coating has been established and boron coated sensor elements for neutron detectors supplied as and when required.

8. Acknowledgement

The authors gratefully acknowledge the contribution of many of their colleagues who have nurtured this programme from inception to the present stage. Amongst the many who have made significant contribution, special mention may be made of Dr. C.K. Gupta who has admirably led this programme from the front and many others who have implemented such as Late Shri B.R. Mahindra, Dr. T.K. Mukherjee, Dr. D.K. Bose, Dr.M.K.Totlani, Shri.A.K.Grover, Dr. K.U. Nair, Shri C. Narayanan, Shri S.M. Shetty, Smt. T.K. Roy, Shri. Shaikh Baba,

<table>
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<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Density (g/m$^3$)</td>
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<tr>
<td>Hardness (GPa)</td>
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<tr>
<td>Young's Modulus (GPa)</td>
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<tr>
<td>Shear modulus (GPa)</td>
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<tr>
<td>Bulk modulus (GPa)</td>
<td>261</td>
</tr>
<tr>
<td>Flexural Strength at RT (MPa)</td>
<td>363</td>
</tr>
<tr>
<td>Flexural Strength at 600°C (MPa)</td>
<td>271</td>
</tr>
<tr>
<td>Fracture toughness $k_F$ (MPa.m$^{1/2}$)</td>
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<tr>
<td>Coefficient of thermal expansion (ppm/K) @900°C</td>
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</tr>
<tr>
<td>Electrical Resistivity @ RT ( $\mu$cm)</td>
<td>1.27</td>
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<td>Electrical Resistivity @ 600°C ( $\mu$cm)</td>
<td>8.42 x 10$^{-2}$</td>
</tr>
<tr>
<td>Electrical Resistivity @ 1000°C ( $\mu$cm)</td>
<td>6.15 x 10$^{-2}$</td>
</tr>
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</table>
Shri R.D. Bedse and Shri C.D. Singh. The authors also wish to acknowledge the contributions of Shri R.K. Fotedar, Shri. A.L.Pappachan, Shri. Jitendra Sonber, S. Patiram, S.B.Chavan and others from Materials Processing Division, who are presently participating in the programme. The authors also wish to express their sincere gratitude to the Head and staff members of Analytical Chemistry Division and Post Irradiation Examination Division for characterization of these materials.

9. References


