Boron occurs in nature invariably in combination with oxygen. It is present as boric acid (H$_3$BO$_3$); the most important borate minerals include Borax (Na$_2$B$_4$O$_7$.10H$_2$O), Boracite (Mg$_7$B$_{16}$O$_{30}$Cl$_2$), Borocalcite (CaB$_4$O$_7$.4H$_2$O), Boron atrocalcite (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$_{11}$.5 H$_2$O) and Kernite or Raporite (Na$_2$B$_4$O$_7$.4H$_2$O).

2.1 PROPERTIES OF BORON

Physical properties

Boron has an atomic weight of 10.81. Its melting point is 2465 K. Elemental boron has a hardness level of about 5000 HV. Boron exists as amorphous material upto a temperature of 1073 K. It has a crystal structure of rhombohedral nature between 1073 K to 1373 K. From 1373 K to 1573 K, it takes tetragonal crystal structure. Again above 1573 K, it takes up a rhombohedral structure.

Chemical properties

Boron combines very fast with oxygen at high temperatures. The heat of combustion with oxygen is 13.95 kcal/g. Its chemical reactivity depends on its crystal structure and grain size. In general, crystalline boron is relatively non-reactive, whereas micro-sized, amorphous boron reacts readily and sometimes even violently, with a variety of chemical agents. Boron forms borides with metals and metal oxides, boron carbide (B$_4$C) with carbon, boron nitride (BN) with nitrogen, and boron trihalides such as BCl$_3$, BBr$_3$ and BF$_3$ with halogens. Boron reacts with water at elevated temperatures to give boric acid and other products. It reacts with its oxide (B$_2$O$_3$) above 1273 K to give boron monoxide or other boron suboxides.
2.1.1 Applications

Boron has got wide applications even in its elemental forms:

- Boron is used in electronic devices as a doping agent.
- Cubic Boron Nitride is being used as an abrasive.
- In very small percentages, boron increases the hardenability of steels.
- Borided steel surfaces have very high hardness and wear resistance.
- In fibre form, as reinforcing material for composites.

2.2 METAL - BORON PHASE DIAGRAMS

It has been reported that Hannesen\(^2\) determined the Fe-B diagram up to approximately 8.5% boron, while Tschishewki and Herd\(^3\) developed it up to 11.5% boron. These studies were done by thermal analysis and microscopic investigations and the systems were reviewed by Wever and Miller\(^4\). Liao and Spear\(^5\) have reported the various phase diagrams between B-Fe, B-Cr, B-Co, B-Mn, B-Ti, B-Ni, B-Mo, B-V while Carlson\(^5\) has reported the phase diagrams of B-Al. Olesinski and Abbaschian\(^5\) have reported the B-Si phase diagram.

These phase diagrams indicate the solubility of boron in different elements and they also indicate the formation of various borides. From these phase diagrams, the melting points of the different borides can be determined. Iron-boron phase diagram is shown in Figure. 2.1.
2.3 DIFFUSION AND SOLUBILITY OF BORON IN IRON AND STEEL

In 1917, Tshischewsky\cite{6} found that iron heated in powdered boron or ferroboron acquired a hard, boron-rich case. Later, Campbell and Fay\cite{7} confirmed this case-hardening effect of boron and reported that boron penetrates steel in much the same manner as carbon.

Diggers, Irish and Carwile\cite{8} 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\cite{9}, 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\(^{[10]}\). They reported that the diffusion coefficient of boron in austenite can be represented by the equation:

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

Within the limits of experimental error, \(D_{\text{gamma}}\) appears to be independent of carbon content 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 \% but increases rapidly with temperature above 1198 K. The solubility of boron in alpha iron at 1108 K is about 0.002\%, which is 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\(^{[11]}\) subsequently calculated the diffusion coefficient of boron in alpha iron as:

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

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. McBride, et al.\(^{[12]}\) have also arrived at a similar conclusion based on theoretical considerations. Similarly, on examination of the rate of deboronisation and decarburisation of steel, Diggers et al.\(^{[8]}\) concluded that boron (just like carbon) occupies interstitial sites in austenite. Hayashi and Sugeno\(^{[13]}\) suggested that boron in alpha iron can occupy both interstitial and substitutional positions; on that basis they modified the D value as:

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

by considering the mechanism of dissociative diffusion.
Walser and Sherby\textsuperscript{[14]} have determined the grain boundary self diffusion activation energy of iron in alpha iron and gamma iron as 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. Brakeman et al\textsuperscript{[15]} have stated that the $Q_{\text{FeB}}$ is 175 kJ/mole and $Q_{\text{Fe2B}}$ is 157 kJ/mole for bilayer growth. Kunst and Schaaber\textsuperscript{[16]} have stated that 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 Lu\textsuperscript{[17]}, $Q_{\text{FeB}}$ is 82.5 kJ/mole and $Q_{\text{Fe2B}}$ is 105.5 kJ/mole for gas boriding of armco iron; and the activation energy for boriding is 132 kJ/mole, when both the layers are treated as one (with very little FeB) and boriding is carried out in Ekabor 2 powder. Matiasovsky\textsuperscript{[18]} reported the value of activation energy for boriding of low carbon and low alloy steels using electrolytic boriding process and as 175.51 kJ/mole in the range of 1023 - 1173 K for low carbon low alloy steel. Permyakov\textsuperscript{[19]} reports the activation energy for diffusion of boron in austenite of commercially pure iron as 84.2 kJ/mole (20.14 kcal/ g-atom). Danek and Matiasovsky\textsuperscript{[20]} have reported the activation energy for diffusion of boron in iron as 210 kJ/mole. According to Busby and Wells\textsuperscript{[11]}, activation energy for diffusion of boron in iron is 260 kJ/mole. Ozsoy and Yaman\textsuperscript{[21]} reported the value of diffusion coefficient (D) as $2.997 \times 10^{-9}$ cm$^2$/sec for conventional boriding processes at 1173 K.

### 2.4 BORIDING TECHNIQUES

Over the years, a number of workers from almost all over the world have worked on one or other form of boronising. 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 procedures.
2.4.1 Powder Pack Method

Powder pack bonding was the earliest known method of boriding and it is based on the use of amorphous boron, ferroboron, iron-boron-aluminium alloy, boron carbide, etc., as the packing medium around the components. The pack is placed 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, silicon carbide etc. Finally to accelerate the process, ammonium fluoride or chloride, or more popularly potassium tetra fluoborate is added.

Ferroboron was the first used boron source for pack boronising\textsuperscript{[6]}, by Tschischewsky in 1917. However, Von Mattushca\textsuperscript{[22]} states that the case was a discontinuous and degenerated one. Samsonov and Tseitina\textsuperscript{[23]} in 1955 adopted a method using amorphous boron with ammonium chloride for four h at 1173 K, which produced a 70 microns thick case. Gorbanov\textsuperscript{[24]} in 1958 suggested that a reducing hydrogen atmosphere facilitates the formation of thicker cases. Zemskov\textsuperscript{[25]} in 1964 used mixtures containing 84% B\textsubscript{4}C and 16% Borax and treated specimens of steel 45 for 6 h at 1223 K and produced cases of 150 microns thick. Voroshnin and Lyakhovich\textsuperscript{[26]} in 1966 found that the addition of ammonium chloride to boron carbide powder increased the thickness of the case by 15-20%. Protsik et al.\textsuperscript{[27]} in 1973 carried out boriding on steels using boron carbide and borax in the ratio 84:16 at 1223 K for 6 h. The boride layer thickness decreased with alloying elements, Mo and W having the greatest effect and Ni, Mn having lesser effect.

Loskutov et al.\textsuperscript{[28]} in 1973 have studied the kinetics of boronising and the structure and properties of diffusion layers formed after saturation of Armco iron, St20, St 45, U8 (AISI W1), Cast Iron and various cast alloys. Optimum temperature of treatment for St20, St45 & U8 was 1173 - 1223 K. Increase in concentration of carbide forming
elements Zr, V, Ti, Nb in alloys decreased boride layer thickness, with 0.29% Zr causing maximum decrease of 50%. It was further established that the carbon content of the steel had little effect on the hardness of the boride layer.

Zakhariev [29] in 1974 boronised iron and steel by heating components at 1273 -1373 K for 4 h, in contact with metal boride powders. This yielded diffusion layers of thickness about 0.16 mm. V.G.Permyakov et al. [30] (1974) boronised low and medium carbon steels at 1193 K and complex alloy steels (with Cr, W, Mo etc) at 1293 K, using commercial boron carbide. Komatsu et al. [31] 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 h at 1223 K. Moonllkim and Woon Kwan Yeo [32] in 1975 used a mixture of 10-15% potassium tetra fluoborate with Ferroboron to get a dense and thick case. Epik et al. [33] in 1977 presented boriding media and boriding procedures used in industry as shown in Table 2.1.

The choice of boride layer depths and corresponding saturation procedures are determined primarily by the type of boriding material and the purpose of preparation. High quality cases have been obtained in low-carbon steels. Epik and Sosnovski [33] 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 were those containing fluorine (e.g. KBF₄). The use of fluorides as activators makes it possible to produce a good quality surface and prevents B₄C particles from sticking to it.
Table 2.1. Thickness of Boride layer at saturation in different media

<table>
<thead>
<tr>
<th>S.No</th>
<th>Method of boriding</th>
<th>Layer thickness in microns</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Armco iron</td>
</tr>
<tr>
<td>1</td>
<td>Electrolysis in borax 1223 K, 4 hrs</td>
<td>250</td>
</tr>
<tr>
<td>2</td>
<td>70 % Borax + 30 % B4C 1223 K, 4 hrs</td>
<td>200</td>
</tr>
<tr>
<td>3</td>
<td>84 % B4C + 16 % Borax 1223 K, 4 hrs</td>
<td>170</td>
</tr>
<tr>
<td>4</td>
<td>79% Borax + 15% NaCl + Boron powder 1223 K, 4 hrs</td>
<td>240</td>
</tr>
<tr>
<td>5</td>
<td>Pack powder mix, Commercial B4C 1223 K, 4 hrs</td>
<td>220</td>
</tr>
<tr>
<td>6</td>
<td>Pack 98% B4C, 1.5% KBF4 1223 K, 3 hrs</td>
<td>230</td>
</tr>
</tbody>
</table>

Fishcein et al.\textsuperscript{[34]} in 1977 boronised 40KhCr steel with a mixture of boron carbide (initially roasted at 473 K for 2 h) and alumina. The above mixture yielded 110 microns case. Yu.Alimov\textsuperscript{[35]} in 1977 used commercial boron carbide (95%) with sodium fluoride (5%), to boronise Cr-Mn-W steel and medium carbon steel at 1173 - 1193 K for 4 h in containers with fusible seals. Continuous and acicular FeB crystals up to 75-90 micron case could be obtained by them. John and Sammels\textsuperscript{[36]} in 1981 have used a pack mixture of 20 % B4C, 5 % KBF4 and rest graphite. They state that initially Fe2B formed and after 2 h FeB started to form in the case in addition to Fe2B. Tsipas and Perez-perez\textsuperscript{[37]} in 1982 have borided steels, using a solution of Li2B4O7 in methyl alcohol, sprayed over a specimen maintained at 373 K. This resulted in a uniform deposit of Li2B4O7. The amount of Li2B4O7 deposit was about 1% of the
specimen weight. Subsequently each specimen was covered with B₄C and heated in a furnace at 1148 K in an argon atmosphere and in air for times varying between 2 and 48 h. According to the authors the Li₂B₄O₇ act both as generator of elemental boron and activator.

Chatynyan et al. in 1982 have attempted boriding using B₄C with 1.5 % AlF₃ at 1223 K for 2h. The structure showed both FeB and Fe₂B. Ruth Chatterjee-Fisher and Schaaber in 1986 carried out boriding treatment to increase the abrasion resistance of surface on steels and other metals. Steels were borided at 1173 K for 4.5 h 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 volume. During the boriding of C45 steel, an increase of dimension increase of 8 % on each side, was observed. Subrahmanyan studied the pack cementation process for boriding and mild steel, observed both FeB, Fe₂B phases. In this process the source of boron was B₄C and the activator was ammonium biflouride, KBF₄, or NaF. Boron carbide and one of the activators 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 1173 - 1273 K.

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 h to 12 h. The charge mixture based on "EKABOR", the trade name for a commercial boronising powder, has also been utilised as the main ingredient in this project.
2.4.2 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 only in 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.

Aliev\textsuperscript{[42]} in 1978 tried bonding of steel 20 and U8. The steels were first vacuum annealed and then borided using pastes containing (1) 70 % B\textsubscript{4}C and 30 % Na\textsubscript{3}AlF\textsubscript{6} and (2) 60 % B\textsubscript{4}C and 40 % Na\textsubscript{3}AlF\textsubscript{6}. 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.

Volkov et al.\textsuperscript{[43]} 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.

However several researchers are of the opinion that paste boriding is not so effective as pack boriding.

2.4.3 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 disadvantages of a need for regular maintenance,
replenishment of the bath composition, as well as the need to clean the components after treatment. Further, the reactions are usually based on reduction of the boron components and a need for low bath viscosity, both of which require high temperatures (1173 - 1223 K).

Morozava [44] in 1917 used a bath mix containing BaCl₂ - 45%, NaCl - 45% and B₄C - 10% which yielded a 250 micron case on C 45, at 1203 K for 5 h. Orning [45] in 1955 attempted an experimental bath containing 5% B₄C, 95% NaCl and NaBF₄, but satisfactory results were not obtained by him. Natchuki [46] in 1961 used ultrasonic waves to stir the bath and found that ultrasonic waves intensify the molten salt boriding process. Kaidash [47] 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 1273 K for 6 h produced 140 micron thick boride layer. However, it is more appropriate to call this paste boriding than fused salt boriding. The use of elemental boron (upto 12%) in a bath containing borates (Na₂B₄O₇, K₂B₄O₇, Li₂B₄O₇), operated between 1088-1448 K was found to accelerate the boriding process by Hill [48]. 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. Lyakhovich and Brigilevskaya [49] in 1968 borided steel 45 using borax and boron carbide in the ratio 60:40 for 4h at 1233 - 1243 K and they were able to get 0.18 to 0.20 mm. case depth.

Liquid boronizing was carried out by Kwon and Hahn [50] 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, and the melt also started deteriorating fast. The depth of the boronised case in stainless steel was about half that of low-C steel, when it was boronised under the same conditions. The borided case depth on 430 stainless steel was 20-30 % greater than that on 304 stainless steel. The 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 1223 K (approx) and (iii) boronising time 6 h (approx). Kato et al. [51] 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 temperatures as low as 1073 K, 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 rapid 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. Lyakhovich [52] in 1984 employed a number of boriding melts; three melts employed had the following composition:

(i) 80% borax + 20% CaSi
(ii) 70% borax + 20% B₄C + 10% SiC
(iii) 80% borax + 20% Fe Mn of Mn 5 grade

Belyaeva et al. [53] found that addition of oxides of heavy metals (PbO, BiO₂), phosphates (NaPO₄), sulphates (Na₂SO₄), alkalis (NaOH) and chlorides (NaCl) to borax allowed lower processing temperatures (823 - 973 K) by reducing the melting point of borax. Skomorokhov [54] in 1974 found that addition of Al and Mg to molten borax increased the depth of boronising. Boronising was carried out by Belyaeva, et al. [53] in 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 slurry. Boriding rate was two times higher with this mix than with than borax melt containing 40% boron carbide.

Matiasovsky [18] 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 in 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 bonded 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.

2.4.4 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.

Govorov \[55\] in 1944 found that the optimum current density for electrolytic boronising was 0.15 - 0.25 A/sq.cm. Taran and Skvgorova \[56\] in 1957, Boronised St35 in molten borax bath to produce 220 micron thick case in 4 h at 1223 K (current density 0.20 - 0.25 A/sq.cm). A current density of 0.75A/sq.cm was required to boronise St 40 to the same depth under similar conditions.

For economic and technological reasons, a bath composition of 40% borax and 60% anhydrous boric acid was attempted by Galushko \[57\] and proved successful. In such a bath, a 320 micron case was obtained on 0.5% C steel after 4 h, at 1223 K (0.2 - 0.25 A/sq.cm). Commercial grade borax with graphite electrodes as anodes was used to carry out electrolytic boronising by Myl'nikov \[58\] in 1957. Hammer forging dies (made of material 5 KhNV and OHkN3M) were boronised at 1193 - 1223 K for 3 h with a current density of 0.3 - 0.5 A/sq.cm. After subjecting the dies to different heat treatments, their operating life 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. Sorkin \[59\] 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 15h, and the graphite (anode) must be kept completely immersed in borax 15-20 min before starting the process. The distance between the anode and cathode should be atleast 15-20mm.
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 crucible, Shalya and Bordyug [60] (1968) suggested the use of 18 Cr 8 Ni steel or 25 Cr 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/sq. dm. 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 h. At temperature greater than 1273 K, boriding leads to formation of complex eutectics and pores and both of these impair the properties of the boride layer. At elevated temperatures, the sharp acicular borides are also blunted and made more smooth. 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.

Fiedler and Hayes [61] electrochemically borided AISI H11, H12 and H13 steels at 1173 K. 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 1273 K and tempered at 813 K. 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.

Electrolytic boronising has also been carried out by Orning and Schaaber [45] in a bath of 25% NaCl and 75% borax.

Han and Chun [62] investigated the effect of various activators such as Na2CO3, NaCl and NaOH (in molten borax) on the electroboronising of low-carbon steel (1015) at 1073 K. Their experiments showed that Na2CO3 was the most effective activator, followed by B4C, and NaCl. The most economic composition of activators was identified as 10 wt% Na2CO3, 10 wt % B4C, 20 wt % 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 boronised layer was more uniform and two times thicker than that formed with conventional electroboronising methods.

Ikuta and Taguchi [63] electrolytically boronised steel bars of St 45 in a fused borax bath containing 30% SiC at 1123 K. By adding SiC to the borax bath, the electrolyzing current was stabilized and the post-treatment was also improved. With intermittent electrolysis, the boronised layer was sound and thick relative to the one obtained by continuous electrolysis. But, the current efficiency decreased with increasing treatment time. The boronised 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.

Lyakhovich [52] claimed that (i) refining of the borax melt before the process 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 a less harmful effect than iron or nickel oxides, but even this also reduces the case depth and (iv) the cathodic current density must not be less than 0.3 A/sq.cm.

Pasechnik et al. [64] 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 1123 - 1173 K. Lower temperature (1123 K) should be used, for higher carbon steels. The current density was 0.1 - 0.2 A/cm² and the time 2 h.

Investigations were carried out on samples made from steel 20, steel 45 and steel U8A by Byakhova et al [65]. 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 1123 -
1373 K for 1 to 6 h. 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 1173 - 1223 K, in 3-4 h, at a current density of 0.2 A/sq.cm. After boriding the samples were cooled in air, reheated to 1053 - 1073 K and isothermally quenched to about 473 K where they were kept for 2 h. 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 [66]. They explained the results on the basis of correlations to electrode potentials. Boride coatings with hardness up to 1800 VHN were prepared by Khor [67] on AISI 1020 steels using an electrolytic process involving a molten borax - NaF bath. The parameters such as temperature 973 - 1173 K, time (1-6 h) and C.D (0.2 - 0.25 A/sq.cm) were varied during the experiments. This method produced a dual boride layer comprising of FeB and Fe$_2$B. The maximum thickness produced was 200 microns after 6 h of boriding. Khor claimed that treatments below 973 K did not produce any boride coatings on steels. For consistent boride layer thickness, fresh borax bath had to be used instead of refilled baths.

### 2.4.5 Gaseous Boronising

Gaseous boronising is reported to be the fastest among the conventional methods of boronising, because the high activity of the gaseous media leads to a faster diffusion. Its major and serious 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 using B$_2$H$_6$ or BCl$_3$ or BBr$_3$ with hydrogen.

Pchelkina and Lakhtin [68] boronised Carbon steels and high alloy steels including Austenitic steels in a mixture of B$_2$H$_6$ and H$_2$. They found that the case depth varied between 70 to 160 microns, depending on the type of material. The same authors [69] have used a mixture of BCl$_3$ and H$_2$ for gas boronising. In 3 h they obtained a 60 microns thick case on Armco iron at 1023 K and a 250 micron case at 1223 K.
Skugorova et al. [70] made an attempt to perfect the apparatus and technique of gas bonding in a super cooled mixture of \( \text{H}_2 \) with \( \text{BCl}_3 \) or \( \text{H}_2 \) with \( \text{B}_2\text{H}_6 \), by constructing a special laboratory scale apparatus. In this apparatus, the ratio of the concentration of \( \text{BCl}_3 \) and \( \text{H}_2 \) 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 973 to 1223 K. Boronising St20 pipe of diameter 20 x 16 mm and of length 20 mm yielded high quality boride layer of maximum hardness 2200 HV. Gas boronising at 1193 K for 2 h gave a case depth of 120-150 microns.

Linial [71] found that gas boronizing (CVD) method was particularly advantageous when coating has to be controlled 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 \( \text{Me(BH}_4 \text{n)} \) can be carried out at a temperature as low as 573 K under normal pressure. Well-adherent functional coatings, however, can only be obtained above 1073 K. Also he concluded that handling halides is much simpler than handling of inflammable hydrides and also considerably less expensive.

An experimental plant for gas bonding in a mixture of \( \text{BCl}_3 \) and dissociated \( \text{NH}_3 \) has been described by Kuleshov et al. [72]. This apparatus was found suitable for a wide variety of products in laboratory conditions and in actual production conditions. The bonding plant makes it possible to produce high quality hard \((\text{HV 50} =1600\text{-}2000)\) boride layers of practically any depth and phase composition. The plant is simple to operate and permits the hardening of parts directly after bonding without reheating.

P.Gouriet [73] et al. developed a gaseous boriding process which is simple, economical and industrially reliable. In this process, \( \text{B}_4\text{C} \), \( \text{SiC} \), an activator \( \text{BF}_3 \) gas and a moderator (Silica or alumina) are used. In the reactor, the \( \text{BF}_3 \) gas is passed through the silica bed at a temperature greater than 723 K. The \( \text{BF}_3 \) gas gets converted to \( (\text{BOF}_3) \) gas and it is then passed through the boriding agent containing the boridable sample at temperatures in the range 1073 - 1273 K. On plain carbon steels, this produces a single phase \( \text{Fe}_2\text{B} \) layer and on Chromium steels this produces a strongly adherent but brittle case with \( \text{FeB} \).
Boriding has been carried out by Smirnov\textsuperscript{[74]} using a mixture of diborane (B\textsubscript{2}H\textsubscript{6}) 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 398 K in dry air and in the presence of traces of moisture and other hydrates can explode even at room temperature. Boron trichloride (BCl\textsubscript{3}) has proved to be most convenient due to its low boiling point (295.6 K), but it strongly irritates the mucous membrane and in a liquid state it causes burns. Mixing dissociated NH\textsubscript{3} with BCl\textsubscript{3} at 1073 - 1273 K can result in effective boriding of specimens.

Kuleshov\textsuperscript{[75]} states that boride layers on steels, obtained in a gaseous mixture containing BCl\textsubscript{3} 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 BCl\textsubscript{3} than Fe, e.g., Ni.

\textbf{2.4.6 Recent Advances}

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.

\textbf{2.4.6.1 Powder deposition in welding}

Levitsky and Kasumzade\textsuperscript{[76]} found that acceptable 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 30 A/sq.mm. 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{77} reported a novel method for boronising by the use of electrically conductive particulate mixture in a rotary retort.

2.4.6.2 Plasma boriding

Boriding of steel in a cold R.F Plasma of diborane in argon has been investigated by Grill et al.\cite{78}. The advantages of such a process would be low operating temperatures (873 K) 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 M Hz generator. The diborane dissociates in the plasma and the boron is deposited onto the surface of steel and diffuse into the substrate.

Boron deposition on a steel specimen under glow discharge in a $H_2$ with $BCl_3$ mixture has been investigated by Filep et al.\cite{79}. The highest efficiency of the process was found to be 27% at 1073 K, when using an initial $BCl_3$ concentration of 0.2 -10%; this efficiency was higher by an order of magnitude than other 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.

2.4.6.3 Laser boronising

An attempt was made by Molian and Rajasekhara\cite{80} 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 significant hardness gradients along the thickness of laser melted coating. Armco iron, AISI T1 tool steel and M2 high speed steel were initially boronised in a pack mixture, for 2-10 h at 1273 K and air cooled, and subsequently irradiated with 3 continuous wave $CO_2$ lasers with power levels of
1.2, 2.5 and 5 kW. The 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 [M₂B + 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.

2.4.6.4 Superplastic boronising

Xu, et al [81] have attempted 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 obeys a parabolic law and superplastic boronizing follows an approximately linear relation. During superplastic boronizing high defect densities are generated and this increases the rate of boronisation.
2.4.6.5 Multi component boriding

This method involves the simultaneous diffusion of boron and one or more metallic elements, such as Cr, Al, Ti, Si, Zr and V, into the surface of the substrate. These coatings are expected to have better wear resistance, higher toughness values, and better corrosion resistance than conventional boride coatings.

Boro-Aluminzing

This method involves simultaneous insertion of boron and aluminium as evident from the name of the process.

The Russian workers Zemskov and Kaidash \(^{[82]}\) attempted powder boro-aluminizing of steels. They observed that boro-aluminized steels have higher strength and heat resistance. The heat resistance of boronised and then aluminized steels increases by a factor of 40-45 at 1173 - 1273 K. Combined saturation of steels with B and Al was carried out with B\(_4\)C, borax, Fe-Al and NH\(_4\)Cl mixture. The composition employed contained 75% of the (95% Fe-Al + 3% NH\(_4\)Cl) mix and 25% of the (84% B\(_4\)C + 16% Borax) mix. When the process was carried out below 1173 K, only borides formed, but above 1173 K both borides and aluminides were observed. Prosvirin \(^{[83]}\) 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 373 K for 1.5 to 2 h and then heated to 1073 K. When more than 2% of Al was used in the paste, the depth of the diffusion coating decreased. Boriding with a paste containing 10% Al yielded Fe\(_2\)B phase alone and the FeB phase was absent. The lattice constants of the boride were \(a = 5.132 \, \text{Å}, c = 4.220 \, \text{Å}\) and \(c/a = 0.822\). Boro-aluminizing produced 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{[84,85,86]} had attempted simultaneous diffusion of boron with other elements – Cr, Al, Zr. According to them, 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 almost 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 the reaction with borax, but remains in the ionic condition. As a consequence, one would expect the discharge of Cr ions on the cathode during boro-chromizing.

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 boro-aluminizing, aluminium is deposited on the cathode due to “the sodio-thermic reaction”:

\[ 3 \text{Na} + 2 \text{Al}_2\text{O}_3 = 3 \text{Na}_2\text{Al}_2\text{O}_4 + \text{Al} \]

For C45 steel, the formation of iron borides alone was observed at current densities below 0.15 A/cm$^2$. Above 0.15 A/cm$^2$, chromium boride and chromium carbide formed in the diffusion coating. When boron and aluminium are diffused into the coatings, stable alpha phase forms first 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 1023 – 1073 K) than that of iron borides.

Boro-aluminide coatings were prepared\textsuperscript{[87]} using a mixture containing 25 wt\% boron – containing component (84\% B$_4$C + 16\% Na$_2$B$_4$O$_7$) and 75 wt \% aluminium – containing component (98\% Fe-Al + 2\% NH$_4$Cl). It is found that iron borides have a lower heat resistance than aluminides.
Zemskov et al. [88] report that Boro-aluminising improves thermal stability, corrosion resistance and fatigue strength. The authors had boro-aluminized commercial iron and C45 steel either by simultaneous or successive diffusion impregnation. For simultaneous impregnation 50% powders of boron and ferro-aluminium, 45% aluminium oxide and 5% NH₄Cl were used in powder form. At 1223 K both B & Al diffuse into the metal. Below 1173 K, only Al diffused, but above 1323 K, the quality of sample deteriorated. The boride phases were FeB (1600 kg/mm²) and Fe₂B (1300 – 1000 kg/mm²).

To obtain boro-aluminized layer, boriding was carried out first using borax + boron carbide at 1173 K for 2 h. The layer was 110 mm thick with FeB and Fe₂B layers. Then this material was aluminized. The hardness of the aluminized zones were 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 aluminized (1223 K, 2 h) and then borided (1223 K, 2 h), 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 towards the core, while borides and aluminides were formed on the surface.

Parketa, et al. [89] report that aluminizing and then boriding reduces the hydrogen permeability of Kh 18 N 10 T steel. Aluminizing was carried out in powder mixtures with Al₂O₃ – 82%, Al – 15%, NH₄Cl – 3% at 1173 K, 1 h and boriding in 84% B₄C + 16% borax at 1223 K, 6 h. An aluminized layer of 90 μm 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 1073 K – 813 K 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 1073 - 673 K and at elevated temperatures hydrogen accelerates a redissolution of diffusion layer. Kaidash et al. [90] achieved a boro-aluminised layer over steels with case depths in the range of 150 – 375 microns in six h by pack method, using B₄C (84 %) + Na₂B₄O₇ (16 %) as the boron source and FeAl (97 %) + NH₄Cl (3 %) as the aluminium source in various ratios.
**Boro-Chromising**

Meirer et al. have stated that chromizing increases the oxidation and corrosion resistance of ferrous alloys. A typical pack mixture for chromising is 30% (Cr or Fe-Cr), 5% halide activator and 55% filler (Al₂O₃ by weight). The halide activators used were CrCl₂, FeCl₂, NH₄Cl and NH₄F. The samples embedded in the packs were heated to 1423 K for 0.1 to 28 h and cooled to 873 K in 2 h.

Alimov et al. found that boride coatings are very hard (1800 – 2200 HV) 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 only to applications which experience friction during a static loading and applications which require resistance to wear in an abrasive medium. According to them, diffusion chromizing gives a hardness up to 1500 – 1800 HV. Chromized steels are characterised by an increased 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 three types of chromium borides, namely, CrB₂, Cr₂B and Cr₅B₃. Boron prefers to combine with Cr than Fe because B has greater affinity for Cr than for Fe. The boro-chromized layer has lower hardness compared to boride layer but shows an improved wear resistance and improved plasticity. Kal'ner et al. state that successive boro-chromizing increases the heat resistance, wear resistance and corrosion resistance of steels. Boro-chromizing 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 chromizing was done in a vacuum furnace by the non-contact method. The working space was first evacuated to 1.33 Pa pressure and then CCl₄ vapour is filled into the reaction space. The chromizing source was chromium lumps (1-5 mm). During boriding, FeB and Fe₂B layers are formed, and during chromizing 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 boro-chromium glass seals the defects, and this layer gives the greatest oxidation resistance at 1173 K. Kogan et al. prepared a boro-chromized layer by the successive
method of the two-stage technique. This boro-chromizing technique, as compared to boriding alone, results in greater hardness, higher corrosion resistance, oxidation resistance and more toughness. The boro-chromized samples were subjected to cyclic loading and then the fracture topography and 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 boro-chromizing by 40%. Carburizing and nitriding increases the fatigue limit by 20 to 60%. Boro-chromizing increases the corrosion fatigue strength of steel 45 by 2.5 times in a 3% NaCl solution.

Ruth Chatterjee et.al. [95] concluded that boro-aluminising coating is ideal for wear resistance applications under humid conditions where as boro-chromising coatings are both wear resistant and corrosion resistant.

2.5 STRUCTURE AND PROPERTIES OF BORONISED SURFACES

2.5.1 Structure

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 depends on the composition of steel, boronising method, activity of boron in the boriding medium, temperature, time and other treatment conditions.

Effect of composition

According to Carbucicchio et al. [96] mainly FeB and Fe₂B acicular borides are formed in carbon steels. These borides are oriented perpendicular to the surface. In addition to these borides, in high carbon steels elongated inclusions are seen whose orientation differ from that of borides. These inclusions are probably boro-cementite whose microhardness is 900-1100 kg/mm². 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 Fe₃(C,B). When boron concentration increases from 0 to 5.2 wt%,
the lattice parameter 'b' changes from 5.079 to 5.405 Å while the parameter 'a' decreases from 4.515 to 4.450 Å and 'c' from 6.748 to 6.669 Å, according to Lyakhovich et al. [97].

In general, the presence of alloying elements reduces 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 moderate influence and nickel, manganese, and cobalt have only a marginal influence. During boronising, redistribution of the alloying elements takes place depending on the solubility of the elements in the iron boride 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. The formation of this soft layer has been observed in high silicon steels and siliconised steels. The displacement of silicon from the iron boride during its growth can result in the formation of iron silicon borides. 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. In plain carbon and low alloy steels, the borides grow as columnar aggregates of crystals giving rise to tooth like morphologies of the FeB / Fe₂B and Fe₂B / Fe interface and on alloy steels almost flat boride matrix interface was created [98].

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 [99].

In steels C and Si diffuse ahead of boron and concentrate in a layer immediately beneath the boride, while Cr and Mn diffuse into the FeB layer [100]. Carbon segregates towards the matrix [101].
Effect of Cr

Cr reduces boride layer thickness and flattens out the characteristic tooth shaped morphology. When it is in excess of what FeB and Fe$_2$B could absorb, it segregates along the boride-metal interface. When Cr concentration is higher, distinct Cr borides (CrB) form. In the case of 304 steel chromium concentrates at the interface between the boride layer and the matrix. Chromium has a more pronounced effect on coating thickness and morphology than Manganese.$^{102}$

Cr, upto 5.65 wt %, was able to fatten appreciably the Fe$_2$B / Fe interface. Cr and Mn preferentially enter the Fe$_2$B phase, depleting the underlying unborided matrix.$^{98}$ It was found that both the elements (Cr and Ni) enter iron borides, thus substituting for iron in the lattice. Cr however concentrates in the coatings, depleting the underlying unborided matrix, while Ni preferentially concentrates beneath the boride coatings, allowing low-Ni iron borides to be formed. Growth of boride crystals are in [002] preferred direction.$^{103}$

FeB is orthorhombic, (a = 4.061 Å, b = 5.506 Å, c = 2.952 Å) and Fe$_2$B is BCT, (a=5.109 Å, c= 4.249 Å, c/a = 0.832). Iron borides have covalent - metallic bonds with a predominance of metallic nature (particularly in the case of Fe$_2$B, in which the bond is almost metallic).

The chromium boride Cr$_2$B is isomorphous with Fe$_2$B. The type of bond in Cr$_2$B is same as in Fe$_2$B. The lattice constants of these two borides are fairly close to each other (a = 5.180 Å and c =4.316 Å for Cr$_2$B). The difference in atomic radius is 1.5%. Thus Fe$_2$B and Cr$_2$B must be mutually soluble to a considerable extent. However, between Cr$_2$B and FeB, the mutual solid solubility is low.$^{104}$

Effect of Ni

Ni reduces boride layer thickness and flattens out tooth shaped morphology. Ni has been found to concentrate beneath the boride coatings, enter the Fe$_2$B layer and in some cases precipitate as Ni$_3$B out of the FeB layer. Ni is partially incorporated in FeB and Fe$_2$B. When it is in excess, Ni borides will form.$^{105}$
During boriding, Ni segregates towards the surface and chromium is scarcely affected. The Ni segregation to the surface at high boron reactivity severely hinders the successful boriding of highly alloyed steels like austenitic stainless steels.

**Effect of Mn**

Mn also reduces boride layer thickness and flattens out tooth shaped morphology. Mn is also found to concentrate in Fe$_3$B layer.

**Effect of Mo**

In molybdenum steels, concentration is lower in FeB than the original concentration in the Fe$_2$B boride. The transition zone is enriched with Mo, since during boriding Mo is forced from the boride zone into the base metal.$^{[106]}$

**Effect of Ti**

Ti is mainly concentrated in Fe$_2$B. The Ti concentration in FeB matches the original concentration in steel and there is impoverishment of Ti in the transition zone.$^{[106]}$

During boriding of carbon steels, a ‘transition zone’ differing in the structure from the core, forms 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 base 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.$^{[102]}$
Si is also strongly displaced from the surface and concentrates below the boride layer. Its amount in the zone adjoining the boride layer rises to such an extent that it results in gamma to alpha transformation \cite{102}.

Ti, Mo, Cr and Si reduce the depth of boron penetration and Ni has practically no effect on it. The intensity of the inhibiting effect exerted on the diffusion rate of boron in austenite (0.4 %C) decreases from Ti to Si.

Ti, Mo and Cr largely neutralise the adverse effect of carbon and boron on the growth of austenite grains in the transition zone. Ni and Si have practically no effect on this phenomenon.

Lyakhovich and Voroshnin \cite{105} have found that if the carbon content is increased from 0.1 to 0.4%, the depth of the boronized layer decreases considerably. If the carbon content is increased from 0.4 to 0.75%, the depth of the case is not influenced, but if the carbon is increased to 1%, the depth decreases considerably. The same workers have found that in electrolytic boronizing the carbon content has no influence on the depth of the boride layer but affects the total depth of the case.

It has been found that most of the alloying elements slow down the growth of the boronized layer. The greatest decrease in growth rate is caused by molybdenum, tungsten, chromium, aluminum and copper have a less pronounced influence, while nickel, cobalt and manganese have little influence on the depth of the boronized layer. All these alloying elements except aluminum and copper, increase the FeB content in the case.

Lyakhovich and Voroshnin \cite{105} report that borided layers on mild steel, low alloy and high alloy steels have same composition and consist of iron borides (FeB, Fe₂B) and an alpha - solid solution. Alloifying elements do not affect the phase composition of the boride layer, but change the proportion of the boride phases. The lattice parameters of

\[
\text{Fe}_2\text{B} \quad a = 5.100 \text{ Å}, \quad c = 4.241 \text{ Å}, \quad c/a = 0.841
\]

\[
\text{FeB} \quad a = 4.059 \text{ Å}, \quad b = 5.495 \text{ Å}, \quad c = 2.952
\]
Certain alloying elements replace iron atoms in the borides. Si probably replaces boron atoms in the borides. Mo and W, during boron impregnation move from surface towards core. Ni and Si diffuse towards surface. The boride coating deposited from the sodium melt with no carbon consists of four layers with a total thickness of up to 200 microns. According to the results of structural examination methods, the very thin external layer of the specimen consisted of iron diboride (FeB₂) which was difficult to etch and could not be easily detected by metallographic examination. This phase was determined by layer-by-layer - X-ray diffraction analysis. Two subsequent layers are the main layer in the coating and consists of FeB and Fe₂B borides.

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 the area in which FeB predominates is characterised by the formation of tensile stresses; however, compressive stresses form in the underlying zone with Fe₂B.

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 boro-cementite, Fe₃(B,C), where up to 80% of carbon can be replaced by boron.

**Effect of reactivity**

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; the interface Fe₂B / Fe assumes a strong columnarity; when all active boron can be consumed as Fe₂B with low reactivity (e.g. Armco iron in contact with crystalline boron), the interface assumes a low columnarity. 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 Fe$_2$B / Fe interface. Cr and Mn preferentially enters the Fe$_2$B phase, depleting the underlying unborided matrix. Ni on the contrary, concentrates beneath the Fe$_2$B / 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 Fe$_2$B / 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 [98].

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. Crystalline boron (too mild a boronizing medium) on annealed high purity iron samples, carburised upto 0.3% C, and cold rolled upto 22% thickness reduction, even 1273 K, for 15h 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 [107].

When 2-4% Cu powder was added to the boriding mix (84 % B$_4$C + 16% Borax), the case depth was reduced by a factor of 1.5 – 2 [108].

When low C or medium C Steel were borided with low boron content media only Fe$_2$B 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 [104].

Low boron activity (gaseous boriding) can produce good quality Fe$_2$B layer with reduced Ni segregation [101].

When reactivity is high both FeB and Fe$_2$B will form and when activity is low only Fe$_2$B will form [109].
When bonding of AISI 1008 steel was carried out using 20 mole % $\text{B}_4\text{C}$, 5 mole % $\text{KBF}_4$ and 75 mole % graphite, coating developed a good crystalline structure only after heating times greater than 1 h. At times greater than 2 or 3 h, the FeB phase began to dominate the surface layer \cite{100}. The columnar morphology of the coating grows with time \cite{103}. 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 Fe$_2$B 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 $\text{FeC}_0.2\text{B}_{0.8}$ beneath the boride layer, longer processes produce pure cementite.

Pchelkina and Lakhtin \cite{111} 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 973 - 1023 K, no diffusion of boron takes place whatever the method of boronizing, except gas boronizing which proceeds at a considerable rate even at 773 - 823 K. Boronising in powder mixtures of boron carbide and borax at about 1050 K produces cases consisting of Fe$_2$B and an intermediate layer. Boronized cases produced at 1123 - 1273 K 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 1373 K, the diffusion of boron into steel is uniform and the resulting layer consists not of acicular but of grains of a uniformly distributed eutectic. Boronizing at 1473 K 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 a considerable hardness which are described by some authors as cementite, while others believe them to be boro-carbide. 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 h of boronising) and an increase in
the carbon content from 0.2 to 1.2% decreases only slightly the depth of the case. If the process duration is increased, the influence of the carbon content becomes more pronounced (the depth of the case decreases by 20-25% in processes lasting 6 h).

2.5.2 Properties

Iron borides are quite resistant to naphthenic acids present in oil refineries. Also iron borides are highly resistant to high temperature oxidation, according to Trash [112]. He stated that boride layer gives improved corrosion - erosion properties, used for increasing adhesive and abrasive wear resistance of metals, quite resistant to attack by molten metals and acid media corrosion. Also, the formation of Fe₂B alone is desirable, because of its lower degree of brittleness compared to FeB.

Compared to paste technique, powder technique produces a layer with less proportion of FeB, and this layer has less cracking tendency[114].

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 a difference between the maximum and minimum values of penetration depth may impart a brittle behaviour to the very hard brittle borides [98].

Mechanical compactness and hardness of the layers appear to be linked to the extent of crystallographic order [115].

Hardening and high temperature annealing of borided steel 45, does not have much influence on the hardness of borides. The micro hardness of FeB in 0.2 & 0.45 % C steel is 1800-1900 kg / mm² and Fe₂B phase is 1450 kg/mm², while in 0.8 % C steel the microhardness of Fe₂B phase is 1600 kg/mm². Hardening and high temperature annealing of borided 45 steel has no influence on the microhardness of borides because of their high thermal stability. Heating to 1103 -1113 K produces no structural or concentration change. The dimensional changes during boriding is less for steel 45 when compared to steel 20. Boriding reduces surface finish [100].
Kunst and Schaaber [16] have suggested a layer evaluation system to predict the performance of boronised surfaces, Figure 2.2.

**Figure 2.2 Type of boride layers**

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
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. 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.

![Figure 2.3 Typical two phase layers of borided steel](image)

The microstructure of typical two phase layers (FeB and Fe$_2$B) is shown in Figure 2.3. 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 /sq.cm.\textsuperscript{116}.
Pokhmurskii et al.\textsuperscript{[108]} also state that electrolytic boriding to a depth of 0.15 mm, followed by a heat treatment, markedly lowers the fatigue limit of constructional chromium-silicon steel. Contact boriding in a mixture of $\text{B}_4\text{C}$ and borax to a depth of about 0.15 mm without subsequent heat treatment raises the fatigue limit of type 20 steel by about 15\% and that of type 45 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 case thickness and subsequent vacuum annealing raises the fatigue limit of type 45 steel specimens of 8 and 5 mm in diameter by about 15 and 30\%, respectively.

From the viewpoint of corrosion-fatigue behaviour, through-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.

Karpenko et al.\textsuperscript{[117]} 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.

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 arbitrary corrosion fatigue limit. Thus, for Type 45 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. Roughly similar relationships are observed also for Type 20 and U8 steels. For Kh17 steel, the highest fatigue limit is recorded at a layer thickness of about 0.06 mm. The fatigue limit of Kh17N2 steel sharply falls with increase in layer
thickness, the decrease being particularly intense in the layer thickness range 0.01-0.1mm. At a boride layer thickness of about 0.12-0.13mm, the fatigue limit is approximately equal to the arbitrary corrosion fatigue limit.

The arbitrary corrosion fatigue limit of carbon steels has a tendency to rise with increase in layer thickness, while that of Kh17 steel passes through a distinct maximum at a layer thickness of about 0.06 mm.

The improvement in the fatigue limit of carbon steels may be attributed to the presence of high residual compressive stresses (up to 80 kg/mm²), 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 Kh17 stainless steel is attributed 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 increases 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 Kh17N2 steel 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 subboride zone, in which carbides are precipitated along the grain boundaries. Such boundaries in the subboride layer act as structural stress raisers, lowering the fatigue strength of the steel.
Trush et al. [112] claimed 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 1073 K. Above this temperature the thickness of the FeB layer decreases, and thus the percentage of this phase in the boride layer also decreases. This leads to an increase in the thickness of Fe2B above 1173 K until the disappearance of FeB. Fe2B phase is stable up to 1273 K, 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 Fe2B. The microhardness values of borides remain unchanged at all temperatures where they remain stable.

Lyakhovich et al. [118] reported that up to 1123 K, 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 1123 - 1173 K. This may probably be due to the beginning of dissociation of boride (FeB) in air atmosphere. At 1173 K, the oxidised borided surface is much more porous. The presence of atmospheric oxygen accelerates the diffusion processes taking place during heating, so that they begin at lower temperatures than in the case of heating in a non-oxidising atmosphere.

Lyakhovich et al. [119] reported that in electrolytic boriding, the following three zones are observed. FeB; FeB + Fe2B; and Fe2B + 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 the borided steels were reheated and quenched in water, the residual stress in the Fe2B and Fe2B + substrate zone decrease. This decrease is due to volume effect. Tempering borided steels in the range 473 - 873 K, leads to an increase in the magnitude of the residual compressive stresses in the boride layer.

Bloyce et al. [120] stated 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 Fe2B. 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 1173 K. 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.

Kogan et al [121] state 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 must 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 an 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 borides (FeB and Fe₂B) have different coefficient of linear expansion. The coefficient of linear expansion at upto 673 K are 9.97 x 10⁻⁶ and 7.67 x 10⁻⁶ mm/mm for FeB and Fe₂B respectively (and for steel with low carbon, the coefficient of thermal expansion is around 13.4 x 10⁻⁶ to 13.7 x 10⁻⁶ mm/mm). On cooling from boronizing temperature, the core contracts to a greater degree and boride layer with relatively lower contraction impedes 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 and FeB is lacking in the diffusion layer. The maximum value of compressive stress is shifted from the surface towards the core when the layer depth increases. Maximum compressive stress decreases and also shifted towards core, when layer depth increases. At a depth of the boronized layer of less than 100-200 microns, 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.

Summarising on the fatigue properties, we can say that boronizing only slightly increases the fatigue strength of steel 45 regardless of the method used. 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%. However, the increase in corrosion fatigue limit of medium carbon steels due to boronising is marginal.

2.5.3 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.

1. Golego et al [122] arrived at a number of interesting characteristics on finely dispersed boride structure. St 45 specimens were powder boronised and were induction heated and rapidly cooled to produce finely dispersed boride structures.

Dispersed boride structures were also found to have the highest load bearing capacity.

Wear resistance of boride layers under vibratory motion and contact loading was also 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 St 45 with a significant decrease in coefficient of friction.

The working capacity of boride coatings was found to be retained at upto 600 kg/sq.cm specific load. With varying amplitude, the wear decreases but coefficient of friction increases, as the temperature of surface layers increases favouring oxidation process.
2. 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 [122]. After boriding to obtain a 120-130 micron two-phase layer, the specimens were subjected to friction and wear tests in vacuum (2 x 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 substantial wear occurred, caused by brittle fracture and galling, both in vacuum and air. At higher slip rates the wear was less, with decreased coefficient of friction, due to probably increased temperature and tendency of oxides to melt and act as liquid lubricant.

3. Eyre [123] had extensively studied the friction and wear characteristics of boronised surfaces on various substrates. His study on ferrous materials 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, namely, inherent brittleness. Therefore it was recommended that boriding for applications involving impact loads and for components with sharp edges be avoided.

The life of the boronised layer was inversely related to applied load and the layer was found to have a higher load bearing capacity than tufftrided specimens. Boronised layers were able to retain their hardness upto 1273 K.

4. The improvement of wear resistance of carbon steels was attributed, not solely to the high hardness of the Fe₂B phase, but also to its tetragonal structure and chemical composition. Under abrasive conditions, resistance to wear was determined mainly by hardness, and was also proportional to layer thickness. Further, the abrasive wear resistance was found to be affected by the metallurgy of the substrate matrix.

5. Iyer and Sridhar [41] investigated the weight loss on boronised and untreated carbon steels by sand blasting. The superiority of boronised samples was established by their low abrasive wear rates.
6. The effective use of scanning electron microscope with debris analysis was made by Subhramanyam and Gopinath\cite{124} to study the wear characteristics of boronised mild steel containing FeB, Fe₂B or both phases.

The boride layers give a very high hardness compared to surface layers hardened by other processes, as shown in Table-2.2. The boride layers also improve the wear resistance considerably.

**TABLE 2.2**

*Surface hardness of borided steels in comparison with other materials*

<table>
<thead>
<tr>
<th>Material</th>
<th>Microhardness Kg/mm² or HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borided mild steel</td>
<td>1600</td>
</tr>
<tr>
<td>Quenched carbon steel</td>
<td>900</td>
</tr>
<tr>
<td>High speed steel</td>
<td>900 - 920</td>
</tr>
<tr>
<td>Carburized steel</td>
<td>650 - 950</td>
</tr>
<tr>
<td>Nitried steel</td>
<td>650-1400</td>
</tr>
<tr>
<td>Hard chromium plating</td>
<td>1000 - 1200</td>
</tr>
<tr>
<td>Cemented carbides</td>
<td>1100 - 1800</td>
</tr>
<tr>
<td>Al₂O₃ + ZrO₂ ceramic</td>
<td>1500</td>
</tr>
<tr>
<td>TiN</td>
<td>2000</td>
</tr>
<tr>
<td>TiC</td>
<td>3500</td>
</tr>
<tr>
<td>SiC</td>
<td>4000</td>
</tr>
<tr>
<td>B₄C</td>
<td>5000</td>
</tr>
<tr>
<td>Diamond</td>
<td>&gt; 10000</td>
</tr>
</tbody>
</table>

Eyre\cite{125} compared the wear life of boronized layers with those from other surface treatment such as Tufftriding and showed that boronizing is superior to other treatments. They proposed on oxidative and mechanical type of wear mechanism.
The diverging views on the wear mechanism of the boronized layers could arise because boronizing can produce surface layers containing FeB or Fe2B or both the phases. FeB is a hard brittle phase and Fe2B is the softer and more ductile phase. In combination these borides may exhibit complex wear behaviour. FeB, Fe2B and both the phases were obtained on mild steel using a pack cementation process \[124\]. In this process a source of boron and an activator were mixed thoroughly. The specimen was packed in stainless steel retort. Ammonium biflouride and boron carbide were used, as activator and boron source respectively. The boride layers were obtained with 1-2\% activator at temperature in the range 1173 - 1273 K. By suitable choice of the pack composition and temperature, surface layers containing Fe2B alone or FeB alone or both phases were obtained.

Wear tests were carried out using a pin-on-disc machine under unlubricated dry sliding conditions \[124\]. The worn surfaces were examined using a scanning electron microscope.

With increase in time, current density and temperature, the depth of the borided layer increases, but the boride needles oriented perpendicular to the surface of the part gradually come together and the boundary separating the iron-borides from the base metal becomes almost rectilinear as a result of which the contact area and the strength of the bond between the borided layer and base metal decreases. Such a deviation from the optimum boriding conditions therefore reduces the wear resistance of the borided parts.

Sorkin \[126\] claimed that due to acicular structure of the borided layer in plain-carbon steel, the bond with the base metal is stronger in carbon steels than in the case of alloy steels, where the interface of the borided layer is a straight line.

2.5.4 Limitations of Borided Structures

In general the borides produced in plain carbon steels and low alloy steels have a saw-tooth shape. These sharp tipped borides in the microstructure result in reduced toughness by acting as internal notches or stress risers. Bloyce, Deargley and Bell \[120\] very clearly expressed the main disadvantage of borided layer with saw toothed structure. There are not many workers who have reported on attempts to modify such structures.
In order to reduce their embrittling effect, a variation in the boriding treatment was attempted \(^{[127]}\). The boriding process was interrupted every one hour by cooling the specimen to a temperature well below the critical temperature (\(A_1\)). The boriding container was removed from the furnace after every one hour of boriding and cooled to a temperature below 873 K. Instead of boriding continuously for four hours, four one hour boriding passes were given. The interrupted boriding gave borides of slightly different shapes. The tips were more rounded, shorter in lengths and thicker. Consequently they showed better mechanical properties like toughness, though maximum hardness value attained was lower than that in continuous boriding.

Bloyce et al \(^{[120]}\) have tried surface remelting done on boronized ferrous materials using laser beam. The resolidified boride layer hardness profile and as borided hardness profile are discussed in their paper. The boron is taken into solution during melting and is redistributed throughout the melt depth, the magnitude of which depends on laser treatment parameters and substrate properties. It is substantially deeper than the case achieved directly by boronizing.

Yan and Zhu \(^{[128]}\) tried to remelt surface by micro beam plasma arc, with some limited success on Fe-Cr-Si-B over layer. Lin and Han \(^{[129]}\) worked to modify the borided needles using flame spray. Depending on the flame spray coating material, the boride case thickness and morphology of microstructure also showed a marked variation. Agarwal and Dahotre \(^{[130]}\) worked on pulse electrode deposition of super hard boride coating on ferrous alloy. Deger et al \(^{[131]}\) attempted to introduce soft crystals of aluminium and silicon in small particulates into the boriding agents. These soft crystals, when they occupy positions in between the boride teeth, reduce the effective brittleness by deforming.

It is also known that attempts have been made to modify the boride case using a microplasma arc. These techniques which exhibit varying levels of success, are however not suitably established for reliability and reproducibility. Industrially viable technology of high repeatability for effective modification of borided layers is yet to be announced.