Chapter 2

Literature Survey
LITERATURE SURVEY

Since we are interested in the diffusion of Boron into steels, it will be worthwhile to take a bird's eye view of the various aspects of Boron.

2.1 History and Occurrence:

Elemental Boron, the fifth element in the periodic table was first obtained in 1807 by Sir Humphry Davy by the electrolysis of boric acid. Soon afterwards Joseph Gay-Lussac and Louis Jacques Thenard independently succeeded in isolating boron by heating boric oxide with potassium\(^1\). The name 'Boron' is a portmanteau word derived from borax and carbon because boron is present in borax and it shares some properties with carbon.

Although widespread in nature, boron has been estimated to constitute only 0.001% of the earth's crust and occurs exclusively in combination with oxygen. In addition to boric acid (H\(_3\)BO\(_3\)), which is sometimes found naturally in volcanic steam jets, the most important borate minerals include Borax (Na\(_2\)B\(_4\)O\(_7\).10H\(_2\)O), Boracite (Mg\(_2\)B\(_6\)O\(_9\)Cl\(_2\)), Borocalcite (CaB\(_4\)O\(_7\).4H\(_2\)O), Boron atrocite (Na\(_2\)B\(_4\)O\(_7\).Ca\(_2\)B\(_6\)O\(_{11}\).16H\(_2\)O), Ulexite (CaNaB\(_5\)O\(_9\).8H\(_2\)O), Colemanite (Ca\(_2\)B\(_6\)O\(_{11}\).5H\(_2\)O) and Kernite or Rasorite (Na\(_2\)B\(_4\)O\(_7\).4H\(_2\)O)\(^2\).
2.2 Properties of Boron:

Physical Properties[^2]:

The physical properties of Boron are as listed below.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Atomic Weight.</td>
<td>10.811</td>
</tr>
<tr>
<td>2</td>
<td>Melting Point</td>
<td>2192 °C</td>
</tr>
<tr>
<td>3</td>
<td>Boiling Point</td>
<td>3660 °C</td>
</tr>
<tr>
<td>4</td>
<td>Hardness</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mho's hardness (crystalline boron)</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>Knoop, HK</td>
<td>2110</td>
</tr>
<tr>
<td></td>
<td>Vickers, HV</td>
<td>5000</td>
</tr>
<tr>
<td>5</td>
<td>Density gms./cc</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid (Just Above M.P)</td>
<td>2.08</td>
</tr>
<tr>
<td></td>
<td>Rhombohedral</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>Tetragonal</td>
<td>2.46</td>
</tr>
<tr>
<td></td>
<td>Rhombohedral</td>
<td>2.35</td>
</tr>
<tr>
<td>6</td>
<td>Structural Modifications at Temperature, °C</td>
<td>&lt;800</td>
</tr>
<tr>
<td></td>
<td>Amorphous</td>
<td>800-1100</td>
</tr>
<tr>
<td></td>
<td>Rhombohedral</td>
<td>1100-1300</td>
</tr>
<tr>
<td></td>
<td>Tetragonal</td>
<td>&gt;1300</td>
</tr>
</tbody>
</table>

Chemical Properties[^2]:

Heat of combustion with oxygen = 13.95 kcal/g

Reacts with:

- Fluorine - instantaneously at room temperature
- Chlorine - above 500°C
- Bromine - over 600°C
- Iodine - about 900°C
- Hydrochloric acid - none
Hydrofluoric acid - none
Nitric acid, hot, concentrated - slow
Oxygen - room temp.- slight, 1000°C - rapid
Hydrogen Iodide - explosive
Hydrogen - above 840°C
Nitrogen - bright red heat
Sodium Hydroxide - slow - over 500°C
Boron Nitride - none
Metals-Over 900°C many metals react rapidly, and the reactions are exothermic.

The chemical properties of elemental boron appears to depend on its morphology and particle size. In general, crystalline boron is relatively unreactive, whereas micro-sized, amorphous boron reacts readily and sometimes violently, with a variety of chemical agents. Boron forms borides with metals and metal oxides, boron carbide (B₄C) with carbon, boron nitride (BN) with nitrogen, and boron trihalides such as BI₃, BCl₃ and BBr₃ with halogens. Boron reacts with water at elevated temperatures to give boric acid and other products. It reacts with its oxide (B₂O₃) above 1000°C to give boron monoxide or other boron suboxides.

Applications²:

- Boron in the form of small diameter filaments has been used as reinforcing material for composites.
Boral, a substance made by suspending B\textsubscript{4}C in molten aluminium is used in the manufacture of neutron-absorbing materials for control rods in nuclear reactors and for protective radiation shields.

- Elemental boron is used in electronic devices as a doping agent.
- Boron has been studied as a catalyst for olefin polymerisation and dehydration of alcohols.
- Cubic Boron Nitride is being used as an abrasive to impart superior durability to cut-off wheels.
- Boron has been found to be effective as an element in ultra-high pressure gaskets. In metallurgy, the addition of very small percentages of boron has been found to increase the hardenability of heat-treatable steels.
- Finally, Boron coated or diffused into iron and steel produce extremely hard and wear resistant surface finding innumerable applications in industries.

### 2.3 Metal - Boron Phase Diagrams:

It has been reported that Hannesan\textsuperscript{3} determined the Fe-B diagram upto approximately 8.5\% boron while Tschishewki and Herd\textsuperscript{4} developed it upto 11.5\% boron. Wever and Miller investigated the phase equilibria of iron boron alloys\textsuperscript{5}. Liao P.K. and Spear K.E.\textsuperscript{6} had reported the various phase diagrams between B-Fe (Fig.2.1), B-Cr (Fig.2.2), Olesinski R.W and Abbaschian G.J.\textsuperscript{6} had reported the B-Si phase diagram (Fig.2.3) and Thaddeus B. Massalski has reported the B-C (Fig.2.4) phase diagram\textsuperscript{6}. 

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Some Refinements to Boriding Processes
These phase diagrams indicate the solubility of B in the other elements and they also indicate the formation of various borides. From these phase diagrams the melting points of the various borides can also be determined.

Borides have high melting point that render them of potential value in certain very high temperature applications. These properties include high melting points ranging from 2000 to 3000°C, low volatality, low electrical resistivity, high hardness and high stability. Borides are slightly more stable than carbides at high temperature.

Several of the boride are decomposed by ammonia gas at moderately elevated temperature, to form boron nitride and metal nitride.

2.4 Methods of preparation of borides:

There are a number of general methods which can be used for the preparation of the borides. Those which have been used most extensively are listed below:

1. Carbothermic or aluminothermic reduction of metal oxide-boron oxide mixtures.

2. Reduction of boric oxide-metal oxide mixtures with reducing agents such as Si, Mg, C, B, B₄C, ferrosilicon, ferroboron, etc.

3. Electrolysis of fused salt mixtures containing metal oxide and B₂O₃ in an inert atmosphere.

4. Deposits from the vapour phase (Hydrogen reduction of the mixed chlorides of boron and of the desired metal component (from vapour state) on a heated surface.

Some Refinements to Bonding Processes 2.5
2.5 Diffusion and Solubility of Boron in Iron and Steel:

In 1917, Tshischewsky[^8] found that iron heated in powdered boron or ferroboron acquired a hard, boron-rich case. Later, Campbell and Fay[^9] confirmed this case-hardening effect of boron and reported that boron penetrates steel in much the same manner as carbon does.

Diggers, Irish and Carwile[^10] showed that boron is removed along with carbon in the decarburized zone of steel. The relative ease with which deboronisation may occur was emphasised by Shyne and Morgan[^11], who observed that under carburising condition and under Argon gas shielding, boron may diffuse out of a surface zone without decarburisation of steel, and only in vacuum (10^{-5} mm Hg) deboronisation could be controlled.

Although earlier investigation had established a similarity in the diffusion rates of boron and carbon in austenite, the first systematic investigation of the diffusion of boron in iron and steel was that of Busby, Varga and Wells[^12].

They reported that the diffusion coefficient of boron in austenite can be represented by the equation.

\[ D_{\gamma} = 2 \times 10^{-3} e^{- \frac{21000}{RT}} \]

Within the limits of experimental error, \( D_{\gamma} \) appears to be independent of carbon and boron content (upto 0.43 % and 0.003 % respectively). The solubility of boron in austenite at normal heat treating temperature is less than 0.001 % boron but increases rapidly with temperature above 925 °C. The solubility of boron in alpha iron at 835 °C is about 0.002%, i.e., considerably higher than that in gamma iron at the same temperature. The solubility in both alpha and gamma phases appear to be unaffected by carbon content unless the austenite is saturated with carbon in which case the solubility may be lowered.
Busby and Wells\textsuperscript{[13]} subsequently calculated the diffusion coefficient of boron in alpha iron as:

\[ D_{\text{alpha}} = 10^6 \times e^{-62000/RT} \]

Studying the relative values for the diffusion coefficient of boron in gamma and alpha irons, Busby and Wells concluded that boron forms an interstitial solid solution in alpha iron. The same conclusion was tentatively reached by Mc.Bride, et al.,\textsuperscript{[14]} from theoretical considerations.

Similarly, on examination of the rate of deboronoisation and decarburisation of steel, Diggers, et al.,\textsuperscript{[10]} concluded that boron (like carbon) is interstitial in austenite.

Hayashi and Sugeno\textsuperscript{[15]} suggested that boron in alpha iron can occupy both interstitial and substitutional positions, therefore they modified the D value as,

\[ D_{\text{effective}} = 3 \times 10^6 \exp(-68000/RT) \text{ cm}^2/\text{sec} \]

by considering the mechanism of dissociative diffusion, i.e., \( Q = 284.24 \text{ kJ/mole} \) for boron diffusion in alpha iron.

Walser and Sherby\textsuperscript{[16]} had determined the grain boundary self diffusion activation energy of iron in alpha iron and gamma iron are 170 kJ/mole and 163 kJ/mole respectively, while the lattice diffusion activation energy in alpha iron and gamma iron are 252 kJ/mole and 270 kJ/mole respectively. C.M.Brakman et al\textsuperscript{[17]} had stated that the \( Q_{\text{FeB}} \) is 175 kJ/mole and \( Q_{\text{Fe}_2\text{B}} \) is 157 kJ/mole for bilayer growth. Kunst and Shaaber\textsuperscript{[18]} had stated activation energy for boron diffusion is 176 kJ/mole for treating both the layers as one, during boriding of armco specimens using amorphous boron. According to M-J.Lu\textsuperscript{[19]} \( Q_{\text{FeB}} \) is 82.5 kJ/mole and \( Q_{\text{Fe}_2\text{B}} \) is 105.5 kJ/mole for gas boriding of armco iron, and activation energy for boriding is 132 kJ/mole while both the layers are treated as one (with very little FeB) and boriding being carried out in Ekabor 2 powder. K.Matiasovsky\textsuperscript{[20]} had determined the value of activation energy for boriding for
low carbon and low alloy steels using electrolytic boriding process and reports it as 175.51 kJ/mole in the range of 750-900°C for low C, low alloy steel. V.G.Permyakov\textsuperscript{[21]} reports the activation energy for diffusion of boron in the austenite of commercial pure iron as 20140 cal/ g-atom (84.2 kJ/mole). V.Danek and K.Matiasovsky\textsuperscript{[22]} had reported the activation energy for diffusion of boron in iron as 210 kJ/mole and these authors had also reported that the error in activation energy calculation is due to the inaccuracies in the determination of the thickness of the boride layer, due to its dendritic character. According to R.E.Busby and C.Wells\textsuperscript{[33]} activation energy for diffusion of boron in iron is 260 kJ/mole. N.G.Kaidash, et al.,\textsuperscript{[23]} used 84% B\textsubscript{4}C and 16% Borax for pack boriding and determined the value of Q as 367 kJ/mole for commercial pure iron. G.I.Belyaeva\textsuperscript{[24]} had reported Q = 187 kJ/mole for boriding of high carbon steels. A.Ozsoy and Y.M.Yaman\textsuperscript{[25]} had reported the value of diffusion coefficient (D) as 2.997 x 10\textsuperscript{-9} cm\textsuperscript{2}/Sec for conventional boriding processes on medium carbon steel at 900 °C, using borax based melts. There is thus a wide variation in the activation energy values reported for both boron diffusion as well as the process of boriding.

2.6 Methods of Boriding:

Over the years, a number of workers from almost all over the world have worked on one or other form of boronizing. Principally there are many methods like pack boriding, paste boriding, molten salt boriding with or without electrolysis, gas boriding, vacuum boriding, etc. Among them the following are the most studied processes.

2.6.1 Powder Pack Method:

Powder pack boriding was the earliest method of boriding and it is based on the use of amorphous boron, ferro-boron, iron-boron aluminium alloy,
boron carbide, etc., as the packing medium around the components. The pack is contained in a steel box which is then heated to the boriding temperature in a suitable furnace. To prevent caking and sticking of powders to the component the pack composition must contain inert medium like alumina, chamotte, etc. Finally to accelerate the process ammonium chloride, borax or more popularly potassium tetra fluoborate is added. Ferroboron was the first to be discovered as a boron source for pack boronising\textsuperscript{[8]}, by Tschischewsky in 1917. However, Von Matushca\textsuperscript{[26]} states that the case was a discontinuous and degenerate one. Samsonov and Tseitinap\textsuperscript{[7]} in 1955 adopted a method using amorphous boron with ammonium chloride for four hours at 900\textdegree C, which produced a 70 microns thick case. N.Gorbanov\textsuperscript{[28]} in 1958 had suggested that a reducing hydrogen atmosphere facilitates the formation of thicker cases. Zemskov\textsuperscript{[29]} in 1964 used mixtures containing 84\% B\textsubscript{4}C and 16\% Borax and treated specimens of steel 45 for 6 hours at 950\textdegree C and produced cases of 150 microns thick. Voroshnin and Lyakhovich\textsuperscript{[30]} in 1966 found that the addition of ammonium chloride to boron carbide powder increased the thickness of the case by 15-20\%. V.G. Protsik , et al \textsuperscript{[31]} in 1973 carried out boriding on steels using boron carbide and borax in the ratio 84:16 at 950 \textdegree C for 6 hours. V.F. Loskutov , et al \textsuperscript{[32]} in 1973 had studied the kinetics of boronising and the structure and properties of diffusion layers formed after saturation of Armco iron, low carbon, medium carbon, and high carbon steels, Cast Iron and various cast synthetic alloys. Optimum temperature of treatment for steels had been stated to be 900-950\textdegree C while that for cast iron
had been stated to be 950-1000 °C. It was further established that the carbon content of the steel had little effect on the hardness of the boride layer. Pokhmurskii, et al.,[33] in 1973 had attempted boron-copper plating using a powder mixture of 84 % B₄C and 16 % borax with an addition of 2-8 % Cu powder at 950 °C for 6 hours. The author had stated that due to this treatment, the case depth and transition zone were reduced by a factor of 1.5 to 2, the microhardness decreased from 1800 to 1600 VHN, yield strength decreased by 5-7 kg/mm², elongation increased by 60 %, toughness increased from 4.5 to 5.5 kg-m/cm². Ductility and fatigue strength of steel increased with boriding alone but B+Cu plating did not influence the fatigue strength appreciably. Zakhariev[34] in 1974 boronised iron and steel by heating components at 1000 - 1100°C for 4 hours in contact with metal boride powders. This yielded diffusion layers whose thickness were about 0.16 mm. V.G.Permyakov, et al.,[35] 1974 boronised low and medium carbon steels at 920 °C and complex alloy steels (with Cr, W, Mo etc.) at 1020 °C, using commercial boron carbide. Komatsu, et al.,[36] in 1974 used a mixture of potassium tetra fluoborate and silicon carbide in the ratio 1 : 9 and produced a 90 micron case on a 10 mm. diameter carbon steel rod when heated for 4 hours at 950°C. Moonllkim and Woon Kwan Yeo[37] in 1975 used a mixture of 10-15 % potassium tetra fluoborate with Ferro boron to get a dense and thick case. A.P.Epik[38] in 1977 presented boriding media and boriding procedure used in industry as shown in Table-1. The choice of boride layer depth and corresponding saturation procedures are determined primarily
by the type of boriding material and the purpose of preparation. High quality cases are obtained in low-carbon steels as shown in Table-2. Epik had stated that Sosnovski in 1977 investigated the process of boriding in boron carbide powder by the addition of halide activators. All such activators were found to accelerate the process to some extent but the most effective was those containing fluorine (e.g. KBF₄). Thus on boriding at 1100°C for 3 hours in B₄C with addition of 1-1.5% KBF₄ a layer of 54-57 microns thick could be produced on molybdenum alloy steel and 55-58 microns on niobium alloy steel. At times these results exceed the thickness of boride layers in liquid and vacuum boriding produced at the same temperatures and time ranges. Fishcein, et al.,[39] in 1977 boronised a high chromium steel with a mixture of boron carbide (initially roasted at 200°C for 2 hours) and alumina. When heated with high frequency currents at 1000°C for 20-25 minutes the above mixture yielded 110 microns case. Yu.Alimov[40] in 1977 used commercial boron carbide (95%) with sodium fluoride (5%) to boronise Chrome-Manganese alloy steel and medium carbon steel at 900-920°C for 4 hours in containers with fusible seals. Continuous and acicular FeB crystals up to 75-90 micron case could be obtained by them. M.R.S. John and A.F. Sammels[41] in 1981 had used a pack mixture of 20 % B₄C, 5 % KBF₄ and rest graphite. They state that initially Fe₂B formed and after 2 hours FeB started to form in the case in addition to Fe₂B. D.N.Tsipas and C.Perez-perez[42] in 1982 had borided steels, using a solution of Li₂B₄O₇ in methyl alchocol, sprayed over a specimen maintained at 100°C. This resulted in
a uniform deposit of Li$_2$B$_4$O$_7$. The amount of Li$_2$B$_4$O$_7$ deposit was about 1% of the specimen weight. Subsequently each specimen was covered with B$_4$C and heated in a furnace at 875 °C in an argon atmosphere and in air for times varying between 2 and 48 hours. According to the authors the Li$_2$B$_4$O$_7$ act both as generator of elemental boron and activator. Honda, T, in 1982 had attempted boriding of sintered iron compacts using Ferroboron and sodium carbonate (20%). He had stated that the structure showed presence of both FeB and Fe$_2$B. The rate of growth was inhibited by the addition of alloying elements and the thickness of the boride layer was independent of the density of the sintered compact. Chatynyan, et al., in 1982 had tried boriding using B$_4$C with 1.5% AlF$_3$ at 950°C for 2 hours.
Table-2.1
Saturating media and boriding procedure

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Composition of saturating media</th>
<th>Recommended temperature of saturation (°C)</th>
<th>Time necessary to produce layer of 100-200μm (hrs)</th>
<th>Presence of boride layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Powder of commercial B&lt;sub&gt;4&lt;/sub&gt;C particle size 80-160</td>
<td>900 - 1000</td>
<td>2 - 4</td>
<td>yes yes</td>
</tr>
<tr>
<td>2</td>
<td>The same powder with 1.2% fluoride activator (NaF, KBF&lt;sub&gt;4&lt;/sub&gt;, (NH&lt;sub&gt;4&lt;/sub&gt; Cl etc.)</td>
<td>900 - 1000</td>
<td>2 - 3</td>
<td>yes yes</td>
</tr>
<tr>
<td>3</td>
<td>Borax  (electrolysis at cd 0.2-0.25A/cm&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>900 - 950</td>
<td>1 - 2</td>
<td>yes yes</td>
</tr>
<tr>
<td>4</td>
<td>70-80% borax plus reducing agent (silicon manganese, silicon calcium, ferromanganese, ferro silicon)</td>
<td>950 - 1000</td>
<td>2 - 3</td>
<td>no yes</td>
</tr>
</tbody>
</table>
Table -2.2

Thickness of boride layer at saturation, in different media

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Method and procedure of boriding</th>
<th>Layer thickness in microns</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Armco - Fe</td>
</tr>
<tr>
<td>1</td>
<td>Electrolysis in borax (950°C, 4 Hrs)</td>
<td>250</td>
</tr>
<tr>
<td>2</td>
<td>Liquid composition 70% borax + 30% B₄C (950°C, 4 Hrs)</td>
<td>200</td>
</tr>
<tr>
<td>3</td>
<td>Molten mixture 84% B₄C + 16% borax (950°C, 4 Hrs)</td>
<td>170</td>
</tr>
<tr>
<td>4</td>
<td>liquid composition 79% borax + 15% NaCl + 6% B powder (950°C, 4 Hrs)</td>
<td>240</td>
</tr>
<tr>
<td>5</td>
<td>Pack powder mixture commercial B₄C (950°C, 4 Hrs)</td>
<td>220</td>
</tr>
<tr>
<td>6</td>
<td>Pack mixture 98% B₄C + 1.5% KBF₄ (950°C, 3 Hrs)</td>
<td>230</td>
</tr>
</tbody>
</table>

The structure showed both FeB and Fe₂B. Alloy steels containing Cr and Ni were first plated with iron and then borided at 1000°C for 7 hours. The boride layer showed iron borides and alloy borides particularly chromium.
Md. Mammiuddin[45] in 1982 has discussed the merits and demerits of carburising, carbonitriding, steam oxidation, chromising and boronising on sintered ferrous alloys. In his method, the sintered parts were embedded in boron carbide powder and heated in a reducing atmosphere (cracked ammonia) at 900 °C for 1-3 hours. Carbucchio, et al.,[46] in 1983 state that in several applications, high alloy materials could be advantageously substituted by surface borided low alloy steels, and they had borided low alloy steels at 850 °C in 4 to 15 hours using 20 % B₄C, 2.5 % KBF₄ and rest SiC. J. Rus, et al.,[47] in 1985 had attempted boriding using two different mixtures of powders. (i) B/NaF/Al₂O₃ mixture and (ii) B₄C/SiC/KBF₄ on 304 stainless steels and found that the second mixture produced a deeper and more uniform case than the first mixture. R. Chatterjee-Fisher and O. Schaaber[48] in 1986 carried out boriding treatment to increase the abrasion resistance of surface on steels and other metals. Steels were borided at 900 °C for 4.5 hours in a boriding powder mix with 2.5 % B₄C. According to them, reducing B₄C from 5 to 2.5 % produced a layer free from FeB and containing only Fe₂B. With higher proportions B₄C (7.5 and 10%), the treatment produced a very rough surface. When the layer contained both FeB and Fe₂B, cracks appear at the interface between these two boride layers on cooling. Further, with high alloy content, FeB formation is more pronounced. Also, with more B₄C in the mixture, the surface roughness is more. Boriding is always associated with an increase in size. During the boriding of C45 steel, an increase of dimension increase of 8 % on each side, was observed.
J. Subramanyam in 1986 using the pack cementation process on mild steel, observed both FeB, Fe₂B phases. In this process the source of boron was B₄C and the activator was ammonium bifluoride or KBF₄ or NaF). Boron carbide and one of the activator were mixed thoroughly and the specimen was packed with the powder mixture in a stainless steel retort. Good boride layers were obtained with 1-2% activator, at temperatures in the range 900-1000°C. A.D. Nachinkov also attempted diffusion coatings on several alloy steels. These steels were borided from a powder mixture, with a composition of 80 % B₄C and 20 % Na₂CO₃, at 950 °C for 6 hours to produce about 100 microns case. V.T.Bondar in 1987 has used a powder mixture containing B₄C and 2 % teflon which when coated on hard alloy cutting tools (at 1100 °C for 5-6 hours) reduced the wear of the tools by half. Badini, et al., 1987 suggests a mixture of B₄C 20-30 %, KBF₄ 5 % and SiC 65-75 % for boriding of ferrous alloys. K.J.L. Iyer, et al., in 1989 had reported the use of powders (98 % FeB + 2 % Na₂CO₃) for pack boriding low alloy steel samples for durations ranging from 4 hours to 12 hours. Ni-Si-Cr steels were boronised by A.V.Reddy in 1992 using 92 % SiC, 5 % B₄C and 3% KBF₄. The boronising behaviour was similar to that of many low alloy steels and the interface layer was a boride layer of type Fe₃(SiB). Goeuriot, et al., 1987 suggest the mechanism of boriding using boron carbide and KBF₄. The KBF₄ breaks down at temperature to yield BF₃, assumed to be the actual activator - which acts as a Lewis acid having a vacant orbital able to accept an electron pair. A diluent or moderator in the form of...
metal oxide is thus required in the pack composition to provide the electron pair e.g., Al₂O₃, B₂O₃, → MgO, SiO₂, etc.

The reaction then proceeds with the formation of complex co-ordinates, thus:

\[
\text{BF}_3 + \text{MO} \leftrightarrow (\text{BOF})_3 + \text{MF} \\
(\text{BOF})_3 \leftrightarrow 3 \text{BOF}
\]

3 BOF or (BOF)₃ posses on their oxygen atoms, pair which can be readily accepted by the molecules of BF₃. This allows just sufficient quantities of BF₃ to be released during the activation of B₄C. Once the boron carbide is activated, the boron travels via a gas phase to the component surface where it is reduced to atomic boron and diffuses into the metal. The above process has been commercialised under the name "Borudif".

The kinetics of the boronising process has been established in more detail in a recent study by G. Wahl [56]. The reactions were calculated from thermodynamic data for 1200°C and selected from 40 possible reactions, as the most probable reactions. Here SiC was used as the moderator and an interesting conclusion was that oxygen was a necessary part of the reaction, an issue which had been in contention for some time.

The above charge mixture is based on "EKABOR", the trade name for a commercial boronising powder, a type of which has also been utilised as the main ingredient in this project. The actual reactions are claimed to be as follows:
In conclusion, most of the successful pack boriding methods are based on boron carbide which is very expensive. Ferroboron has been rarely used with very little success. According to A.G. Von Matuschka\cite{26} ferroboron gives a degenerate case of borides. Therefore, the investigation is focussed on the use of ferroboron for pack boriding, since it is less expensive and easily available.

2.6.2 Paste Method:

The paste method is a more specialised process than the powder pack process as it combines the advantages of the latter with the additional ability to boronise components in-situ or in only selected portions. The method involves heating the component with a paste which is generally made up of boron carbide and flux additions like ammonium chloride, cryolite etc.

V.I. Prosvirin and L.V. Gerasimov\cite{57} in 1973 had attempted Boroaluminising using pastes. The paste was prepared from amorphous boron and aluminium powder in amounts ranging from 2.5 to 10% of the weight of boron and a binder made up of a 2% aqueous solution of silicate cement. The samples were ground and degreased, a layer of paste of 2 mm thick was applied. It was dried in air and then in a desiccator at 100°C for 1.5 to 2 hours. The
stacks were placed in a sealed container at a distance of 5-10 mm from each other with a covering of Al₂O₃ or fire clay containing small amounts of Al or Mg powder. The container was placed in an electric shaft furnace and heated to 800°C. Boroaluminising of carbon and stainless steels with pastes containing 2-10% aluminium, produces high-quality diffusion coatings with a high hardness, heat resistance, and resistance to abrasion. Boronising of steel a low carbon steel (St. 3) produces a more ductile diffusion coating than simple boriding. Aliev A, A [58] in 1978 tried boriding of steel 20 and U8. The steels were first vacuum annealed and then borided using pastes containing (1) 70% B₄C and 30% Na₃AlF₆ and (2) 60% B₄C and 40% Na₃AlF₆. The binder was prepared using nitrocellulose in a mixture of butyl acetate and acetone. They reported that the rate of growth of boride layer was greater with paste (1) than paste (2) and that the boronised layer had an acicular structure and the wear resistance was twice that of conventionally treated steel samples. Belski [59] tried Case hardening of stamping dies using B₄C 60%, B₂O₃ 5%, NaF 5% and iron oxide scale 30%. The boronised layer consisted of both FeB and Fe₂B in the various die steels. V.A.Konopel'skii and V.D. Dubko [60] in 1987 attempted diffusion impregnation of 5 KhNM and U8 steels by boron using pastes containing 55% B₄C and 45% cryolite. A 20% solution of sodium silicate in water was used as a binder. The minimum thickness of the paste was found to be 1.5 mm. The service life of the coated plungers used for hot deformation made from an alloy steel increased by 1.5 to 4 times as a result of boriding from pastes. Volkov, et al., [61] in 1987 studied boronising from pastes under fast electric heating rates. Flat samples of Armco iron and U8 annealed in vacuum were boronised in paste compositions of boron carbide with cryolite and borax. The addition of cryolite and boron yielded layer growth rates of 1.3 to 4 times more than that in impregnation by powders under similar conditions. It was found that the reason for the acceleration of the process was the fact that in the case of internal source of heating, a liquid interlayer was formed on the surface of the sample at the boronising temperature which was retained
throughout the impregnation period ensuring quicker transport of boron atoms to the substrate. Optimum compositions for multi component coatings for wear resistance to hydroabrasive wear were also determined. An interesting technique for the formation of multi component coatings investigated by Zemskov, et al.,[62] in 1987 involved the use of plasters containing boron and other alloys. The plaster consisted of pure alloy powders (3-5 micron size) and amorphous or crystalline boron with a solution of adhesive BF-6 in acetone, hydrolysed ethylsilicate, liquid glass, etc., to serve as binders. Samples of steel were dipped or spray dried with the plaster and dried to form 0.5-1.0 mm. thick coat. A St 40 Kh thus plastered with a B-Cr-Ti composition when diffusion annealed at 1080°C gave a boride layer of Fe2B alloyed with Cr and Ti and of depth 150 microns. They had reported that plungers of distributors of diesel engines treated by the above method showed 3-5 times greater wear resistance than conventionally boronised ones and 10-15 times that of unhardened plungers. Galibois. A., et al.,[63] had reported that paste boriding is not so effective as pack boriding since it very often leads to cracking in the case due to the formation of FeB phase.

It was decided to leave out paste/plaster boriding in this work, and hence the study was restricted to pack, molten salt, and electrolytic boriding only.

2.6.3 Fused Salt Boronizing - Electroless:

This method is widely practised in Eastern Europe former, USSR or C.I.S, and Japan. The method is simple, but it has the disadvantage of regular maintenance and replenishment of the bath composition, as well as that of cleaning the components after treatment. Further, the reaction are usually based on reduction of the boron components and low bath viscosity, both of which require high temperature (900-950°C).

Significant Investigations:
Morozava in 1954 used a bath mix containing $\text{BaCl}_2$ - 45%, $\text{NaCl}$ - 45% and $\text{B}_4\text{C}$ - 10% which yielded a 250 micron case on C 45, at 930°C for 5 hours. Orning in 1955 attempted an experimental bath containing 5% $\text{B}_4\text{C}$, 95% $\text{NaCl}$ and $\text{NaBF}_4$, but satisfactory results were not obtained by him. Natchuki in 1961 used ultrasonic waves to stir the bath and found that ultrasonic waves intensify the molten salt boriding process. N.G. Kaidash in 1965 investigated various molten baths for molten salt boriding and the best molten bath composition was found to be 16% Borax with 84% Boron Carbide. Treatment of steel 45 in such a bath at 1000°C for 6 hours produced 141 micron thick boride layer. However, it is more appropriate to call this pack boriding than fused salt boriding. The use of elemental boron (upto 12%) in a bath containing borates ($\text{Na}_2\text{B}_4\text{O}_7$, $\text{K}_2\text{B}_4\text{O}_7$, $\text{Li}_2\text{B}_4\text{O}_7$), operated between 815-1175°C was found to accelerate the boriding process by Hill. A bath composition similar to the one mentioned above involved the use of a metal, whose free energy of oxidation is higher than that of boron such as Ca, Be, Ce, Li, Mg, Al, Ti which reduced borates to elementary boron. L.S. Lyakhovich and S.S. Brgilevkaya in 1968 borided steel 45 using borax and boron carbide in the ratio 60:40 for 4 hours at 960-970°C and they were able to get 0.18 to 0.20 mm. case depth. They state that borided plain carbon steel shows better wear resistance than high alloyed steels.

The wear properties of boronised stainless steel (304 and 430) was studied by measurement of the case depth and the microhardness, and correlating them with wear test data. Liquid boronizing was carried out by Kwon and Hahn in 1978 in molten borax containing various proportions of SiC. The case depth and case hardness were found to increase with increasing SiC content, boronising time and temperature. However, beyond 40% SiC the increase in case depth was very negligible, also, the melt started deteriorating fast. The depth of the boronised case in stainless steel was about half that of low-C steel, boronized under the same conditions. The borided case depth on 430 stainless steel was 20-30% greater than that on 304 stainless steel.
wear resistance of the boronised specimen was found to increase approx. 100 times over that of the non boronized specimen. The optimum conditions for the best wear resistance were (i) bath composition containing 25-30 % SiC and the rest Na₂B₄O₇, (ii) boronising temperature of 950°C (approx) and boronising time 6 hours (approx). Kochiro Koyama in 1981 found that 75% KBF₄ and 25% KF could be used to boronise nickel at temperatures below 670 °C. Kato et al. attempted boronizing of steel bar in air by reducing fused borax with molten aluminium on the surface of the steel bar. On varying the treating conditions, the composition of the borided layer varied from one of pure Fe₂B alone to a mixture FeB and Fe₂B. Even at temperature as low as 800 °C, a sound boride layer was obtained with a Vickers hardness value of 1800 - 2000 VHN on the FeB layer. As the reduction of fused borax with the molten aluminium was fast enough to supply boron to the surface of steel, the rate of growth of the boride layer was determined only by the diffusion of boron in steel. L.S.Lyakhovich in 1984 employed a number of boriding melts:

(i) 80% borax + 20% CaSi
(ii) 70% borax + 20% B₄C + 10% SiC
(iii) 80% borax + 20% Fe Mn of Mn 5 grade
(iv) 90% borax + 10% FeSi of Si 95 grade, and
(v) 70% borax + 30% SiC

Out of these, only the first three melts were reported to give encouraging results. Lyakhovich also stated that boriding after electroplating helps to boride those alloys which are otherwise difficult to boride (e.g., Copper and its alloys). However, such treatments are mostly inadvisable for increasing the wear resistance of steels.

Belyaeva found that addition of oxides of heavy metals (PbO, BiO₃), phosphates (NaPO₄), sulphates (Na₂SO₄), alkalis (NaOH) and chlorides (NaCl) to borax allowed lower processing temperatures (550 - 700 °C) by reducing the melting point of borax. Boriding steel RIS discs, used for cutting glass streamers from Pyrex, increased their life by 4-5 times. Belyaeva, G. I. in Some Refinements to Boriding Processes 2.22
molten salts containing boron powder of composition 73-79 wt % Borax, 15-20 % NaCl and 6 - 7% boron powder. Additions of boron powder were found to accelerate the process to a greater degree than boron carbide. Also, it reduced the solid waste in the bath and thus restricted the tendency to form a slurry. Boriding rate was two times higher with this mix than with than borax melt containing 40% boron carbide. Using the above setup the kinetics of liquid phase boronising was studied in the temperature range of 800-950 °C. At each temperature the variation in thickness of the borided coating with time showed a parabolic relationship corresponding to the equation:

\[ X^2 = 1.55 \exp\left(- \frac{Q}{RT}\right) t, \text{ cm}^2 \]

where \( X = \) layer thickness in cm,
\( Q = \) activation energy (44000 Cal)
\( R = \) gas constant
\( T = \) process temperature (k)
\( t = \) process duration, in sec

It was found that boronising 46 Nos. drawing dies of U8 (high carbon spring) steel increased their wear resistance by 6-30 times. Boriding of steel for 2-6 hours was done at 850-1000°C. The boriding rate depended on the boron activity in the powder addition and increased with the transition from the CaB₆, B₄C powders to B powder. Use of the reducing SiC decreased the flowability of the melts and retarded boriding. Wear resistance of high carbon steel parts (with borided layer thickness of 60-70 µm) was 4-9 times higher than unborided specimens, in tests with Fe₂O₃ powder. When dies made of steel high carbon steels boronized to 100 microns depth, was used in place of alloy steels the service life increased by two times. Molten salt boronizing in melts of borax, NaCl or NaF and B powder is suitable for parts working under the conditions of abrasive wear.

Matiasovsky\(^{[20]}\) states that (although higher rate of boriding is possible in the electrolytic process) thermochemical boriding in molten salts mixtures or powders are often preferred to electrolytic boriding because it is technologically
simpler and can coat intricate surfaces uniformly. The rate of growth of borides and phase composition in thermochemical boriding can be controlled by the activity of boron at the substrate surface. By decreasing the activity of boron, the formation of the FeB phase can be partially or fully suppressed. When high alloy steels are borided, the formation of the borided layer is accompanied by the redistribution of the alloying elements, apparently with the formation a "diffusion barrier". This affects both the rate of growth and phase composition. To overcome this problem, it was recommended that iron may be coated on these steels and boriding can be carried out.

Wang, et al., [174] in 1992 attempted to strengthen cold-upsetting moulds by boriding and sulphurising treatment. The life of moulds made of cemented carbide greatly increased when it was borided and sulphurised. The composition of the boriding media was 65% Na2B4O7 + 20% SiC + 10% NaCl +3% Na2CO3 + 2 % B4C. The boriding temperature was 950°C for 5 to 6 hours. The surface hardness is 2100-2200 HV. The composition of the sulphurising media was 1.5-2% S + (45-50)% NaOH + H2O. The surface reaction can be represented by is Fe2B + S +O2 = FeS + B2O3. The process includes sulphurising at 130-140°C for 3-5 hrs, air drying & hot oil soaking (120-130°C) for 30 min. The sulphurised surface has better anti-friction and anti-seizure properties. The borided treatment can prolong the life of the mould five fold, and the subsequent sulphurised process could add another 10 %.

2.6.4 Fused Salt Boronizing - Electrolytic Method:

This method is based on the cathodic treatment of articles in molten baths containing borax or other boron bearing materials. More recent metalliding baths use molten salts containing fluorides of lithium, sodium, potassium, along with boron for the electrodeposition of boron on to the metal.
Significant Investigations:

A. Govorov [75] in 1944 found that optimum current density for electrolytic boronising was 0.15 - 0.25 A/cm². Taran and Skvgorova [76] in 1957, boronised St 35 in molten borax bath to produce 220 micron thick case in 4 hours at 950°C (current density 0.20 - 0.25 A/cm²). A current density of 0.75 A/cm² was required to boronise St 40 to the same depth under similar conditions.

For economic and process reasons, a bath composition of 40% borax and 60% anhydrous boric acid was attempted and proved successful. In such a bath, a 320 micron case was obtained on 0.5% C steel after 4 hour, at 950°C (0.2 - 0.25 A/cm²) [77]. Commercial grade borax with graphite electrodes as anodes was used to carry out electrolytic boronising by Mylnikov [78] in 1957. The bath was heated with gas and hammer forging dies made of material 5 KhNV and OHkN3M were boronised at 920 - 950°C for 3 hours with a current density of 0.3 - 0.5 A/cm². After subjecting the dies to different heat treatments, their life in operation was shown to have increased in most cases. Ultrasonic Vibration during boronising reduced boronising time by 25-30% but did not improve adherence of boride case to base material [79]. According to Galushko, et al., [80], when Na₂CO₃ is added to borax at high temperature Na₂CO₃ dissociate to Na₂O and CO₂ leading to a change in ratio between Na and B oxides, they suggest that as much as 30% Na₂CO₃ can be added to the bath to decrease the viscosity. They measured the viscosity by capillary rise. Boriding temperatures were 800 - 820°C. Sorkin, L.M. [81] states that in order to remove defects in boriding, the various impurities must be removed from borax, crucible must be first boronised for 10 to 15 hours, and the graphite (anode) must be completely immersed in borax 15-20 min before starting the process. The distance between the anode and cathode should be at least 15-20 mm. One of the drawbacks of electrolytic boronising in molten borax is the short work life of the crucibles. After studying the deterioration on one such crucibles, Shalya and Bordyug [82] (1968) suggested the use of 18Cr 8Ni steel or 25Cr. 

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2.25
20 Ni steels with addition of Ti or Mo to the crucible material. They also recommended the use of similar welding electrodes as those of the parent material in fabrication. Also they advised the adoption of cathodic protection, with a protective current of 0.7 A/dm². Switching on and off the protective current, during warm up and cool down periods respectively, allowed for continuous protection. Adopting the above practices increases the reliable life of the crucibles up to 4000 hours. L.M. Sorkin [83] in 1969 conducted boriding of forging dies using molten borax at 0.15 A/cm² for 3.5 hours at 920-950°C. Higher boriding time leads to FeB formation, which reduces the wear. At temperature greater than 1000°C, boriding leads to formation of complex eutectics and pores and both of these impair the properties of the boride layer. At elevated temperature, the acicular borides are also smoothed out, as a result the adherence of the boride layer to the base metal is reduced. The elements Mn, Ni, Cr, Mo and W increase the amount of FeB in the boride layer while increase in carbon content reduces the proportion of FeB, thus increasing the wear resistance in use.

H.C. Fiedler and W.J. Hayes [84] electrochemically borided AISI H11, H12 and H13 steels at 900°C. The sample was cathode and elemental boron in copper basket was anode. The bath was 20 mole % KF, 30 mole % NaF and 50 mole % LiF. 0.2 mole % BF₃ was dissolved in this salt. An atmosphere of 90% N₂ and 10% H₂ was used to cover the salt at all times. The samples were hardened at 1000°C and tempered at 540°C. A soft layer (450 VHN) formed between the case and core which contained excess Si. It is advisable to avoid the soft layer because it can lead to spalling.

Fiedler and Sieraski [85] in 1971 boronised tool steels in a specially designed electrolytic bath with molten salts containing fluorides. The part to be treated was made the cathode, while pieces of elemental boron in a copper basket constituted the anode. The bath was covered by inert gas to prevent contamination. It was possible to borided components at temperatures as low as 600°C. The normal range being 800-900°C, with a current density of 0.5 - 2.5
A/dm², 0.5-2.0 mils thick coating could be obtained. Falex tester was used to establish the superiority in wear behaviour of boronised steel compared to those of heat treated, hard-chrome plated and nitrided steels. Applying the above coating to AISI 4340 steel mandrel (against previously used AISI D4 steel) and for dies for copper parts made of AISI A2 steel gave productivity increase of 5 times. More remarkably, replacing AISI D2 deep drawing dies with boronised AISI A6 tool steel allowed the production of 34 times the number of components that could be made using uncoated dies, before polishing was necessary. The life of the dies themselves was atleast doubled.

G.I.Yukin⁶⁶ gives the generally accepted mechanism in electrolytic boronising in borax based baths as follows:

Partial thermal dissociation: \[ \text{Na}_2\text{B}_4\text{O}_7 \rightarrow \text{Na}_2\text{O} + 2\text{B}_2\text{O}_3 \] (in fused state)

Electrolytic dissociation: \[ \text{Na}_2\text{B}_4\text{O}_7 \rightarrow \text{Na}^+ + \text{B}_2\text{O}_7^{2-} \]

Deposition of Na on cathode: \[ \text{Na}^+ + e^- \rightarrow \text{Na} \]

Discharge of anions on the anode and evolution of O₂: \[ \text{B}_2\text{O}_7^{2-} \rightarrow 2\text{B}_2\text{O}_3 + 2e^- + \frac{1}{2} \text{O}_2 \]

Reduction of Boron with Na on cathode yielding high boronising: \[ 6\text{Na} + \text{B}_2\text{O}_3 \rightarrow 2\text{B} + 3\text{Na}_2\text{O} \]

Oxidation of graphite anode: \[ \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \]

Electrolytic boronising has also been carried out by Örming and Shaaber⁶⁵ in a bath of 25% NaCl and 75% Borax. Han.H, and Chun, J.S⁷¹ investigated the effect of various activators such as \( \text{Na}_2\text{CO}_3, \text{B}_4\text{C}, \text{NaCl} \) and \( \text{NaOH} \) (in molten borax) on the electroboronising of low-carbon steel (1015) at 800°C. The effect of superimposed a.c on the penetration depth of B was also investigated. Their experiments showed that \( \text{Na}_2\text{CO}_3 \) was the most effective activator, followed by \( \text{B}_4\text{C} \), and \( \text{NaCl} \). The most economic composition of activators was identified as 10 wt % \( \text{Na}_2\text{CO}_3 \), 10 wt % \( \text{B}_4\text{C} \), 20 wt % \( \text{NaCl} \) and...
the rest borax. Applying superimposed a.c resulted in a considerable advantage. This was because cathodic polarization, affected by frequency and amplitude, was decreased resulting in increase in effective current densities. The boronized layer was more uniform and two times thicker than that formed with conventional electroboronizing methods.

Ikuta and Taguchi\cite{88} electrolytically boronised steel bars of St 45 in a fused borax bath containing 30% SiC at 850 °C. By adding SiC to the borax bath, the electrolyzing current was stabilized and the post-treatment was also improved. With intermittent electrolysis, the boronized layer was sound and thick relative to the one obtained by continuous electrolysis. But, the current efficiency decreased with increasing treatment time. The boronized case was composed of an outer FeB layer and an inner Fe2B layer. The Vickers hardness values of FeB was found to be about 2000, and Fe2B 1300-1500, respectively.

L.S.Lyakhovich\cite{23} claimed that (i) refining of borax is very important during electrolytic boriding, (ii) impurities of about 3 % Iron oxide or Nickel oxide in borax can completely prevent surface alloying of steel with boron, (iii) Chromium oxide has less harmful effect, but also reduces the case depth and (iv) the cathodic current density must not be less than 0.3 A/cm².

S.Ya.Pasechnik, et al.,\cite{89} borided steels in fused salts baths containing borax and upto 40% of boric acid anhydride. According to them, addition of upto 7.5% NaCl to the electrolyte accelerated the boron dissolution in steels. NaF had a similar effect and the amount advised was 20% NaF. Boriding of plain C steels was carried out at 850-900°C. Lower temperatures (850°C) should be used, for higher carbon steels. The current density was 0.1 - 0.2 A/cm² and the time 2 hours. The effect of ultrasonic waves on the basic parameters of electrolytic boriding of medium carbon steel and Armco iron had been investigated by Shcherbakok\cite{90}, et al., Studies were carried out with ultrasonic waves impinging directly on the concentrator or through the molten salt. For specimens in the former setup, increase in the amplitude of vibration increased the layer thickness for short holding times. Thickest layers
were obtained for a hold time of 60 minutes, and small amplitude, when the vibrations were passed directly through the molten salt, the thickness of the boride layer on armco iron was double that without ultrasonic vibration.

Investigations were carried out on samples made from low carbon, medium carbon and high carbon steels by A.V. Byakhova, et al., [91]. For electrolytic boriding, a melt of technical grade borax was used. Borax was melted with the help of the arc between two electrodes and later on, for accelerating the process, the third electrode was introduced into the crucible.

The use of the rotating cathode and two anodes made it possible to obtain uniform diffusion layer over the entire area of the samples irrespective of their shape. Diffusion impregnation of samples was carried out in the temperature range of 850 - 1100°C for 1 to 6 hours. It was established that the coating thickness should not exceed 150 microns for carbon steels and 100 microns for alloy steels, in order to ensure good performance. Such coatings could be obtained at 900-950°C, in 3-4 hours, at a current density of 0.2 A/cm². After boriding the samples were cooled in air, reheated to 780 - 800°C and isothermally quenched to 220-200°C where they were kept for 2 hours. The life of components increased by 3-5 times.

Electrolytic processes occurring during the electrolysis of borax melt were investigated by Afanas'ev and Paschnik [92]. They correlated them to electrode potentials. Based on the physicochemical investigations of the cathode deposit, and also on thermodynamic analysis, the authors had represented the electrolysis of borax by a number of stepwise reactions, as given below:

\[
\begin{align*}
\text{Na}_2\text{B}_4\text{O}_7 &= \text{NaBO}_2 + \text{Na} + 3\text{B} + 2.5\text{O}_2 \quad ; \quad E^\circ_{1173} = 1.86\text{V} \\
\text{Na}_2\text{B}_4\text{O}_7 &= 2\text{Na} + 4\text{B} + 3.5\text{O}_2 \quad ; \quad E^\circ_{1173} = 1.89\text{V} \\
\text{Na}_2\text{B}_4\text{O}_7 &= \text{Na}_2\text{O} + 4\text{B} + 3\text{O}_2 \quad ; \quad E^\circ_{1173} = 1.98\text{V} \\
\text{Na}_2\text{B}_4\text{O}_7 &= 2\text{B}_2\text{O}_3 + 2\text{Na} + 0.5\text{O}_2 \quad ; \quad E^\circ_{1173} = 3.08\text{V} \\
\text{Na}_2\text{B}_4\text{O}_7 &= 2\text{NaBO}_2 + 2\text{B} + 1.5\text{O}_2 \quad ; \quad E^\circ_{1173} = 1.78\text{V}
\end{align*}
\]

The values of reversible emf of the reactions were calculated thermodynamically using the equation \( G^\circ_T = nFE \). According to R.L Muller [79],

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Boron glass is chemically inhomogeneous on the microscopic scale, containing associated polar groups of borates, known as structural units (S.U). If the concentration of polar S.U is low, polar S.U are blocked by nonpolar S.U. In order to minimise energy used up in the process of electrolysis, it is necessary to reduce the boriding force in the polar complex. For this it is necessary to decrease the number of nonpolar S.U which block the polar S.U. Skomorokhov[79] claimed that addition of NaF or Na₂O in the molten borax or B₂O₃ led to a reduction of nonpolar S.U (BO₃⁻ /₂) and thus reduced energy used up in the process of electrolysis. The author had used as much as 30% NaF. Addition of NaF decreased the voltage across the electrolyte bath and also decreased the temperature of the process of electrolysis (700-750°C). When Boriding was conducted at a temperature of 850 °C, with cathode C.D - 0.15 A / cm², for 1.5 to 2 hours, boride layer with a thickness in the range 60 -70 μm formed. Lateral ultrasonic vibrations, (frequency 18-22 KHz, amplitude 15-20 mm in air) directed along the bonds in structures of the polar groups Na⁺ B⁻ O₄⁻ /₂ did not increase the degree of electrolytic dissociation, but they greatly affected the strengthening process of the metal and increased the layer depth by 20%.

V.V.Bakhmat [93] state that proper selection of the schedule for the final heat treatment is one of the factors which has a bearing on the effectiveness of thermochemical strengthening of the dies. Tools made of 5 KhNM, 38 KhS and U 8 steel were electrolytically borided in a bath containing 40% borax + 50% B₂O₃ (boric anhydride) + 10% NaCl at 950 10°C, C.D - 0.15 - 0.2 A/cm² and t = 2-3 hours. Dies removed from crucible were cooled to 70 - 100°C in air before washing them in hot water. After boriding, austempering ensures a higher plasticity than when quenching is carried out in oil. Horic, H, [94], et al., investigated the boronising treatment of spheroidal graphite cast iron, by means of electrolysis in a molten salt mainly consisting of B₂ O₃, K₂O and Na₂O at different ratios and temperatures and over different periods of time. The microhardness values and the thickness of boride layers were measured and the
distributions of B, Si and C on the surface of specimens were examined by an X-ray microanalyser. Microscopic examination and the results of X-ray microanalysis showed that the boride layer consisted of two layers; an outer FeB layer and an inner Fe₂B layer. The microhardness of these boride layers ranged from approximately HVN 1500 to 1800. The thickness of the boride layer increased in proportion to the square root of treatment time, at constant temperatures. The activation energy for diffusion of boron in the specimen was 19.5 kcal /mol, as obtained from the slope of Arrhenius plots. A Si-rich layer was formed in a region outside the boride layer in specimens after boronising. Moreover, graphite formation was observed in the Si-rich layer in specimens boronised at austenitising temperatures for a prolonged time. Graphite formation in the Si-rich layer can be considered to be the consequence of the precipitation of carbon, during the cooling process, after boronising. Boron diffused from spheroidal graphite to the austenite matrix at the boronising temperature. Large amounts of graphite formed in the Si-rich layer resulted in a crack passing through these graphite particles.

Boride coatings with hardness upto 1800 VHN were prepared by K.A.Khor [95] on AISI 1020 steels using an electrolytic process involving a molten borax - NaF bath. The parameters such as temperature (700-900)° C, time (1-6 hours) and C.D (0.2 -0.25 A/cm²) were varied during the experiments. This method produced a dual boride layer comprising FeB and Fe₂B. Maximum thickness produced was 200 microns after 6 hours of boriding. He states that treatments below 700°C, did not produce any boride coatings on steels and for consistent boride layer thickness, fresh borax bath must be used, instead of refilled baths.

2.6.5 Gaseous Boronising:

Gaseous boronising is reported to be the best among the conventional methods of boronising, because of the high activity of the gaseous media leads to a faster diffusion. Its major disadvantages are the high toxicity of the gases used and the possibility of explosion during the process which has
inhibited its applications in industry. Gaseous boronising is usually carried out either in diborane (B₂H₆) or mixtures of BCl₃ or BBr₃ with hydrogen.

M.Pchelkina and Yu.Lakhtin[96] boronised Carbon steels and high alloy steels including Austenitic steels in a mixture of B₂H₆ and H₂. They found that case depth varied between 70 to 160 microns, depending on the type of material. The same authors[97] had used a mixture of BCl₃ and H₂ for gas boronising. In 3 hours they obtained a 60 microns thick case on Armco iron at 750°C and a 250 micron case at 950°C. Skugorova, et al.,[98] made an attempt to perfect the apparatus and technique of gas bonding in a super cooled mixture of H₂ with BCl₃ or H₂ with B₂H₆, by constructing a special laboratory scale apparatus. In this apparatus, the ratio of the concentration of BCl₃ and H₂ was 1:15, and the pressure inside the chamber was maintained at 0-500 mm Hg. Under the above conditions, bonding could be carried out in the range 700 to 950°C. Boronising a low carbon steel pipe of diameter 20 x 16 mm and of length 20 mm yielded high quality boride layer of maximum hardness 2200 VHN. Gas boronising at 920°C for 2 hours gave a case depth of 120-150 microns.

Linial, A.V.[99] found that gas boronizing (CVD) method was particularly advantageous when coating has to be controlled thoroughly in respect to thickness and homogeneity such as needed for precision parts, very small objects, pieces of complicated geometrical shape, long narrow tubes, jet nozzles, etc. Thermal decomposition of boron-hydrides Me(BH₄)ₙ can be carried out at a temperature as low as 300°C under normal pressure. Well-adherent functional coatings, however, can only be obtained above 800°C. Hard coating of TiB₂ are obtained by thermal decomposition of Ti(BH₄)₃, AlB from Al(BH₄)₃ and of ZrB from Zr(BH₄)₄. Also he concluded that handling halides is much simpler than handling of inflammable hydrides and also considerably less expensive. The halide BBr₃ can be reduced by H₂ at lower temperatures than BCl₃. It is a two step process, wherein the halide is reduced to elemental boron forming an overlay coating at first and then the boron diffuses into the substrate, forming an
alloy of intermetallic compound. With BBr₃, diffusion coatings could be produced at temperatures as low as 350 to 400°C, whereas with BCl₃ coatings could be possible only above 550°C in appreciable amounts. Technically the best substrate materials for the CVD gaseous process are Cobalt alloys, Ni and Ni alloys, cemented carbides, Co-WC, Ni-TiC, Ferro-titanites, precipitation hardenable stainless steels, nitriding steels and refractory metals. Tool steels and stellite can also be borided reasonably well. Very limited success has been observed with cast iron, low C steel, soft iron, stainless steel, Cr, Ti and Ti alloys. An experimental plant for gas boriding in a mixture of BCl₃ and dissociated NH₃ has been described by Kuleshov, et al.,[100]. This apparatus was found suitable for a wide variety of products in laboratory conditions and in actual production conditions. The boriding plant makes it possible to produce high quality hard (HV₅₀ = 1600-2000) boride layers of practically any depth and phase composition. The plant is simple to operate and permits the hardening of parts directly after boriding without reheating.

P.Gouriet, et al., developed a gaseous boriding process which is simple, economical and industrially reliable. In this process, B₄C, SiC, an activator BF₃ gas and a moderator (Silica or alumina) are used. In the reactor, the BF₃ gas is passed through the silica bed at a temperature greater than 450°C. The BF₃ gas gets converted to (BOF)₃ gas and it is then passed through the boriding agent containing the boridable sample at temperatures in the range 800-1100°C. On plain carbon steels this produces a single phase Fe₂B layer and on Chromium steels this produces a strongly adherent but brittle case with FeB.
A. Bloyce[^101] listed the properties of major boron bearing gases for boriding:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Boron content wt%</th>
<th>Melting point, °C</th>
<th>Boiling point, °C</th>
<th>Remarks</th>
<th>Suitable</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF₃</td>
<td>15.95</td>
<td>-127.1</td>
<td>-100.3</td>
<td>High stability</td>
<td>No</td>
</tr>
<tr>
<td>BCl₃</td>
<td>9.23</td>
<td>-107.3</td>
<td>12.5</td>
<td>Corrosive</td>
<td>Yes</td>
</tr>
<tr>
<td>BBr₃</td>
<td>4.32</td>
<td>-46</td>
<td>90</td>
<td>Explosive reaction with H₂O</td>
<td>No</td>
</tr>
<tr>
<td>B₂H₆</td>
<td>39.08</td>
<td>-165.5</td>
<td>-92.5</td>
<td>Toxic, Explodes on contact with air</td>
<td>No</td>
</tr>
<tr>
<td>(CH₃)₃B</td>
<td>19.35</td>
<td>-161.5</td>
<td>-20</td>
<td>Carburising tendency</td>
<td>No</td>
</tr>
<tr>
<td>(C₂H₅)₃B</td>
<td>11.04</td>
<td>-95</td>
<td>95</td>
<td>Carburising tendency</td>
<td>No</td>
</tr>
</tbody>
</table>

Boriding has been carried out by A.V. Smirnov[^102] using a mixture of diborane (B₂H₆) and hydrogen. However, this process could not be practically applied because of the explosive nature and toxicity of the gaseous mixture. Pure diborane is inflammable at 125 °C in dry air and in the presence of traces of moisture and other hydrates can explode even at room temperature. Boron trichloride (BCl₃) has proved to be most convenient due to its low boiling point (12.6°C), but it strongly irritates the mucous membrane and in a liquid state it causes burns. Mixing dissociated NH₃ with BCl₃ at 800 - 1000°C can result in boriding of specimens.

Yu.S. Kuleshov[^103] states that boride layers on steels, obtained in a gaseous mixtures containing BCl₃ are characterised by high porosity. One effective way of preventing porosity is by preliminary passivation of the steel surface by metals which are less active in respect to BCl₃ than Fe, e.g., Ni. About 5-10 mm thick layer of electrolytic Ni deposit can be employed for this. Without Ni deposit, the boride layer consisted of FeB and Fe₂B phase with small quantities of alpha Fe, Fe₂₃(C,B)₆ and Fe₃ C. With the Ni deposit, a Ni boride band (Ni₄B₃, NiB and Ni₂B) and predominantly single phase region of...
Fe₂B with small inclusions of FeB phase could be seen on the surface. The life of the dies was also significantly improved by boriding after depositing nickel.

M.Olsson, et al., had used both uncoated and TiC-coated cemented carbide cutting tool inserts as substrate materials, and boron carbide coatings had been deposited in a hot-wall reactor by CVD from a reaction gas mixture of BCl₃, CH₄ and H₂. The results suggest that the nucleation of boron carbide was strongly influenced by the vapour composition on the uncoated cemented carbide substrates. Continuous coatings were easily formed at low CH₄ concentrations. For high CH₄ concentrations in the vapour, only scattered islands of deposits were obtained. Further, extensive formation of various borides (W₂B₅, CoB and Co₂B) was observed on the WC/ Cobalt substrate.

2.6.6 Plasma Boriding:

In gaseous boriding one another method involves the introduction of plasma, which significantly reduced the amount of toxic gases generated during processing.

Laboratory trials on ion boriding were carried out by Wierzchon with a specially constructed equipment. Temperature range was 700°C-800°C and a pressure of 2-6 torr was maintained with gas additions of 10-15% boron trichloride or boroethene in hydrogen carrier gas. Treatment times ranged from one to 4 hours.

The process has a number of advantages such as:

1. No powder adhesion as in pack boronising.
2. No crucible corrosion problems as in salt bath boronising.
3. High degree of control of boride layer composition.
5. Elimination of high temperature furnaces.
6. Savings in energy and gas consumption.

Thus the process is claimed to be highly attractive for practical implementation.
Boriding of steel in a cold R.F Plasma of Diborane in Argon has been investigated by Grill, et al.,\textsuperscript{[106]}. The advantages of such a process would be low operating temperatures (600°C) and the possibility of controlling plasma parameters to produce predominantly single phase borides. Samples of AISI 4340 steel were plasma borided in a plasma initiated in a gas mixture of 2.7% diborane in Argon. The plasma was sustained by inductive coupling to a 27.12 MHz generator. The diborane dissociates in the plasma and the boron is deposited onto the surface of steel and diffuse into the substrate. Depending on the plasma conditions, orthorhombic FeB, tetragonal Fe\textsubscript{2}B or cubic Fe\textsubscript{4},Ni\textsubscript{18},B\textsubscript{6} are formed and high surface hardness values upto 1000 kgf / mm\textsuperscript{2} are obtained.

Y.G.Veksler, et al.,\textsuperscript{[107]} investigated boron coatings applied by plasma flame spraying on nickel - chromium matrix. They state that Chromium borides have a microhardness of order 2300 - 2500 kg/mm\textsuperscript{2}, and are firmly bound to nickel- chromium matrix, and are randomly distributed.

Boron deposition on a steel specimen under glow discharge in a H\textsubscript{2} with BCl\textsubscript{3} mixture has been investigated by Filep, et al.,\textsuperscript{[108]}. The maximum efficiency of the process was found to be 27% at 800°C when using an initial BCl\textsubscript{3} concentration of 0.2 -10 % and this efficiency was higher by an order of magnitude than CVD or thermochemical processes. The deposited boron crystals had a helical appearance and were shown to play a fundamental role in controlling the porosity of the boride layer by acting as a diffusion barrier.

Wierzchon, et al.,\textsuperscript{[109]} had attempted depositing Ni upto 5\textmu m using chemical electroless method (at 370k) and further plasma borided (at 923k) the 1045 steel under glow discharge conditions. The layer was found to have good frictional resistance, high hardness and good corrosion resistance. It was better than plain borided specimens in these aspects.
2.7 Special Techniques of Bonding:

Along with the establishment of process conditions for some conventional boronising processes, investigators also turned their attention to more exotic methods and processes for the formation of boride layers.

2.7.1 Hardfacing:

Levitsky and Kasumzade \cite{110} reveals that satisfactory boride layers have been formed on steel using powder filled wire under flux. It was found that stable high boron alloys could be formed at current densities greater than 30A/mm². Below this current density poor bead formation and base metal fusion occur. Crack formation in the cooled structure was found to be a problem when high contents of alloying elements were used in the powders (>3%B). The main cause for the cracking was attributed to the presence of liquid inter layers which develop in the solidus to liquidus range when the alloy was in the solid-liquid state. Reduction of cooling rates of alloys lead to reduction in the tensile stresses and prevents crack formation. The powder composition ranges were 0.2 - 0.4 % C, 1.6-2.9 % B, 0.4 - 1.1 % Si, 0.7-1.4 % Mn.

Rashkov\cite{111} had also reported a novel method for boronising by the use of electrically conductive particulate mixture in a rotary retort.

2.7.2 Laser Boronising:

An attempt was made by Molian and Rajasekhar \cite{118} to determine the feasibility of producing amorphous or microcrystalline coatings of very high hardness by Laser glazing of iron and tool steels. While the results in amorphisation were unsatisfactory, it was found that laser processed coatings were substantially thicker and harder than the initial boride coatings and exhibited hardness gradients along the thickness of laser melted coating. Armco iron, AISI T1 tool steel & M2 high speed steel were initially boronised in a pack mixture, for 2-10 hrs at 1000°C and air cooled, and subsequently irradiated with 3 continuous wave CO₂ lasers with power levels of 1.2, 2.5 & 5 kW. Scanning speed was maintained between 21-212 mm/Sec. Hardness gradient
was found to decrease with increase in scanning speed. Hardness values greater than 2100 HV were observed in some regions of the laser melted coating. Laser treatment produces Fe₂B + eutectic in boronised pure iron and M₆B + M₂₃(B,C)₆ + ternary eutectic in boronised tool steels.

Boronising does not provide significant strengthening of the matrix beneath the layer. Hence, in certain applications the wear resistant qualities of the layer cannot be fully exploited because the strength of the substrate is insufficient to support the layer. One way to provide a more gradual transition in properties is to laser-melt the boronised layer. Laser melting facilitates greater penetration of the boron into the substrate and, beneath the melt depth, transformation hardening occurs. Depending upon the original boride layer thickness and laser treatment parameters, different phases and structures are obtained in the melt. The overall effect is a less abrupt hardness gradient than that found in conventional boronising.

2.7.3. Super Plastic Boronising:

Xu, et al.,[113] had tried Isothermal superplastic boronising of high carbon and low alloy steels. Super plasticity and superplastic deformation of steel and ferrous alloys offer a new method of forming complex parts for industrial applications, such as dies and gears. Boriding gives high hardness, good wear resistance, good corrosion resistance and oxidation resistance. Superplastic boronising combines boronizing with superplastic deformation. Since two processes are done together, energy and time can be saved. Further, superplastic boriding produces fine equiaxial grains while conventional borided specimen show a comb-like shape. Conventional boronising obey a parabolic law and superplastic boronizing follow a approximately linear relation. During superplastic boronizing high defect densities are generated and this increases the rate of boronisation.

2.7.4 Multi Component Coatings:

Ruth Chatterjee- Fisher[47] states that multi component treatments with boron as one of the components has been investigated by several Russian
authors\textsuperscript{[114,115]}, but has only quite recently been the subject of detailed study in the west.

The method involves the simultaneous diffusion of boron and one or more metallic elements into the surface of iron and steel. The coatings usually have greater hardness and wear resistance than conventional thermo chemical treatments, including boronising. Some of these are briefly discussed below:

2.7.4.1 Carburising And Boriding:

Feng, et al., \textsuperscript{[116]} stated that three methods carburising (C), boriding (B) and carbo - boriding (C-B) were used to prolong the life of 20 steel hammers for fodder pulveriser. The 'C-B' method is the best. The process sequence is as follows: (1) gas carburising at 930°C for 4.5 hours, air cool (2) boriding at 930°C for 5 hours, water quench, and then (3) tempering at 250°C for 1 hour. The life is increased by 1.81 times that of carburised hammers and cost is 1.7 to 2 times higher. The C-B method reduces the fodder production cost by 18%. However for nodular iron boriding is better than carbo - boriding.

2.7.4.2 Boro-Aluminising:

Zemskov and Kaidash \textsuperscript{[114]} attempted Boro-aluminising of steels. They state that boroaluminised steels have higher strength and heat resistance. The heat resistance of preboronised and aluminised steels increase by a factor of 40-45 at 900-1000°C. Combined saturation of steels with B and Al could be carried out with B\textsubscript{4}C, borax, Fe-Al and NH\textsubscript{4}Cl mixtures. The composition employed contained 75% of (95% Fe-Al + 3% NH\textsubscript{4}Cl) and 25% of (84% B\textsubscript{4}C +16% Borax). When the process was carried out below 900°C, only borides formed, but above 900°C both borides and aluminides formed. Prosvirin ,et al.,\textsuperscript{[57]} prepared pastes from amorphous boron powder, aluminium powder in amounts of 2.5 to 10%, of the weight of boron used and a binder of 2 % solution of silicate cement. The sample was subjected to surface grinding and subsequently degreased. The layer of paste was 2 mm thick and the sample coated with paste was placed in a stack and heated to 100°C for 1.5 to 2 hours and then heated to 800°C. More than 2% of Al in the paste, decreases the depth
of the diffusion coating. With a paste containing 10% Al the FeB phase was absent and Fe$_2$B phase alone was observed. The lattice constants were $a = 5.132$ Å, $c = 4.220$ Å and $c/a = 0.822$. Boroaluminising produces a high quality case with high hardness, heat resistance and resistance to abrasive wear as well as greater ductility than simple boriding.

Pasechnik, et al.,\textsuperscript{[117]} had attempted simultaneous diffusion of boron with other elements - Cr, Al, Zr. They state that the addition of chromium oxide (Cr$_2$O$_3$) to the melt of borax decreases the decomposition voltage of the electrolyte. With the addition of 10 wt % Cr$_2$O$_3$ it becomes equal to the decomposition voltage of pure chromium oxide, which was determined by thermodynamic calculations. With increasing concentration of chromium oxide, the activity of the electrolyte increases, due to the fact that part of the Cr$_2$O$_3$ does not enter into reaction with borax, but remains in the ionic condition. As a consequence, one would expect the discharge of Cr ions on the cathode during borochromising.

With the addition of Al$_2$O$_3$ to the melt of borax, the decomposition voltage of electrolyte remains unchanged. This is evidently due to the fact that Al$_2$O$_3$ does not dissociate, but interacts partially with borax, forming intermediate compounds with a decomposition voltage near that of 'pure' borax. As a result, during electrolytic boroaluminising, aluminium is deposited on the cathode due to "the sodio - thermic reaction":

$$3\text{Na} + 2\text{Al}_2\text{O}_3 = 3\text{NaAlO}_2 + \text{Al}$$

For C45 steel, the formation of iron borides was at current densities below 0.15A/cm$^2$. Above 0.15A/cm$^2$, chromium boride and chromium carbide formed in the diffusion coatings. When boron and aluminium are diffused into the coatings, stable alpha phase is formed and then the nuclei of iron borides form. The presence of Al in the coating changes the lattice constants of the borides to values different from that of pure iron borides. The aluminium borides have higher oxidation resistance (at 750-800°C) than that of iron borides.
Boroaluminide coatings were prepared by N.G.Kaidash, et al., using a mixture containing 25 wt% boron-containing component (84% B₄C+16% Na₂B₄O₇) and 75 wt% aluminium-containing component (98% Fe-Al+2% NH₄Cl). It is found that iron borides have a lower heat resistance than aluminides.

G.V.Zemskov, report that Boroaluminising improves thermal stability, corrosion resistance and fatigue strength. The authors had boroaluminised commercial iron and C45 steel either by simultaneous or successive diffusion impregnation. For simultaneous impregnation 50% powders of boron and ferroaluminium, 45% aluminium oxide and 5% NH₄Cl were used in powder form. At 950°C both B & Al diffuse into the metal. Below 900°C, only Al diffused, but above 1050°C, the quality of sample deteriorated. The boride phases were FeB (1600 kg/mm²) and Fe₂B (1300-1000 kg/mm²).

To obtain boroaluminised layer, boriding was carried out first using borax + boron carbide at 900°C for 2 hours. The layer was 110 mm thick with FeB and Fe₂B layers. Then this material was aluminised. The hardness of the aluminised zones was 520 kg/mm² and that of borides were 1870 kg/mm². The phases were FeAl₃, Fe₂Al₅ and FeAl, from the surface toward core, respectively.

When samples of pure iron were first aluminised (950°C, 2 hours) and then borided (950°C, 2 hours), fine needle-shaped FeB (2100 kg/mm²) phase was observed. When C45 steel was studied, the results (structure and composition) were similar to that of iron. This was because the carbon was forced away from the surface toward the core, while borides and aluminides were forming on the surface.

Parketa, et al., report that aluminising and then boriding reduces the hydrogen permeability of Kh 18 N 10 T steel. Aluminising was carried out in powder mixtures with Al₂O₃ - 82%, Al - 15%, NH₄Cl - 3% at 900°C, 1h and boriding in 84% B₄C + 16% borax at 950°C, 6h. An aluminised layer of 90μm and borided layer 80μm were formed. The diffusion impregnation of steel Kh
18 N 10 T with aluminium, lowers its hydrogen permeability in the temperature range 800-540°C by 3 to 5 times. The diffusion impregnation of this steel with boron lowers its hydrogen permeability by 13 to 70 times in the temperature interval 800 -400°C and at elevated temperatures hydrogen accelerates a redissolution of diffusion layer.

Further, boro-zirconising was studied with borax + 5% ZrO₂ electrolyte at different temperatures and different current densities and processing times. The coating could be intensified by reversing the polarity of the current.

2.7.4.3 Boro-Chromising:

Meirer[121] states that Chromising increases the oxidation and corrosion resistance of ferrous alloys. A typical pack mixture is 30% (Cr or Fe-Cr), 5% halide activator and 55% filler (Al₂O₃ by weight). The halide activators used were CrCl₃, FeCl₂, NH₄Cl and NH₄F. The samples embedded in the packs were heated to 1150°C for 0.1 to 28 hours and cooled to 600°C in 2 hours.

Yu. A. Alimov[122] found that boride coatings are quite hard (1800-2200 VHN) but they are quite brittle. The coatings are also prone to oxidation and have an inadequate corrosion resistance. Therefore, the use of boriding is limited to working conditions such as friction during a static application of external force and resistance to wear in abrasive medium. He further states that diffusion chromising gives a hardness upto 1500-1800 VHN. Chromised steels are characterised by an increased in resistance to wear under friction, action of abrasives and also by an increased resistance to oxidation in an oxygen atmosphere.

If boron and chromium are present in steel together, they form CrB₂, Cr₂B and Cr₃B₃ - type of chromides since B has greater affinity for Cr than for Fe. The borochromised layer has lower hardness compared to boride layer but show an improved wear resistance and improved plasticity. V.D. Kal'ner, et al.,[123] states that successive borochromising increase the heat, wear and corrosion failure resistance of steels. Borochromising also decreases the tendency for deboronisation of steel. Boriding was done by contact gas method.
using boron carbide-base powder mixture with NaF as activator. Subsequent chromising was done in a vacuum furnace by the non-contact method. The working space was first evacuated to 1.33 Pa pressure and then with CCl₄ vapour is supplied to the reaction space. The chromizing source was chromium lumps (1-5 mm). During boriding FeB and Fe₂B layers are formed and during chromising the boride layer thickness increases and a defect free layer (without deboronisation) is obtained. The surface layer is (Cr, Fe)₂B. The formation of low melting borochromium glass seals the defects and this layer gives greatest oxidation resistance at 900°C. R.L.Kogan, et al.,[124] prepared a borochromised layer, by the successive method of the two-stage technique. This technique as compared to boriding alone, gives greater hardness, higher resistance to corrosion and oxidation and less brittleness. The borochromised samples were subjected to cyclic loading and fracture microstructure was studied. Also fatigue tests were carried out by bending of rotating specimens. It is found that borided samples (steel 45) increase the fatigue limit by 20 % and borochromising by 40%. Carburising and nitriding increases the fatigue limit by 20-60%. Borochromising increases the corrosion fatigue strength of steel 45 by 2.5 times in a 3% NaCl solution.

2.7.4.4 Boro Chromo Titanising:

G.V.Zemskov et al. [125] had attempted multi component boriding. Steel 45 was surface alloyed with boron (using borax + B₄C) at 850 - 900°C to get 50-120 mm case. Subsequently diffusion metallisation was carried out at 1050°C (for 5 hours) in a mixture containing powders of the impregnating metals (Cr, Ti), an inert addition (Al₂O₃) and an activator (NH₄Cl). The boro chromo titanised layer has a higher microhardness and contains less iron in the surface layers than that of borochromised and borotitanised layers. The tensile strength of multi component borided specimens was more than that of borided samples, but plasticity was lesser. On boriding, the tensile strength increased by 10-15%, on borochromising by 20-25% and on borochromo titanising by 30-40%. Boriding increases fatigue resistance in corrosive mediums (3%NaCl solution).
Borochromo titanising confers very high wear resistance on steels. G.V.Zemskov, [125] also had stated that Titanium diboride, TiB₂, has many valuable properties such as high hardness, wear and heat resistance, corrosion resistance and resistance to attack by non ferrous metallic melts. Obtaining a dense and strongly adhesive layer of this compound offers a promising means of protecting metals. TiB₂ can be formed by first diffusing boron on steels and then titanium. Diffusion boriding by these authors was carried out by a mixture of 84% B₄C and 16% borax, at 900°C for 2 hours. Then titanium enrichment was carried out at 900-1100°C for 2h using a mixture with 70% Ti, 25% Al and 5% NH₄Cl. This method produced a 25 mm thick case on the surface with a hardness of 3180 kg/mm² followed by 35 mm thick layer with a hardness of 480 kg/mm². This is an α-iron based solid solution and below this layer Fe₂B type of borides are observed.

2.7.4.5 Boro-Siliconising:

Yu.V.Kolesinkov, et al.,[126] state that Chemico thermal treatment (CCT) is one of the effective methods of increasing the surface life of machine components and high hardness values are recorded for boronised layers. However, at high loads these layers are brittle. Addition of Cu, Al, etc., increase the activity of the diffusion layers but, at the same time reduce hardness. Borosiliconised layer have high hardness and satisfactory wear resistance under the effect of high loads. Boro-siliconising using 60% Na₂B₄O₇ + 40% SiC at 1100°C using RF heating greatly increases dynamic strength of the steel. L.A.Sosnovski[127] siliconised steels using the mixtures Si - 60%, Cu - 35%, NaF - 5% and Si 85, Cu 10, NaF- 5 at 1000°C, 3 hours and at 1100°C, for 3 hours respectively.

2.7.4.6 Electrolytic Deposition:

A.P.Epik, et al.,[128] had evolved a process for producing composite boride coatings by the method of electrolytic deposition of dispersed boron particles, along with nickel and by subsequent diffusion annealing. The antifrictional properties of the composite boride coatings were studied in...
comparison with those of boride and hard chromium coatings. It is shown that composite boride coatings have a higher wear resistance.

Investigating multi component coatings, Ruth Chaterjee-Fischer concluded that the most interesting and functional coating processes are the following:

**Boro-chromizing**: These coatings are both wear resistant and corrosion resistant. They find applications in enhancing wear resistance of austenitic steel parts and dies for forming ceramics.

**Boro-chromo-vanadizing**: These coatings have the maximum wear resistance, among the coatings investigated, under conditions of metal to metal (adhesive) wear. Though boro-chromo-vanadized and boro-vanadized coatings exhibit very high hardness of 3000 HV, they were quite ductile also making them very promising coatings for applications undergoing impact loads.

**Boro-chromo-titanizing**: These layers have extremely high hardness of 5000 HV and were found to be the most wear resistant coating under abrasive wear conditions. They are also corrosion resistant and find applications in parts for plastic processing machinery.

**Boro-aluminizing**: This coating has been found to be ideal for wear resistance applications under humid environmental conditions.

### 2.8 Effect of Variables on Morphology, Microstructure and Properties:

During boriding of iron and steel, distinct intermetallic phases of definite composition form, in contrast to carburising where there is a gradual transition of concentration of carbon from surface to substrate. The structure of the boride layer and the transition zone depend on the composition of steel, boronising method, activity of boron in the boriding medium, temperature, time and other treatment conditions.
2.8.1. Morphology, Microstructure and Effect of Composition:

2.8.1.1 Effect of Carbon:

In plain carbon and low alloy steels, the borides grow as columnar aggregates of crystals, giving rise to "saw tooth" like morphologies at the FeB / Fe$_2$B and Fe$_2$B / Fe interface. On high alloy steels almost flat boride-matrix interface was observed. In carbon steels acicular borides FeB and Fe$_2$B oriented perpendicular to the surface are formed. The FeB is orthorhombic with $a = 4.061$, $b = 5.506$, $c = 2.952$ and Fe$_2$B is BCT with $a = 5.109$, $c = 4.249$, $c/a = 0.832$. The nature of bonds in Iron borides is covalent - metallic bonds with a predominance of metallic bonding. In the case of Fe$_2$B, bond is almost metallic.

Kunst and Schaaber have suggested a layer evaluation system to predict the performance of boronised surfaces (Fig 2.5). It is recommended that a type E, or at least a type F layer be obtained for successful commercial application of boronising. Both these layers contain only Fe$_2$B phase which apart from having a lower hardness than FeB and hence more ductility, also possesses a coefficient of thermal expansion which is comparable with iron and steel, thus allowing components to be quenched after treatment with least residual stress formation. Where formation of FeB phase is unavoidable, it can be readily converted to Fe$_2$B by diffusion annealing in an inert atmosphere or a salt bath for oxidation protection.

In addition to these borides, in high carbon steels elongated inclusions are seen whose orientation differs from that of borides. It has been stated that these inclusions are probably boro-cementite FeC$_{0.2}$B$_{0.8}$ whose microhardness is 900-1100 kg/mm$^2$. These inclusions are so very fine that it is difficult to measure their microhardness. Boron can replace up to 80% of the carbon in cementite without changing its orthorhombic lattice. This ternary phase is called boro-cementite Fe$_3$ (C,B). In addition to these, iron borocarbides Fe$_{23}$ (C,B)$_6$ may also form. When boron concentration increases from 0 to 5.2 wt%, the
lattice parameter 'b' changes from 5.079 to 5.405 Å, the parameter 'a' from 4.515 to 4.450 Å and 'c' from 6.748 to 6.669 Å.[134]

G.V. Karpenko[133] reported that the depth of the boronized layer decreased considerably when the carbon content is increased from 0.1 to 0.4%. Further, when carbon was increased from 0.4 to 0.75%, the depth of the case is not changed, but when it was increased to 1%, the depth again decreases considerably. The author had further stated that in electrolytic boronizing, the carbon content has no influence on the depth of the boride layer.

2.3.1.2. Effect of Alloying Elements:

In general, the presence of alloying elements reduce the diffusivity of boron in the steel, and consequently decreases the thickness of the boride layer. While carbon, molybdenum, and tungsten dramatically reduce the boride layer thickness, silicon, chromium and aluminium have a more moderate influence. Nickel, manganese, and cobalt have only a marginal influence[26]. During boronising, redistribution of the alloying elements takes place depending on the solubility of the elements and the ability of the elements to form stable compounds with boron. Various investigations have led to the conclusion that chromium and molybdenum are dissolved uniformly in the Fe₂B layer and nickel, carbon, silicon, and aluminium concentrate at the boride/steel interface. The concentration of silicon at the boride/steel interface results in the formation of a soft ferrite layer at the interface. Steels containing over 0.5 wt-% silicon are stated to be unsuitable for boronising because of the formation of this soft ferrite region and the difficulty in producing thicker boride layers[55].

The layer thickness is found to decrease with increasing alloy content. The elements causing maximum inhibition to growth of layer, in descending order are Mo, Al, W, Cr, Si, C, Mn, Co, Ni[26] All the above said elements except Al and Cu increase the FeB content in the case. Alloying elements in the steel lead to the formation of a more complex boride structure; however, the influence of alloying elements is not additive[133]. It has been stated that that the composition of carbon steel and of low-alloy steel has little effect on the
diffusion rate of boron and the composition of the boride layer, but it influences both the structure of the boride phases and the quantitative relationship between them.\textsuperscript{[133]} Qian and stone reports that at the boriding temperature, carbon atoms are rejected from the iron lattice and are pushed toward the core and when the solubility of the carbon in iron is exceeded carbides are formed \textsuperscript{[135]}. In steels C & Si diffuse ahead of boron and concentrates in a layer immediately beneath the boride\textsuperscript{[136]}.

Chromium either enters iron borides or concentrate at the interface between the boride layer and the substrate and in certain cases also forms boride layers entirely composed of Chromium boride (CrB)\textsuperscript{[130,131]}. Nickel has been found to concentrate beneath the boride layer, enter the Fe\textsubscript{2}B layer and in some cases precipitate as Ni\textsubscript{3}B out of the FeB layer. Both Cr and Ni reduce boride layer thickness and flatten out the tooth shaped morphology generally observed in low carbon steels. Manganese also behaves similar to Ni in reducing boride layer thickness, enter the Fe\textsubscript{2}B layer\textsuperscript{[130]}. Lyakhovich, Puchkov, et al.,\textsuperscript{[132]} had stated that Cr and Mo have high solubility in Fe\textsubscript{2}B whereas Ti in FeB. The chromium boride Cr\textsubscript{2}B is isomorphous with Fe\textsubscript{2}B. The type of bond in Cr\textsubscript{2}B is same as in Fe\textsubscript{2}B. Cr\textsubscript{2}B and FeB mutual solid solubility is low. Molybdenum boride Mo\textsubscript{2}B is also isomorphous with Fe\textsubscript{2}B. Highest solubility of TiB is expected in FeB\textsuperscript{[132,135]}. Flat case- core interface, and strong (002) preferred crystallographic orientations are present simultaneously on borided high Cr alloys. So, growth of the case can not be explained by assuming that growth is controlled by the (002) preferred orientation \textsuperscript{[137]}. M. Carbucicchio, et al., report that when an alloy with 5.65 wt\%Cr, 0.2 wt\% C and rest iron was powder borided, FeB and FeB\textsubscript{x} (x>1) were observed. With increase in Cr, FeB phase increased, whereas when Ni was added the opposite effect was observed (FeB decreased)\textsuperscript{[66]}. Tsipas and Rus\textsuperscript{[138]} had reported that Cr enter into FeB and Fe\textsubscript{2}B. When Cr is in excess, more than what iron borides could absorb, it segregates along the boride-metal interface. When Cr is in excess, distinct chromium borides will form. In the case of 304 stainless steel Cr concentrates at the...
interface between the boride layer and the matrix. Cr has a more pronounced effect on coating thickness and morphology than Mn. Epik et al.\textsuperscript{[139]} reported that alloying elements (W, Mo, Cr, Mn, and Si) enhance the hardness of boride layer from 1400-1800 (in plain carbon steels) to 2000-2500 VHN in alloy steels. Gouriet, et al.,\textsuperscript{[140]} reported that Cr up to 20% does not affect the formation of boride phases significantly apart from its influence on the boride morphology. Ni however segregate strongly to the surface of stainless steels at high boron activities. Palombarini, Carbucicchio, et al.,\textsuperscript{[141,142]} have stated that both the elements (Cr & Ni) enter iron borides, substituting for Iron. However, Cr concentrates in the boride layer depleting the underlying unborided matrix, while Ni preferentially concentrates beneath the boride coatings, allowing low-Ni iron borides to be formed. V.P. Smirnov\textsuperscript{[143]} had stated that Fe, Cr and Ni have different affinities for boron. Out of these three elements, Cr form the most stable borides, then iron forms the borides. Ni form the least stable borides. When Cr and Fe form the borides in the surface layer of the steel, Ni concentration increases at a distance below the surface and a new Nickel rich boride phase is formed. L.S. Lyakhovic and Voroshnin\textsuperscript{[144]} had stated that Ni and Si diffuse during boriding toward the surface of the article and when alloy steels are borided the borides formed may be designated as (Fe,AE)\textsubscript{2}B and (Fe,AE)B where AE stands for alloying element.

2.3.1.3. Region Below the Boride Layer:

Puchkov, et al.,\textsuperscript{[136]} report that during boriding of carbon steels a 'transition zone' differing in the structure from the core form immediately under the boride layer. With low and medium carbon steels air-cooled after boriding, the transition zone has a pearlitic or near pearlitic structure, which shows no significant variation over the whole depth of the transition zone. In borided high carbon steels, precipitated carbide inclusions, the number of which decreases with increase in the distance from the boride layer, are found in the transition zone immediately under the boride layer. In the transition zone of carbon steels, the true size of the austenite grain is much greater than in the basis metal. The
simultaneous action of boron and carbon lead to the pearlite formation in the transition zone. The presence of boron in the transition zone severely inhibits ferrite formation during normalising treatment. Si is also strongly displaced from the surface and concentrates below the boride layer.

2.3.1.4. Reactivity between the substrate and bonding medium:

V.V. Drobit, et al., [145] had reported that the boride coating deposited from the sodium melt with no carbon consists of four layers with a total thickness of up to 200μm. The very thin external layer was difficult to etch and could not be analysed by metallographic examination. This phase was determined by layer-by-layer X-ray diffraction analysis, to be Fe₂B. Two subsequent layers are the main layer in the coating and consists of FeB and Fe₂B borides, which are the major constituents. The internal diffusion layer with the structure which differs only slightly from the microstructure of the matrix represents a solid solution of boron in iron. This zone forms in all cases, regardless of the low solubility of boron in iron. The multiphase boride coatings are characterised by the presence of a very large number of cracks which propagate both in the direction parallel to the surface between FeB and Fe₂B layers and in the direction normal to the surface in the FeB layer. It is found that in the area in which FeB predominates is characterised by the formation of tensile stresses and compressive stresses form in the underlying zone with Fe₂B[145].

Saturation with boron from the sodium melt enriched with carbon results in the formation of a multilayer coating with the main phase being Fe₂B boride. In addition to this X-ray diffraction patterns of the powders taken from the surface layer reveal the presence of borocementite Fe₃(B,C), where up to 80% of carbon can be replaced by boron.

In the case of very high reactivity (e.g. armco iron in contact with concentrated B₄C activated powders) the interface is strongly columnar and products richer in boron than Fe₂B are allowed to grow. With low reactivity
(e.g. Armco iron in contact with crystalline boron) the interface assumes a low
columnarity, and Fe₂B is the main constituent. Alloying elements other than
carbon seem to influence the morphology of the coating-substrate interface.
Upto 8.85% Ni, the interface columnarity was reduced only slightly. Cr upto
5.65 wt% was able to fatten appreciably the Fe₂B/Fe interface. Cr and Mn
preferentially enters the Fe₂B phase, depleting the underlying unborided matrix.
Ni on the contrary, concentrates beneath the Fe₂B/Fe interface. High alloy iron
and steels display a higher reactivity towards boron than pure iron, but a lower
reactivity than low alloy iron and steels. Consequently the morphology of the
Fe₂B/Fe interface appears to be columnar for low alloy materials instead of
rounded in shape as for pure iron or nearly flat for high alloy steels\(^{129}\).

On low alloy steels, decreasing boron carbide from 5 to 2.5% in the
boriding mixture reduced the FeB layer formation. But in high alloy steels FeB
layer cannot be avoided particularly at the edges\(^{146}\). Crystalline boron (too mild
a boronizing medium) applied on annealed high purity iron samples, which
were carburised upto 0.3% C, and cold rolled upto 22% thickness reduction,
even 1000°C, even for 15 hours, produced boride only in a few places. On
Armco iron a continuous layer could be produced. In pure iron carburising (upto
0.3 wt% C) or 22% cold reduction was not able to improve the reactivity to the
level of Armco iron but punching (severe work hardening) led to increased
reactivity and more reaction products between iron and boron\(^{147}\).

Compared to paste technique (containing 55% cryolite), the powder
technique with FeB produced a layer with less proportion of FeB. In both the
techniques the layer had FeB and Fe₂B along with Fe₂(B, Si) and Fe₃C\(^{69}\).

When low C or medium C Steel were borided with low boron content
media only Fe₂B phase formed. But when chromium (13%) was present in steel
it formed FeB phase and it also reduced the thickness of the boride layer and fattened the coating/substrate interface.\[131]\)

Low boron activity (gaseous boriding) can produce good quality Fe$_2$B layer with reduced Ni segregation\[139].

When reactivity is high both FeB and Fe$_2$B will form and when activity is low only Fe$_2$B will form\[137].

G. Palombarini, et al.,\[148] reports that the presence of oxygen in large amount is detrimental to the boriding process, leading to high losses of active boron powder and powder agglomeration. The role of a limited amount of oxygen either in the form of oxygen gas or oxides in the powder mix is controversial.

2.3.1.5. Temperature:

Lakhtin and Pchelkina investigated the dependence of the depth of boronized cases on temperature and found that the case grows much faster on alpha-iron than on gamma-iron, due apparently, to difference in the diffusion coefficient.

Below 700-750°C, no diffusion of boron takes place whatever the method of boronizing, (except gas boronizing which proceeds at a considerable rate even at 500-550°C). Boronising in powder mixtures of boron carbide and borax at about 800°C produces cases consisting of Fe$_2$B and an intermediate layer. Boronized cases produced at 850-1000°C by any method (except boronizing in powder mixtures of a low activity) produces case consisting of a layer of acicular boride and an intermediate zone. At 1100°C, the diffusion of boron into steel is uniform and the resulting layer consists not of acicular borides, but grains of a uniformly distributed eutectic. Boronizing at 1200°C produces regions with a eutectic of a clearly dendritic structure in which the individual crystals are separated by globular pearlite. Beneath this boride layer there are globular inclusions of considerable hardness which are described by some authors as cementite, while others believe them to be borocarbide. At elevated temperatures, boron diffuses mainly along the grains boundaries. It has
been found that if the content of carbon in the steels increases from 0.45 to 1.1%, the depth of the case is reduced to one third (for 1-3 hours of boronising). If the process duration is increased, the influence of the carbon content becomes more pronounced.

2.3.1.6. Time:

When boriding of AISI 1008 steel was carried out using 20 mole % B₄C, 5 mole % KBF₄ and 75 mole % graphite, coating developed a good crystalline structure only after heating times greater than 1 hours. At times greater than 2 or 3 hours, the FeB phase began to dominate the surface layer. The columnar morphology of the coating grow with time [45]. The dependence of the thickness of the boronized layer on the duration of the process is governed by a parabolic law. At the beginning of the process the thickness of the layer considerably increases with time but then this increase slows down. The duration of the process influences the relationship between the FeB and Fe₂B contents of the layer. Thus, an increase in the duration of the process increases the amount of the FeB phase. The duration of boronizing in slightly active media considerably influences the composition of the case. While short processes produce a layer of boride-cementite FeC₀₂B₀₈ beneath the boride layer, longer processes produce pure cementite [134].

2.3.2. Mechanical and Chemical Properties:

2.3.2.1. Microhardness and Tensile Properties:

As a result of boronising, the yield strength is increased by 8-15%, the elongation is reduced by 8-15%. After electrolytic boronizing and slow cooling, the elongation decreases by up to 35%. Boronizing decreases the reduction in area by 25-40% and the toughness by 25%. Boronizing of carbon steel in powder media increase the fatigue strength of smooth specimens by 18-25% and of notched specimens by 200%.

In plain carbon and low alloy steels, the boride phases are found to be acicular giving rise to tooth like morphologies of FeB / Fe₂B and Fe₂B / Fe interface. A reasonable columnarity can improve the mechanical adherence at
the interfaces which gives resistance to spalling under wear conditions. However, too high difference between the maximum and minimum values of penetration depth may impart a brittle behaviour to the very hard brittle borides\footnote{129}.

The micro hardness of FeB in 0.2 & 0.45 % C steel is 1800-1900 kg / mm\(^2\) and Fe\(_2\)B phase is 1450 kg/mm\(^2\), while in 0.8 % C steel the microhardness of Fe\(_2\)B phase is 1600 kg/mm\(^2\). Hardening and high temperature annealing of borided 45 steel have no influence on the microhardness of borides because of their high thermal stability. Heating to 830-840\(^\circ\)C produces no structural or concentration change. The dimensional changes during boriding is less for steel 45 when compared to steel C 20.\footnote{133}

The layer thickness is found to decrease with increasing alloy content. The elements causing maximum inhibition to growth of layer, in descending order are Mo, Al, W, Cr, Si, C, Mn, Co, Ni.\footnote{130}

Boriding sharply increases the brittleness of the steel when 2-4% Cu powder was added to the boriding mixture (84% B\(_4\)C + 16% Borax), the case depth was reduced by a factor of 1.5 - 2, the hardness was reduced from 1800 to 1300 - 1600 VHN, the yield strength was reduced by 5-7 Kg/mm\(^2\), increases elongation by 60% and toughness increased from 4.5 to 5.5 kg -m /cm\(^2\).\footnote{146}

2.2.2 Fatigue and Corrosion Fatigue:

Carburising or nitriding increase the fatigue limit by 50-100%, whereas boriding increases only by 15-20%.

V.I.Pokhmurskii,\footnote{149} states that electrolytic boriding to a depth of 0.15mm, followed by a heat treatment, markedly lowers the fatigue limit of constructional chromium- silicon steel. Contact boriding in a mixture of B\(_4\)C and borax to a depth of about 0.15mm without subsequent heat treatment rises the fatigue limit of type 20 steel by about 15% and that of type C45 steel by about 20-25%. Quenching a borided steel with subsequent low-temperature tempering (to form tempered martensite in the core) lowers its fatigue limit to a quarter of that of the quenched unborided steel and to one-half the fatigue limit.
of the borided steel which has not been subjected to quenching. Varying the mean thickness of the borided steel in the range 0.07 - 0.21 mm has been found to have virtually no effect on the fatigue limit of medium - carbon steel. Electrolytic boriding giving the same layer thickness and subsequent vacuum annealing raise the fatigue limit of type 45 steel specimens 8 and 5 mm in diameter by about 15 and 30% respectively.

Electrolytic and gaseous-phase contact boriding to a depth of 0.10 - 0.15 mm, both without subsequent heat treatment and vacuum annealing, may double the arbitrary corrosion-fatigue limit of low-and medium-carbon unalloyed steels on a basis of $2.5 \times 10^7$ loading cycles. From the view point of corrosion-fatigue behaviour, thorough-quenching of borided parts is undesirable owing to the cracks produced due to the difference in the coefficients of linear expansion of the basis metal and diffusion layer. These cracks act as stress raisers and increase the degree of discontinuity of the layer.

G.V.Karpenko, et al.,[150] report that the fatigue and corrosion fatigue of the steels with and without coatings were studied in pure rotary bending, using specimens of 8-mm diameter. Investigations have shown that boriding increases the fatigue limit of carbon steels by 18-22%, the strengthening effect being slightly less for steel of lower carbon content. Boriding hardly affects the fatigue limit of stainless steel.

The corrosion fatigue limit of carbon steels increases 1.5-2.0-fold, the limited fatigue strength of carbon steels increasing with rise in their carbon content. An investigation into the effect of impregnation time on the fatigue and corrosion fatigue of the steels shows that, for each steel, there is an optimum impregnation process (or an optimum diffusion layer thickness), which results in the highest fatigue limit or corrosion fatigue limit. Thus, for C45 steel, the fatigue limit is a maximum at a layer thickness of about 0.15 mm and shows a tendency to fall at greater layer thicknesses.

The improvement in the fatigue limit of carbon steels may be attributed to the presence of high (up to 80 Kg/mm²) residual compressive stresses,
which, without being the dominant factor, have a beneficial effect on the fatigue behavior of steel. In the increase in fatigue strength, an important part is played also by the zone enriched in the carbon driven out of the surface layer. The size of this zone increases, like the strengthening effect induced by boriding, with rise in the carbon content of steel. The increase in the arbitrary corrosion fatigue limit of carbon steels may be linked with the formation on their surface of a corrosion-resistant protective layer.

The increase in the fatigue limit of stainless steel is attributable also to the formation under the boride layer of a comparatively uniform carbide from the surface and by the removal of carbon from the surface and by the counterdiffusion of the alloying element. In all probability, it is this zone that is responsible for the over-all strengthening effect in spite of the presence of a fairly brittle layer of complex borides on the surface. As the thickness of the boride layer is increased to 0.1mm, the layer begins to crumble locally, as a result of which the fatigue limit falls to the level characteristic of uncoated specimens.

The sharp reduction in the fatigue limit of stainless steels after boriding can presumably be associated with the presence in the steel of nickel, which affects diffusion processes and alters the character of the diffusion layer structure. A marked difference is observed in the structure of the sub-boride zone, in which carbides are precipitated along the grain boundaries. Such boundaries in the sub-boride layer act as structural stress raisers, lowering the fatigue strength of the steel.

2.5.2.3. Oxidation Resistance:

I.Kh.Trush, et al.,\cite{51} reports that Boronizing may be an effective means of improving oxidation resistance of low-carbon steel. It was found that FeB is relatively unstable and decomposes around 800°C. Above this temperature the thickness of the FeB layer decreases, and thus the percentage of this phase in the boride layer also decreases as per the reaction,

\[
2\text{FeB} = \text{Fe}_2\text{B} + \text{B}
\]
and this leads to an increase in the thickness of Fe$_2$B above 900°C until the disappearance of FeB. Fe$_2$B phase is stable up to 1000°C, but decomposes rapidly at higher temperatures. In amounts up to 1.5% Vanadium increases the stability of FeB but does not increase the stability of Fe$_2$B. The microhardness of borides remain unchanged at all temperatures where they remain unstable.

L. S. Lyakhovich, et al.,\textsuperscript{[152]} reports that up to 850°C, the oxidation resistance of borides is satisfactory. A drastic decrease in the oxidation resistance (measured using weight gain) of borided specimens was observed, when the temperature was raised from 850°C to 900°C. This may probably be due to the beginning of dissociation of boride FeB in the air atmosphere.

2.3.2.4. Residual Stresses:

L. S. Lyakhovich, et al.,\textsuperscript{[153]} due to electrolytic boriding, the following zones occur, (i) FeB (ii) FeB + Fe$_2$B and (iii) Fe$_2$B + substrate. The dimensions of each zone depend on the carbon content of the sample. Independent of the carbon content of the samples, compressive stresses develop in the boride layers and at the coating-substrate interface these stresses change to tensile stresses.

When FeB and Fe$_2$B are formed together, residual tensile stresses will occur in FeB outer layer and residual compressive stresses will be found in Fe$_2$B layer during cooling of the Steel. Cracks appear on the boundary level of both these layers parallel to the surface when mechanically stressed\textsuperscript{[145]}. Formation of Fe$_2$B alone is desirable, because of its lower degree of brittleness compared to FeB\textsuperscript{[55]}.

When the borided steels were reheated and quenched in water the residual stress in the Fe$_2$B zone and Fe$_2$B + substrate zone decrease. This decrease is due to volume effect. Tempering borided steels at 200 to 600°C, leads to an increase in the magnitude of the residual compressive stresses in the boride layer.

A. Bloyce, et al.,\textsuperscript{[149]} state that commercial boronising of steels is confined to the pack (or paste) technique(s) and these frequently result in a dual phased layer of FeB and Fe$_2$B. The disparities in the coefficients of thermal...
expansion of the two phases produces residual tensile stresses in the exterior FeB, which causes exfoliation under mechanical loading. It is therefore desirable to obtain a monophased layer of Fe₂B. Conventionally, this has normally been satisfactorily accomplished, in the case of engineering steels, by a subsequent diffusion treatment at about 900°C. An alternative is to boronise using plasma or gaseous media, which in principle, allows a broader range of boron potential, facilitating the production of monophased layers.

R.L.Kogan, et al., states that as a result of boronizing of steel, residual compressive stresses arise in the diffusion layer, reaching 30-120 kg/mm². Variation in these stress values shall be due to variation in chemical composition of the steels and various boronizing methods and procedures. When steels were borided deeper than 50 microns, two zones were observed. (The outer FeB layer and inner Fe₂B layer). Layers less than 50m consisted essentially a single phase (Fe₂B) layer. The residual compressive stresses in Armco iron were appreciably greater than in carbon steels. With increase in depth of the layer, the compressive stresses decline and the maximum is shifted downward in the layer. Residual stresses appear during cooling after boronizing as a result of elastic interaction between the diffusion layer and the core, since the two and have different coefficient of linear expansion. The coefficient of linear expansion in the range of 20 to 400°C are 9.97 x 10⁻⁶ and 7.67 x 10⁻⁶ mm/mm for FeB and Fe₂B respectively, whereas for steel with low carbon content this value is around 13.4 x 10⁻⁶. On cooling from boronizing temperature, the core contracts to a greater degree and boride layer with relatively low contraction impede this, leading to appearance of tensile stresses in the core balanced by compressive forces in the boride layer. The compressive forces are influenced also by the volume ratio of layer and core. With increase in the depth of the layer the residual compressive stresses decline. The maximum value of compressive stresses is observed at the surface only if the layer is less than 50 microns thick and FeB is lacking in the diffusion layer. The location of maximum compressive stress is shifted from the surface toward core
and the value of maximum compressive stress decreases, when layer depth increases. At a depth of the boronized layer of less than 100-200m, the maximum value of compressive stresses in Armco iron is considerably greater (2 to 2.5 times) when compared to low, medium or high carbon steels. This is due to the fact that the coefficient of linear expansion for Armco iron is greater than for carbon steels. Increase in carbon content in steel from 0.2 to 0.8% has no effect on the value of maximum compressive stress. The depth of boride layer is significant for Armco iron for which there is a considerable drop in the maximum compressive stress is observed. For carbon steels the effect of depth of the diffusion layer is in significant.

According to Karpenko (133), the data can be summed up thus: (i) Boronizing increases only slightly the fatigue strength of steel 45 regardless of the method used. (ii) Boronizing of carbon steel in powder media increase the fatigue strength of smooth specimens by 18-25% and of notched specimens by 200%. An increase in the carbon content of the steel from 0.2 to 0.8% increases the strength of boronized steel. (iii) The fatigue strength of steel 45 specimens is increased by diffusion layers 0.14-0.15 mm thick. Such a layers are produced by boronizing for 5-6 hours at 950°C. Variations in layer thickness within 0.1-0.2 mm have little effect on the fatigue strength. (iv) Boronizing by pack boriding method increases the corrosion fatigue limit of medium carbon steels by 160-200%. (v) The smaller the stress raiser factor, the smaller is the effect of boronizing on the fatigue strength of steel in air and the greater its effect on the fatigue strength in corrosive media. (vi) Hardening, followed by low-temperature annealing of boronized steel, reduces its fatigue strength and increases slightly its corrosion fatigue limit. Hardening followed by high-temperature annealing is the most favourable heat treatment from the standpoint of increasing the fatigue strength of boronized steel. (vii) The distribution of residual stresses after boronizing under various operation conditions has little influence on the fatigue strength or on the corrosion fatigue limit of medium carbon steel.

Some Refinements to Boriding Processes 2.59
2.2.5. Friction and Wear Characteristics of Borided Layers:

As boriding is primarily a wear resistant coating it has been the subject of numerous friction and wear studies under varying conditions. Reviewed below are some of the major studies along with a brief summary of their conclusions.

(i) L.P. Kolesnichenko and Golego (155) discovered a new method of surface hardening frictional pair components by forming liquid eutectics at the metal-hardening phase interface followed by rapid cooling. Applying this method to a boron paste coated C45, they were able to form boride constituents in the form of discrete and uniformly distributed particles on the metal surface. This was then shown to exhibit superior friction and wear characteristics compared to annealed, quenched and borided surfaces respectively.

(ii) N.L. Golego, et. al., (156) arrived at a number of interesting characteristics on finely dispersed boride structure. C45 specimens were powder boronised and were induction heated and rapidly cooled to produce finely dispersed boride structures. The nature of change in coefficient of friction and wear was studied and found to be essentially the same for all coatings (i.e.) high at small slip speeds and decrease with increasing speed. However, in the low speed region (athermal) of the friction test (0.05 m/sec) wear resistance of dispersed boride layers was 5-6 times that of usual borided coatings and at high speeds (thermal) regions (2-5 m/sec), the appearance of a liquid phase acting as a lubricant, following the formation of oxide B₂O₃ and its melting at low temperatures,
resulted in uniformly low values of wear and friction for all types of coating. Dispersed boride structures were also found to have the highest load bearing capacity. Wear resistance of boride layers under vibratory motion and contact loading had also been studied. At constant amplitude (50 microns), the wear of borided surfaces over the range of loads studied was 1/2 to 1/3 that of uncoated C45 with a significant decrease in coefficient of friction. The working capacity of boride coatings was found to be retained up to 600 kg/cm² specific load. With varying amplitude, wear decreases but coefficient of friction increases, as the temperature of surface layers increases, favouring oxidation processes.

(iii) The effect of slip rate (rubbing wear) on the friction and wear of St 45 rings in vacuum and in air was the subject of another study by N.L. Golego et al. After boriding samples using pure B₄C to obtain a 120-130 micron two-phase layer, the specimens were subjected to friction and wear tests in vacuum (2*10⁻⁵ torr) and in air, at slip rates of 0.5-5.0 m/sec and a constant pressure of 10 kg/cm². It was found that at relatively low slip rates (athermal), 0.05-0.5 m/sec, substantial wear occurred, caused by brittle fracture and galling, both in vacuum and air. In the region of 0.5-1.5 m/sec in vacuum, the boride coatings cracked and individual particles were embedded in the surface. Slightly lower friction and wear coefficients were observed due to even distribution of normal loads over the entire working surface. Above 2.0 m/sec in vacuum, temperatures of rubbing surfaces reached 700°C - 800°C and a easily deformable composite layer of substrate and dispersed boride particles were
formed to a thickness of 10-15 microns. This resulted in lower coefficient of friction. In air, oxidation products (B₂O₃) melted and acted as liquid lubricants to give low friction coefficients and wear rates. Sticking in vacuum occurs at as low as 0.5-0.6 m/sec but only at 3.0 m/sec in air due to protective effect of oxide films.

(iv) T.S. Eyre [157] had extensively studied the friction and wear characteristics of boronised surfaces on various substrates, under the following conditions:

- Wear Test technique: Pin on disc method
- Materials treated (wear pin): EN 1A, EN 8, Grey CI
- Wear disc material: EN 24
- Coating applied:
  - EN 1A: normalised, carburized, boronised
  - EN 8: normalised, boronised
  - GCI: boronised, tufftrided
- Sliding speed: 300 cm/sec const.
- Normal load on pin: 3.1 to 28.0 kgs.
- Environment conditions: 20°C, 65% relv. humidity
- Pin dimensions: 7.5 cm long, * 6.0 mm dia. with flat ends.

It was concluded that Boronising prevented adhesive wear of EN 1A, EN 8 and GCI. It also improved wear characteristics of all materials investigated and had only one major disadvantage of inherent brittleness. Therefore it was recommended that applications involving impact loads and treating of components with sharp edges be avoided. The life of the boronished
layer was inversely related to applied load and the layer was found to have a higher load bearing capacity than tufftride. Wear above mild/severe transition load was inhibited during the lifetime of boronised layer and the coating was established to be far superior to other diffusion treatments investigated. Finally, boronised layers were able to retain their hardness upto 1000°C.

(v) Eyre has also noted that there is some evidence to suggest a relationship between the hardness of the surface layer, its thickness and the hardness of the substrate material. In the case of boronised steel under abrasive conditions a low wear rate was obtained only at 150 gms. on boronished 0.15%C steel whereas the same coating thickness produced a low wear rate at both 150 and 300 gms. on a 0.35%C steel.

(vi) Sliding wear characteristics of gas boronised stator (SAE 1045 pin) against a rotor (vacuum annealed disc) under un lubricated conditions was studied by E. Takeuchi. Using the weight loss method - the loss of weight is converted to weight loss/unit area and represented as wear loss - the mechanism of sliding wear of boronised steel was postulated from the results of wear characteristic curves, X-ray diffraction, SEM and EPMA of boron and oxygen on the sliding surface. Wear of FeB and Fe₂B were shown to be similar and maximum wear rates were obtained under a sliding velocity of 0.3 m/sec for FeB specimen and 0.5 m/sec for Fe₂B specimen. Under such conditions both mechanical and oxidative wear occurred, while under mild wear or wear at high sliding velocity wear loss was mainly by oxidative wear.
Subrahmanyam and Gopinath\textsuperscript{160} carried out unlubricated dry sliding wear tests using pin-on-disc machine on boronised mild steel pins, using hardened tool steel discs. A very significant finding was that single phase boride layers exhibited better wear resistance than two phase boride layers.
Fig 2.1 Fe-B Phase diagram

Fig 2.2 Cr-B Phase diagram
Fig 2.3 Si-B Phase diagram

Fig 2.4 C-B Phase diagram
Layer A: Single-phase layer, exclusively FeB
B: Two-phase layer of Fe₂B and FeB (complete layer)
C: Two-phase layer, FeB layer thinner than in layer B
D: Two-phase layer, but only isolated FeB teeth
E: Single-phase layer, exclusively Fe₂B, strongly toothed
F: Single-phase layer, exclusively FeB, less strongly toothed
G: Layer of individual Fe₂B teeth
H: Layer of very isolated Fe₂B teeth
I: Diffusion zone
K: Degenerate layer
L: Two-phase layer of FeB and Fe₂B, evenly laid on, not toothed
M: Single phase layer of FeB or Fe₂B, evenly laid on, not toothed