AN INVESTIGATION OF BORIDING OF MEDIUM CARBON STEELS

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(MATERIAL SCIENCE AND ENGINEERING)

THESIS
FOR THE DEGREE OF UNDERGRADUATE
IN
MATERIALS SCIENCE AND ENGINEERING PROGRAMME

SUPERVISOR
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İSTANBUL, 2007
An Investigation of Boriding of Medium Carbon Steels

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Submitted in partial fulfilment of the requirements for MSE 498 Senior Project in Materials Science and Engineering

Marmara University
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28.06.2007
I would like to thank to Prof. Dr. İ. Ersan KALAFATOĞLU, for his supervision and support during the course of this research. My special thanks go to Research Assistant Özgür ÇİNAR for helping me both within and out of the laboratory. I also thank Asil Çelik Sanayi ve Tic. A.Ş. for providing me the steel specimens which are used in the experiment. Finally I wish to express my thanks to the Marmara University Faculty of Engineering.
Surface hardening a process which includes a wide variety of techniques is used to improve the wear resistance of parts without affecting the softer, tough interior of the part. This combination of hard surface and resistance and breakage upon impact is useful in parts such as a cam or ring gear that must have a very hard surface to resist wear, along with a tough interior to resist the impact that occurs during operation.

There are two distinctly different approaches to the various methods for surface hardening:

The first group of surface hardening methods includes the use of thin films, coatings, or weld overlays (hard-facings). Films, coatings, and overlays generally become less cost effective as production quantities increase, especially when the entire surface of work pieces must be hardened.

The second group of methods on surface hardening is further divided into diffusion methods and selective hardening methods. Diffusion methods modify the chemical composition of the surface with hardening species such as carbon, nitrogen, or boron.

Boriding is a thermo-diffusion surface hardening process in which boron atoms are diffused into the surface of a work-piece to form borides with based materials. Thermo-chemical diffusion treatments are widely used for improving the friction and wear characteristics of steels unders sliding conditions. Borided steel surfaces can provide excellent resistance against adhesive, abresive and corrosive wear. However, despite their high hardness and wear resistance, their friction coefficients are relatively high against steel and other engineering alloys.

Borided steel has a higher surface hardness than carburized and/or nitrided steel that has been used wear resistant materials. Thermal diffusion treatments of boron compounds used to form iron borides require process temperatures of 700-1000°C.

During the experiment we have performed liquid boriding onto the 1040 steel. Metallographic and Hardness testing process are applied before and after the boridng process.
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PART 1. INTRODUCTION

Mechanical performances vary according to the mass and the surface properties of material. During the usage of the material the interactions are occurred on the surface. With the surface processes the material’s hardness, ductility, fatigue resistance, and wear resistance are improved.

Our country has a big partition of the boron minerals ore around the world. This advantage should be used to improve the surface properties of materials by applying boriding. The usage areas of boron minerals in metallurgical processes are given below;

- Slag former during the steel production,
- Alloyin element for steels,
- Surface hardener for steels.

The boriding is a thermo-diffusion surface hardening process in which boron atoms are diffused into the surface of a work-piece to form borides with based materials. Thermo-chemical diffusion treatments are widely used for improving the friction and wear characteristics of steels under sliding conditions. Borided steel surfaces can provide excellent resistance against adhesive, abrasive and corrosive wear. However, despite their high hardness and wear resistance, their friction coefficients are relatively high against steel and other engineering alloys. [1]

The aim of this senior project is to investigate and understand the effect of the boronizing to the low carbon steels for surface hardening. Firstly, I am going to give general information about the mechanisms of strengthening in metals and types of boriding process that are performed on steels.
PART 2. MECHANISMS OF STRENGTHENING IN METALS

Important to understanding of strengthening mechanisms is the relation between dislocation motion and mechanical behavior of metals. Because macroscopic plastic deformation corresponds to the motion of large numbers of dislocations, the ability of metal to plastically deform depends on the ability of dislocations to move. In contrast, the more unconstrained the dislocation motion, the greater is the facility with which a metal may deform, and the softer and weaker it becomes. Virtually all strengthening techniques rely on this simple principle: restricting or hindering dislocation motion renders a material harder and stronger. [2]

Strengthening mechanisms are varied at 5 main ways;

- Strengthening by grain size reduction,
- Solution strengthening,
- Strain hardening,
- Precipitation hardening,
- Case hardening.

2.1. STRENGTHENING BY GRAIN SIZE REDUCTION

The size of the grains, or average grain diameter, in a polycrystalline metal influences the mechanical properties. Adjacent grains normally have different crystallographic orientations and, of course, a common grain boundary, as indicated in Figure 2.1.1. During plastic deformation, slip or dislocation motion must take place across this common boundary-say, from grain A to grain B in Figure 2.1.1. The grain boundary acts as a barrier to dislocation motion for two reasons:

1. Since the two grains are of different orientations, a dislocation passing into grain B will have to change its direction of motion; this becomes more difficult as the crystallographic misorientation increases.
2. The atomic disorder within a grain boundary region will result in a discontinuity of slip planes from one grain into the other.
It should be mentioned that, for high-angle grain boundaries, it may not be the case that dislocations traverse grain boundaries during deformation; rather, a stress concentration ahead of a slip plane in one grain may activate sources of new dislocations in an adjacent grain.

![Figure 2.1.1: The motion of dislocation as it encounters a grain boundary.](Image)

A fine-grained material (one that has small grains) is harder and stronger than one that is coarse grained, since the former has a greater total grain boundary area to impede dislocation motion. For many materials, the yield strength $\sigma_y$ varies with grain size according to

$$\sigma_y = \sigma_o + k_y d^{-1/2}$$  \hspace{1cm} \text{Eq:2.1.1}

In this expression, termed the Hall-Petch equation, $d$ is the average grain diameter, and $\sigma_y$ and $k_y$ are constants for a particular material. Note that Equation 7.5 is not valid for both very large grain and extremely fine grain polycrystalline materials. [2]
2.2. SOLID SOLUTION STRENGTHENING

Solid solution strengthening is a type of alloying that can be used to improve the strength of a pure metal. Atoms of one element are added to a crystalline lattice comprised of atoms of another. The alloying element will diffuse into the matrix, forming a "solid solution". In most binary systems, when alloyed above a certain concentration, a second phase will form and the material will enjoy the benefits of precipitation strengthening.

Depending on the size of the alloying element, a substitutional solid solution or an interstitial solid solution can form.

In a substitutional solid solution, solute atoms replace solvent atoms in their lattice positions. Based on the Hume-Rathery Rule, solvent and solute atoms must differ in atomic size by less than 5% in order to form this type of solution. Because both elements exist in the same crystalline lattice, both elements in their pure form must be of the same crystal structure. Examples of substitutional solid solutions include the Cu-Ni and the Ag-Au binary systems.

When the solute atom is much smaller than the solvent atoms, an interstitial solid solution forms. This typically occurs when the solute atoms are less than half as small as the solvent atoms. Elements commonly used to form interstitial solid solutions include H, N, C, and O. [3]

2.3. STRAIN HARDENING

Strain hardening is the phenomenon whereby a ductile metal becomes harder and stronger as it is plastically deformed. Sometimes it is also called work hardening, or, because the temperature at which deformation takes place is "cold" relative to the absolute melting temperature of the metal, cold working. Most metals strain harden at room temperature.
It is sometimes convenient to express the degree of plastic deformation as percent cold work rather than as strain. Percent cold work (\% CW) is defined as;

\[
\% CW = \left( \frac{A_o - A_d}{A_o} \right) \times 100
\]

\textbf{Eq. 2.3.1}

where \(A_o\) is the original area of the cross section that experiences deformation, and \(A_d\) is the area after deformation.

The influence of cold work on the stress-strain behavior of a steel is vividly portrayed in Figure 2.3.1.

![Figure 2.3.1: The influence of cold work on the stress-strain behavior.](image)

The strain-hardening phenomenon is explained on the basis of dislocation-dislocation strain field interactions. The dislocation density in a metal increases with deformation or cold work, due to dislocation multiplication or the formation of new dislocations. Consequently, the average distance of separation between dislocations decreases—the dislocations are positioned closer together. On the average, dislocation-dislocation strain interactions are repulsive. The net result is that the motion of a dislocation is hindered by the presence of other dislocations. As the dislocation density increases, this resistance to dislocation motion by other dislocations becomes more pronounced. Thus, the imposed stress necessary to deform a metal increases with increasing cold work.

Strain hardening is often utilized commercially to enhance the mechanical properties of metals during fabrication procedures. The effects of strain hardening may be removed by an annealing heat treatment. [2]
2.4. PRECIPITATION HARDENING

Precipitation hardening, also called age hardening or dispersion hardening, is a heat treatment technique used to strengthen malleable materials, especially non-ferrous alloys including most structural alloys of aluminium and titanium. It relies on changes in solid solubility with temperature to produce fine particles of an impurity phase, which impede the movement of dislocations, or defects in a crystal's lattice. Since dislocations are often the dominant carriers of plasticity (deformations of a material under stress), this serves to harden the material. The impurities, in fact, play the same role as matrix substances in composite materials. Just as the formation of ice in air can produce clouds, snow, or hail, depending upon the thermal history of a given portion of the atmosphere, precipitation in solids can produce many different sizes of particles, which have radically different properties. Unlike ordinary tempering, alloys must be kept at elevated temperature for hours to allow precipitation to take place. This time delay is called aging.

Nucleation occurs at a relatively high temperature (often just below the solubility limit) so that the kinetic barrier of surface energy can be more easily overcome and the maximum number of precipitate particles can form. These particles are then allowed to grow at lower temperature in a process called aging. This is carried out under conditions of low solubility so that thermodynamics drive a greater total volume of precipitate formation.

Diffusion's exponential dependence upon temperature makes precipitation strengthening, like all heat treatments, a fairly delicate process. Too little diffusion (under aging), and the particles will be too small to impede dislocations effectively; too much (over aging), and they will be too few and far between to interact with the majority of dislocations.

Precipitation strengthening is possible if the line of solid solubility slopes strongly toward the center of a phase diagram. While a large volume of precipitate particles is desirable, little enough of the alloying element should be added that it remains easily soluble at some reasonable annealing temperature.
Elements used for precipitation strengthening of typical aluminium and titanium alloys make up about 10% of their composition. While binary alloys are more easily understood as an academic exercise, commercial alloys often use three components for precipitation strengthening, in compositions such as Al(Mg, Cu) and Ti(Al, V). A large number of other constituents may be unintentional, but benign, or may be added for other purposes such as grain refinement or corrosion resistance. [4]

2.5. CASE HARDENING

Surface hardening a process which includes a wide variety of techniques is used to improve the wear resistance of parts without affecting the softer, tough interior of the part. This combination of hard surface and resistance and breakage upon impact is useful in parts such as a cam or ring gear that must have a very hard surface to resist wear, along with a tough interior to resist the impact that occurs during operation. Further, the surface hardening of steels has an advantage over through hardening because less expensive low-carbon and medium-carbon steels can be surface hardened without the problems of distortion and cracking associated with the through hardening of thick sections. [5]

There are two distinctly different approaches to the various methods for surface hardening (Table 2.5.1): diffusion methods, selective hardening methods.

Table 2.5.1: Engineering methods for surface hardening of steels.

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2.5.1. SELECTIVE HARDENING METHODS

Selective hardening methods are defined as no change in surface composition. The processes are classified according to the heating source and these are:

1. Flame hardening
2. Induction hardening
3. Laser beam hardening
4. Electron beam hardening

The obvious requirement for these processes is that the original composition must have sufficient carbon and hardenibility to achieve the required hardness at the surface. Medium carbon steels are usually suited for these processes.

In addition to increased wear resistance the surface hardening also induces residual compressive stresses that result in improved bending and torsional strength as well as fatigue properties. [6]

These processes are applied because of one or more of the following reasons:

- Parts to be heat treated are so large as to make conventional furnace heating and quenching impractical and uneconomical,
- Only a small segment, section or area of the part needs to be heat treated,
- Better dimensional accuracy of a heat treated part,
- Overall cost saving by using inexpensive steels to have the wear properties of alloyed steels.

2.5.1.1. FLAME HARDENING

A high intensity oxy-acetylene flame is applied to the selective region. The temperature is raised high enough to be in the region of Austenite transformation. The "right" temperature is determined by the operator based on experience by
watching the color of the steel. The overall heat transfer is limited by the torch and thus the interior never reaches the high temperature. The heated region is quenched to achieve the desired hardness. Tempering can be done to eliminate brittleness. The depth of hardening can be increased by increasing the heating time.[7]

2.5.1.2. INDUCTION HARDENING

In Induction hardening, the steel part is placed inside a electrical coil which has alternating current through it. This energizes the steel part and heats it up. Depending on the frequency and amperage, the rate of heating as well as the depth of heating can be controlled. Hence, this is well suited for surface heat treatment. The details of heat treatment are similar to flame hardening.[7]

2.5.1.3. LASER BEAM HARDENING

Laser beam hardening is another variation of flame hardening. A phosphate coating is applied over the steel to facilitate absorption of the laser energy. The selected areas of the part are exposed to laser energy. This causes the selected areas to heat. By varying the power of the laser, the depth of heat absorption can be controlled. The parts are then quenched and tempered. This process is very precise in applying heat selectively to the areas that need to be heat-treated. Further, this process can be run at high speeds, produces very little distortion.[7]

2.5.1.4. ELECTRON BEAM HARDENING

Electron Beam Hardening is similar to laser beam hardening. The heat source is a beam of high-energy electrons. The beam is manipulated using electromagnetic coils. The process can be highly automated, but needs to be performed under vacuum conditions since the electron beams dissipate easily in air. As in laser beam hardening, the surface can be hardened very precisely both in depth and in location.[7]
2.5.2 DIFFUSION METHODS

2.5.2.1. CARBURISING

Carburizing is the addition of carbon to the surface of low-carbon steels at temperatures generally between 850 and 950°C (1560 and 1740°F), at which austenite, with its high solubility for carbon, is the stable crystal structure. Hardening is accomplished when the high-carbon surface layer is quenched to form martensite so that a high-carbon martensitic case with good wear and fatigue resistance is superimposed on a tough, low-carbon steel core.

Case hardness of carburized steels is primarily a function of carbon content. When the carbon content of the steel exceeds about 0.50% additional carbon has no effect on hardness but does enhance hardenability. Carbon in excess of 0.50% may not be dissolved, which would thus require temperatures high enough to ensure carbon-austenite solid solution.

Carburizing steels for case hardening usually have base-carbon contents of about 0.2%, with the carbon content of the carburized layer generally being controlled at between 0.8 and 1% C. However, surface carbon is often limited to 0.9% because too high a carbon content can result in retained austenite and brittle martensite.

Most steels that are carburized are killed steels (deoxidized by the addition of aluminum), which maintain fine grain sizes to temperatures of about 1040°C. Steels made to coarse grain practices can be carburized if a double quench provides grain refinement. Double quenching usually consists of a direct quench and then a requench from a lower temperature.

First, in a case-hardened steel, the hardenability of both case and core must be considered. Because of the difference in carbon content, case and core have quite different hardenabilities, and this difference is much greater for some steels than for others.
Moreover, the two regions have different in-service functions to perform. Until the introduction of lean alloy steels such as the 86xx series, with and without boron, there was little need to be concerned about case hardenability because the alloy content combined with the high carbon content always provided adequate hardenability. This is still generally true when the steels are direct quenched from carburizing, so that the carbon and alloying elements are in solution in the case austenite. In parts that are reheated for hardening and in heavy-sectioned parts, however, both case and core hardenability requirements should be carefully evaluated.

The relationship between the thermal gradient and the carbon gradient during quenching of a carburized part can make a measurable difference in the case depth as measured by hardness. That is, an increase in base hardenability can produce a higher proportion of martensite for a given carbon level, yielding an increased measured case depth. Therefore, a shallower carbon profile and shorter carburizing time could be used to attain the desired result in a properly chosen steel.

While the basic principle of carburizing has remained unchanged since carburizing was first employed, the method used to introduce the carbon into the steel has been a matter of continuous evolution. There are five methods:

- Gas carburizing
- Vacuum carburizing
- Plasma carburizing
- Salt bath carburizing
- Pack carburizing

These methods introduce carbon by the use of gas (atmospheric-gas, plasma, and vacuum carburizing), liquids (salt bath carburizing), or solid compounds (pack carburizing). All of these methods have limitations and advantages, but gas carburizing is used most often for large-scale production because it can be accurately controlled and involves a minimum of special handling.
Vacuum carburizing and plasma carburizing have found applications because of the absence of oxygen in the furnace atmosphere. Salt bath and pack carburizing are still done occasionally, but have little commercial importance today.

Process characteristics of the above-mentioned carburizing methods fall into two general groups:

- Conventional methods, which introduce carbon by gas atmospheres, salt baths or charcoal packs
- Plasma methods, which impinge positive carbon ions on the surface of a steel part (the cathode)

The main difference between conventional and plasma methods is the reduced carburizing times achieved in plasma-assisted methods. The quickly attained surface saturation also results in faster diffusion kinetics. Furthermore, plasma carburizing produces very uniform case depths, even in parts with irregular surfaces.

With the conventional methods, carburization always takes place by means of a gaseous phase of carbon monoxide; however, each method also involves different reaction and surface kinetics, producing different case-hardening results.

In general, with conventional methods, carbon monoxide breaks down at the steel surface:

\[ 2\text{CO} \leftrightarrow \text{CO}_2 + \text{C} \quad \text{Eq. 2.5.2.1.1} \]

The liberated carbon is readily dissolved by the austenite phase and diffuses into the body of the steel. For some process methods (gas and pack carburizing), the carbon dioxide produced may react with the carbon atmosphere or pack charcoal to produce new carbon monoxide by the reverse reaction.

Carburizing is most frequently performed between 850 and 950°C (1550 and 1750°F), but sometimes higher temperatures are used to reduce cycle times and/or produce deeper depths of the high-carbon surface layer.[8]
A comprehensive model of gas carburization must include algorithms that describe:

- Carbon diffusion
- Kinetics of the surface reaction
- Kinetics of the reaction between endogas and enriching gas
- Purging (for batch processes)
- The atmosphere control system.

### 2.5.2.2. NITRIDING

Nitriding is a surface-hardening heat treatment that introduces nitrogen into the surface of steel at a temperature range (500 to 550°C, or 930 to 1020°F), while it is in the ferrite condition. Thus, nitriding is similar to carburizing in that surface composition is altered, but different in that nitrogen is added into ferrite instead of austenite. Because nitriding does not involve heating into the austenite phase field and a subsequent quench to form martensite, nitriding can be accomplished with a minimum of distortion and with excellent dimensional control.

The mechanism of nitriding is generally known, but the specific reactions that occur in different steels and with different nitriding media are not always known. Nitrogen has partial solubility in iron. It can form a solid solution with ferrite at nitrogen contents up to about 6%. At about 6% N, a compound called gamma prime (γ’), with a composition of Fe₄N is formed.

At nitrogen contents greater than 8%, the equilibrium reaction product is ε compound, Fe₃N. Nitrided cases are stratified. The outermost surface can be all γ’ and if this is the case, it is referred to as the white layer. Such a surface layer is undesirable: it is very hard profiles but is so brittle that it may spall in use. Usually it is removed; special nitriding processes are used to reduce this layer or make it less brittle. The ε zone of the case is hardened by the formation of the Fe₃N compound, and below this layer there is some solid solution strengthening from the nitrogen in solid solution.
The reasons which we prefer nitriding are:

- To obtain high surface hardness
- To increase wear resistance
- To improve fatigue life
- To improve corrosion resistance (except for stainless steels)
- To obtain a surface that is resistant to the softening effect of heat at temperatures up to the nitriding temperature

Nitrided steels are generally medium-carbon (quenched and tempered) steels that contain strong nitride-forming elements such as aluminum, chromium, vanadium, and molybdenum.

Of the alloying elements commonly used in commercial steels, aluminum, chromium, vanadium, tungsten and molybdenum are beneficial in nitriding because they form nitrides that are stable at nitriding temperatures. Molybdenum in addition to its contribution as a nitride former also reduces the risk of embrittlement at nitriding temperatures. Other alloying elements such as nickel, copper, silicon and manganese have little, if any, effect on nitriding characteristics.

The following steels can be gas nitrided for specific applications:

1. Aluminum-containing low-alloy steels
2. Medium-carbon, chromium-containing low-alloy steels of the 4100, 4300, 5100, 6100, 8600, 8700 and 9800 series
3. Hot-work die steels containing 5% chromium such as HI1, HI2, and HI3
4. Low-carbon, chromium-containing low-alloy steels of the 3300, 8600, and 9300 series
5. Air-hardening tool steels such as A-2, A-6, D-2, D-3 and S-7
6. High-speed tool steels such as M-2 and M-4
7. Nitronic stainless steels such as 30, 40, 50, and 60
8. Ferritic and martensitic stainless steels of the 400 and 500 series
9. Austenitic stainless steels of the 200 and 300 series
There are three types of nitriding process:

1. Gas Nitriding
2. Pack Nitriding
3. Plasma Nitriding

2.5.2.2.1. Gas Nitriding

Gas nitriding is a case-hardening process whereby nitrogen is introduced into the surface of a solid ferrous alloy by holding the metal at a suitable temperature in contact with a nitrogenous gas, usually ammonia. Quenching is not required for the production of a hard case. The nitriding temperature for all steels is between 495 and 565°C.

Because of the absence of a quenching requirement with attendant volume changes, and the comparatively low temperatures employed in this process, nitriding of steels produces less distortion and deformation than either carburizing or conventional hardening. Some growth occurs as a result of nitriding but volumetric changes are relatively small.

2.5.2.2.2. Pack Nitriding

Pack nitriding is a process analogous to pack carburizing. It employs certain nitrogen-bearing organic compounds as a source of nitrogen. Upon heating, the compounds used in the process form reaction products that are relatively stable at temperatures up to 570°C.

Slow decomposition of the reaction products at the nitriding temperature provides a source of nitrogen. Nitriding times of 2 to 16 h can be employed. Pans are packed in glass ceramic or aluminum containers with the nitriding compound, which is often dispersed in an inert packing media.
2.5.2.2.3. Plasma Nitriding

Ion nitriding is an extension of conventional nitriding processes using plasma-discharge physics. In vacuum, high-voltage electrical energy is used to form a plasma, through which nitrogen ions are accelerated to impinge on the workpiece. This ion bombardment heats the workpiece, cleans the surface, and provides active nitrogen.

Metallurgically versatile, the process provides excellent dimensional control and retention of surface finish. Ion nitriding can be conducted at temperatures lower than those conventionally employed. Control of white-layer composition and thickness enhances fatigue properties. The span of ion-nitriding applications includes conventional ammonia-gas nitriding, short-cycle nitriding in salt bath or gas, and the nitriding of stainless steels.[9]
2.5.2.3. BORIDING

Before talking about boriding we have to know the element boron and boron minerals and their application areas.

Boron is a hard, brittle semi-metallic element. Typical properties of boron are given below table 2.5.2.3.1.

Table 2.5.2.3.1: General chemical properties of boron.

<table>
<thead>
<tr>
<th>Chemical symbol</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>5</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>10.81</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>2348 K</td>
</tr>
<tr>
<td>Boiling temperature</td>
<td>4273 K</td>
</tr>
</tbody>
</table>

Boron does not occur in nature as a free element, crude borax occurs in nature as a mineral with associated clay and other impurities. There are over 200 naturally occurring boron containing minerals but the most commercially important and frequently traded minerals (salts, known as borates) are tincal colemanite, ulexite and kernite. Some commercial boron minerals are given below at table 2.5.2.3.2;

Table 2.5.2.3.2: Some commercial boron minerals.

<table>
<thead>
<tr>
<th>Tincal</th>
<th>Na₂B₄O₇.10H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kernite</td>
<td>Na₂B₄O₇.4H₂O</td>
</tr>
<tr>
<td>Colemanite</td>
<td>Ca₂B₆O₁₁.5H₂O</td>
</tr>
<tr>
<td>Ulexite</td>
<td>NaCaB₅O₉.8H₂O</td>
</tr>
<tr>
<td>Datolite</td>
<td>Ca₂B₂O₅.Si₂O₅.H₂O</td>
</tr>
<tr>
<td>Hydroborocite</td>
<td>CaMgB₆O₁₁.6H₂O</td>
</tr>
</tbody>
</table>
Table 2.5.2.3.3 shows the products that are obtained from boron minerals and given below:

<table>
<thead>
<tr>
<th>Products from minerals.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Boric acid</strong></td>
</tr>
<tr>
<td><strong>Anhydrous boric acid</strong></td>
</tr>
<tr>
<td><strong>Anhydrous borax</strong></td>
</tr>
<tr>
<td><strong>Borax pentahydrate</strong></td>
</tr>
<tr>
<td><strong>Borax decahydrate</strong></td>
</tr>
<tr>
<td><strong>Sodium Perborate</strong></td>
</tr>
</tbody>
</table>

In the world, Turkey, USA and Russia have the important boron mines. In terms of total reserve basis, Turkey has a share of %72.20, the other important country USA is %6.8. Total world boron reserves on the basis of B$_2$O$_3$ content are 369 million tons proven. 807 million tones probable and possible, as a total of 1,176 million tons. With a share of %72.20, Turkey has a total boron reserves of 851 million tons on the basis of B$_2$O$_3$ content.

Turkey is the largest producer of boron ore in the world. Important boron minerals of Turkey's are tincal, colemanite and ulexite. Boron minerals contain different amount of B$_2$O$_3$ in their structures. The important factor for industrial application of boron minerals are B$_2$O$_3$ content, so they can replace each other in use. This means one boron mineral can be trade competitor the other one.

Boron minerals can be used in some sectors in the industry as crude minerals. In general, their applications after refining and end-products are wider than crude ones. Borates find use in a different sectors, however the principal markets are: Agriculture, detergents and soaps, flame retardants, glass, glazes, frits, enamels and insulation.

Boron minerals can be used in some sectors in the industry as crude minerals. In general, their applications after refining and end-products are wider than crude ones. Boron minerals, borates and compounds have a very wide range of applications. Table 2.5.2.3.4 gives us information about boron usage at different sectors. [10]
Table 2.5.2.3.4: Application areas of boron and their affects.

<table>
<thead>
<tr>
<th>Application Area</th>
<th>Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agriculture</td>
<td>Essential micronutrient for all plant</td>
</tr>
<tr>
<td>Detergents and Soaps</td>
<td>Act as pH buffer</td>
</tr>
<tr>
<td></td>
<td>Soften the Washing water</td>
</tr>
<tr>
<td></td>
<td>Enhance the solubility of other ingredients</td>
</tr>
<tr>
<td></td>
<td>Act as a gentle but powerful bleaching agent</td>
</tr>
<tr>
<td></td>
<td>Anti-bacterial properties eliminate microorganisms</td>
</tr>
<tr>
<td>Ceramic Glazes and Enamel Frits</td>
<td>Provide good fluxing properties</td>
</tr>
<tr>
<td></td>
<td>Provide a good base for dissolving colouring agents</td>
</tr>
<tr>
<td>Insulation Fibreglass</td>
<td>Reduce the temperature at which fibres are formed</td>
</tr>
<tr>
<td></td>
<td>Improve the durability of the glass fibres</td>
</tr>
<tr>
<td></td>
<td>Reduce the viscosity of the molten glass</td>
</tr>
<tr>
<td></td>
<td>Increase the biosolubility of the glass fibres</td>
</tr>
<tr>
<td>Timber Preservation</td>
<td>Prevent and control the spread of bacteria</td>
</tr>
<tr>
<td></td>
<td>Inhibit corrosion</td>
</tr>
<tr>
<td></td>
<td>Act as flame retardant</td>
</tr>
<tr>
<td>Flame Retardants</td>
<td>Enhance the performance of alumina trihydrate</td>
</tr>
<tr>
<td></td>
<td>Effective as flame retardants</td>
</tr>
<tr>
<td>Nuclear Power Stations</td>
<td>Absorb thermal neutrons</td>
</tr>
<tr>
<td></td>
<td>Used to control nuclear reaction</td>
</tr>
<tr>
<td></td>
<td>Used in nuclear shielding</td>
</tr>
<tr>
<td>Cosmetics and Medicine</td>
<td>Neutralize fatty acid</td>
</tr>
<tr>
<td></td>
<td>Act as emulsifiers in certain creams</td>
</tr>
<tr>
<td></td>
<td>Give mild antiseptic properties</td>
</tr>
<tr>
<td>Metallurgy</td>
<td>Used as cover fluxes</td>
</tr>
<tr>
<td></td>
<td>Dissolve and remove unwanted metal oxides as slag</td>
</tr>
<tr>
<td>Others(Glass, magnets, automobile airbags,</td>
<td></td>
</tr>
<tr>
<td>photography, fuels...)</td>
<td></td>
</tr>
</tbody>
</table>
Boriding, or boronizing, is a thermo-chemical surface hardening process that can be applied to a wide variety of ferrous, nonferrous, and cermet materials. The process involves heating well-cleaned material in the range of 700 to 1000 °C (1300 to 1830 °F), preferably for 1 to 12 h, in contact with a boronaceous solid powder (boronizing compound), paste, liquid, or gaseous medium. Other developments in thermochemical boriding include gas boriding techniques such as plasma boriding and fluidized bed boriding. There is a current trend toward the use of multi component boriding.

During boriding, the diffusion and subsequent absorption of boron atoms into the metallic lattice of the component surface form interstitial boron compounds. The resulting layer may consist of either a single-phase boride or a polyphase boride layer. The morphology as seen at Figure 2.5.2.3.1, growth, and phase composition of the boride layer can be influenced by the alloying elements in the base material. The microhardness of the borided layer also depends strongly on the composition and structure of the boride layer and the composition of the base material are given at table 2.5.2.3.5.

### Table 2.5.2.3.5: Melting point and microhardness of different boride phases formed during boriding of different substrate materials with 100 g and 200 g load.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Constituent phases in the boride layer</th>
<th>Microhardness of layer, HV or kg mm²</th>
<th>Melting point °C</th>
<th>°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe₃B</td>
<td>1900-2100</td>
<td>1350</td>
<td>2490</td>
</tr>
<tr>
<td></td>
<td>Fe₅B</td>
<td>1800-2000</td>
<td>1350</td>
<td>2490</td>
</tr>
<tr>
<td>Co</td>
<td>CoB</td>
<td>1850</td>
<td>. . . . . .</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co₃B</td>
<td>1500-1600</td>
<td>. . . . . .</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co₅B</td>
<td>700-800</td>
<td>. . . . . .</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co₉B</td>
<td>1200 (100 g)</td>
<td>. . . . . .</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co₂B</td>
<td>~1550 (100 g)</td>
<td>. . . . . .</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co₂B (?)</td>
<td>700-800</td>
<td>. . . . . .</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>Ni₃B</td>
<td>1600</td>
<td>. . . . . .</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni₅B</td>
<td>1500</td>
<td>. . . . . .</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni₇B</td>
<td>900</td>
<td>. . . . . .</td>
<td></td>
</tr>
<tr>
<td>Inconel 100</td>
<td>...</td>
<td>1700 (200 g)</td>
<td>. . . . . .</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>Mo₃B</td>
<td>1660</td>
<td>2900</td>
<td>5290</td>
</tr>
<tr>
<td></td>
<td>Mo₅B</td>
<td>2330</td>
<td>~2100</td>
<td>~3790</td>
</tr>
<tr>
<td>W</td>
<td>W₂B</td>
<td>2400-2700</td>
<td>2100</td>
<td>3810</td>
</tr>
<tr>
<td>Ti</td>
<td>TiB</td>
<td>2500</td>
<td>~1900</td>
<td>~3470</td>
</tr>
<tr>
<td></td>
<td>Ti₂B</td>
<td>2870</td>
<td>2980</td>
<td>5390</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>TiB</td>
<td>3000 (100 g)</td>
<td>. . . . . .</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>Nb₂B</td>
<td>3200</td>
<td>3040</td>
<td>5550</td>
</tr>
<tr>
<td></td>
<td>Nb₃B</td>
<td>. . . . . . . .</td>
<td>. . . . . .</td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>Ta₃B</td>
<td>3200-3500</td>
<td>5790-6130</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ta₅B</td>
<td>3500</td>
<td>6300</td>
<td>11620</td>
</tr>
<tr>
<td>Hf</td>
<td>HfB₅</td>
<td>3250</td>
<td>3750</td>
<td>6780</td>
</tr>
<tr>
<td>Zr</td>
<td>ZrB₅</td>
<td>2250</td>
<td>3040</td>
<td>5550</td>
</tr>
</tbody>
</table>
Advantages of boriding include:

- One basic advantage is that boride layers have extremely high hardness values (between 1450 and 5000 HV) with high melting points of the constituent phases.
- The hardness of boride layers produced on carbon steels is much greater than that produced by any other conventional surface (hardening) treatments.
- The combination of a high surface hardness and a low surface coefficient of friction of the borided layer also makes a significant contribution in combating the main wear mechanisms: adhesion, tribooxidation, abrasion, and surface fatigue. This fact has enabled the mold makers to substitute easier-to-machine steels for the base metal and to still obtain wear resistance and antigalling properties superior to those of the original material.
- Hardness of the boride layer can be retained at higher temperatures than, for example, that of nitrided cases.
- A wide variety of steels, including through-hardenable steels, are compatible with the processes.
- Boriding, which can considerably enhance the corrosion-erosion resistance of ferrous materials in nonoxidizing dilute acids and alkali media, is increasingly used to this advantage in many industrial applications.
• Borided surfaces have moderate oxidation resistance (up to 850 °C, or 1550 °F) and are quite resistant to attack by molten metals.

• Borided parts have an increased fatigue life and service performance under oxidizing and corrosive environments.

Disadvantages of boronizing treatments are:

• The techniques are inflexible and rather labor intensive, making the process less cost effective than other thermochemical surface hardening treatments such as gas carburizing and plasma nitriding. Both gas carburizing and plasma nitriding have the advantage over boronizing because those two processes are flexible systems, offer reduced operating and maintenance costs, require shorter processing times, and are relatively easy to operate. It is, therefore, suited to engineering components that need high hardness and outstanding wear and corrosion resistance of the boride layers, and/or where cheaper labor is available.

• The growth (that is, the increase in volume) resulting from boronizing is 5 to 25% of the layer thickness (for example, a 25 µm layer would have a growth of 1.25 to 6.25 µm); its magnitude depends on the base material composition but remains consistent for a given combination of material and treatment cycle. However, it can be predicted for a given part geometry and boronizing treatment. For treatment of precision parts, where little stock removal is permitted, an allowance of ~20 to 25% dimensional increase of the final boride layer thickness must be provided.

• Partial removal of the boride layer for closer tolerance requirements is made possible only by a subsequent diamond lapping because conventional grinding causes fracture of the layer. Thus, precise boronizing is mostly practiced for components with a large cross-sectional area.

• Boriding of most steels provides a marginal increase, if any, in the bending fatigue endurance limit, although some improvement in the corrosion-fatigue strength has been noticed. In general, the rolling contact fatigue properties of borided alloy steel parts are very poor compared to carburized and nitrided steels at high contact loads (2000 N, or 450 lbf). This is why boronizing
treatments of gears are limited to those screw designs where transverse loading of gear teeth is minimized.

- There is frequently a need to harden and temper the tool after boriding which requires a vacuum or inert atmosphere to preserve the integrity of the boride layer.

Unlike carburizing treatment on ferrous materials, where there is a gradual decrease in composition from the carbon-rich surface to the substrate, the boriding of ferrous materials results in the formation of either a single-phase or double-phase layer of borides with definite compositions. The single-phase boride layer consists of Fe$_2$B, while the double-phase layer consists of an outer dark-etching phase of FeB and an inner bright-etching phase of Fe$_2$B. The formation of either a single or double phase depends on the availability of boron.

The formation of a single Fe$_2$B phase (with a sawtooth morphology due to preferred diffusion direction) is more desirable than a double-phase layer with FeB. The boron-rich FeB phase is considered undesirable because FeB is more brittle than the iron subboride Fe$_2$B layer. Also, because FeB and Fe$_2$B are formed under tensile and compressive residual stresses, respectively, crack formation is often observed at or in the neighborhood of the FeB/Fe$_2$B interface of a double-phase layer. These cracks may lead to flaking and spalling when a mechanical strain is applied or even separation as seen at Figure 2.5.2.3.2 when a component is undergoing a thermal and/or mechanical shock. Therefore, the boron-rich FeB phase should be avoided or minimized in the boride layer.

![Figure 2.5.2.3.2: Separation of two-phase boride layer on a low-carbon steel.](image-url)
It has also been reported that the tribological properties depend on the microstructure of the boride layer. The dual-phase FeB-Fe₂B layers are not inferior to those of monophase Fe₂B layers, provided that the porous surface zone directly beneath the surface is removed. Alternatively, a thinner layer is favored because of less development of brittle and porous surface-zone formation and flaking.

Typical properties of the FeB phase are:
- Microhardness of about 19 to 21 GPa (2.7 × 10^6 to 3.0 × 10^6 psi)
- Modulus of elasticity of 590 GPa (85 × 10^6 psi)
- Density of 6.75 g/cm³ (0.244 lb/in.3)
- Thermal expansion coefficient of 23 ppm/°C (13 ppm/°F) between 200 and 600 °C (400 and 1100 °F)
- Composition with 16.23 wt% boron
- Orthorhombic crystal structure with 4 iron and 4 boron atoms per unit cell
- Lattice parameters: \( a = 4.053 \text{ Å} \), \( b = 5.495\text{Å} \), and \( c = 2.946 \text{ Å} \)

The formation of single-phase Fe₂B layers with a sawtooth morphology is desirable in the boriding of ferrous materials. A single Fe₂B phase can be obtained from a double FeB-Fe₂B phase by a subsequent vacuum or salt bath treatment for several hours above 800 °C (1470 °F), which may be followed by oil quenching to increase substrate properties.

Typical properties of Fe₂B are:
- Microhardness of about 18 to 20 GPa (2.6 × 10^6 to 2.9 × 10^6 psi)
- Modulus of elasticity of 285 to 295 GPa (41 × 10^6 to 43 × 10^6 psi)
- Thermal expansion coefficient of 7.65 ppm/°C (4.25 ppm/°F) and 9.2 ppm/°C (5.1 ppm/°F) in the range of 200 to 600 °C (400 to 1100 °F) and 100 to 800 °C (200 to 1500 °F), respectively (Ref 6 and 17)
- Density of 7.43 g/cm³ (0.268 lb/in.3)
- Composition with 8.83 wt% boron
- Body-centered tetragonal structure with 12 atoms per unit cell
- Lattice parameters: \( a = 5.078 \text{ Å} \) and \( c = 4.249 \text{ Å} \)
There are six types of boriding process available in industry which are:

1. Pack Boriding
2. Paste Boriding
3. Gas Boriding
4. Fluidized Bed Boriding
5. Liquid (salt bath) Boriding
6. Plasma Boriding

2.5.2.3.1. Pack Boriding

Pack boriding is the most widely used boriding process because of its relative ease of handling, safety, and the possibility of changing the composition of the powder mix, the need for limited equipment, and the resultant economic savings. The process involves packing the annealed, cleaned, smooth parts in a boriding powder mixture contained in a 3 to 5 mm (0.1 to 0.2 in.) thick, heat-resistant steel box so that surfaces to be borided are covered with an approximately 10 to 20 mm (0.4 to 0.8 in.) thick layer. Many different boriding compounds have been used for pack boriding. They include solid boron-yielding substances, diluents, and activators.

The common boron-yielding substances are boron carbide (B₄C), ferroboron, and amorphous boron; the last two have greater boron potential, provide a thicker layer, and are more expensive than B₄C. Silicon carbide (SiC) and alumina (Al₂O₃) serve as diluents, and they do not take part in the reaction. However, SiC controls the amount of boron and prevents caking of the boronizing agent. NaBF₄, KBF₄, (NH₄)₃BF₄, NH₄Cl, Na₂CO₃, BaF₂, and Na₂B₄O₇ are the boriding activators. There are special proprietary brands of boriding compounds, such as different grades of Ekabor, available on the market that can be used with confidence.

Typical compositions of commercial solid boriding powder mixtures are:

- 5% B₄C, 90% SiC, 5% KBF₄
- 50% B₄C, 45% SiC, 5% KBF₄
- 85% B₄C, 15% Na₂CO₃
- 95% B₄C, 5% Na₂B₄O₇
- 84% B4C, 16% Na2B4O7
- Amorphous boron (containing 95 to 97% B)
- 95% amorphous boron, 5% KBF4

The parts conforming to the shape of the container are packed at Figure 2.5.2.3.1.1, covered with a lid, which rests inside the container and is weighted with an iron slug or stone to ensure an even trickling of the boriding agent during the boriding treatment. It is then heated to the boriding temperature in an electrically heated box or pit furnace with open or covered heating coils or a muffle furnace for a specified time. The container should not exceed 60% of the furnace chamber volume. In principle, boriding should be accomplished in such a way that high internal stresses are relieved, which in turn, eliminates cracks or spalling. With the packing process, the powder may be reused by blending with 20 to 50 wt% of fresh powder mixture. In this case, the powder should be discarded after 5 or 6 cycles.

![Diagram of the packing of a single geometrical part in a pack boriding box.](image)
The thickness of the boride layer depends on the substrate material being processed, boron potential of the boronizing compound, boronizing temperature, and time as seen at Figure 2.5.2.3.1.2. In ferrous materials, the heating rate especially between 700 °C (1300 °F) and the boriding temperature (800 to 1000 °C, or 1470 to 1830 °F) should be high in order to minimize the formation of FeB.

![Figure 2.5.2.3.1.2: Effect of pack boriding temperature and time on the boride layer thickness in a low-carbon steel.](image)

2.5.2.3.2. Paste Boriding

Paste boriding is used commercially when pack boronizing is difficult, more expensive, or time consuming. In this process, a paste of 45% B$_4$C (grain size 200 to 240 µm) and 55% cryolite (Na$_3$AlF$_6$, flux additive), or conventional boronizing powder mixture (B$_4$C-SiC-KBF$_4$) in a good binding agent (such as nitrocellulose dissolved in butyl acetate, aqueous solution of methyl cellulose, or hydrolyzed ethyl silicate) is repeatedly applied at intervals over the entire or selected portion of parts until a layer about 1 to 2 mm (0.04 to 0.08 in.) thick is obtained. Subsequently, the ferrous
materials are heated at 900 °C for 4 h inductively or in a conventional furnace to 800 to 1000 °C for 5 h. In this process, a protective atmosphere (for example, argon, cracked NH₃, or N₂) is necessary. A layer in excess of 50 µm thickness may be obtained after inductively or resistively heating to 1000 °C for 20 min. This process is of special interest for large components or for those requiring partial boriding.

2.5.2.3.3. Gas Boriding

Gas boriding may be accomplished with:

- Diborane (B₂H₆)-H₂ mixture
- Boron halide-H₂/or (75:25 N₂-H₂) gas mixture
- Organic boron compounds such as (CH₃)₃B and (C₂H₅)₃B.

Boronizing with B₂H₆-H₂ mixture is not commercially viable due to the high toxic and explosive nature of diborane. When organic boron compounds are used, carbide and boride layers form simultaneously. Because BBr₃ is expensive and is difficult to handle (with violent reactions with water), and because BF₃ requires high reduction temperature (due to its greater stability) and produces HF fumes, BCl₃ remains the attractive choice for gas boriding.

When parts are gas borided in a dilute (1:15) BCl₃-H₂ gas mixture at a temperature of 700 to 950 °C and a pressure up to 67 kPa (0.67 bar), a boride layer 120 to 150 µm thick is reported to be produced at 920 °C (1690 °F) in 2 h. Recent work has suggested the use of 75:25 N₂-H₂ gas mixture instead of H₂ gas for its better performance because of the production of boride layers with minimum FeB content. The latter phase can be easily eliminated during the subsequent diffusion treatment before hardening. This process can be applied to titanium and its alloys as well.
2.5.2.3.4. Fluidized Bed Boriding

A recent innovation is boriding in fluidized beds which is shown at Figure 2.5.2.3.4.1, which involves bed material of coarse-grained silicon carbide particles, a special boriding powder such as Ekabor WB, and an oxygen-free gas such as N₂-H₂ mixture. When electricity is used as the heat source, the bed serves as a faster heat-transfer medium. This is usually equipped with quench and tempering furnaces.

This process offers such advantages as:

- High rates of heating and flow, as well as direct withdrawal of the parts, provide shorter operating cycle times (that is, rapid boronizing).
- Temperature uniformity with low capital cost and flexibility is ensured.
- A fluidized furnace is very tight because of upward pressure of the gas.
- This process produces reproducibility, close tolerances, and a very uniform finish on mass-produced parts.
• This process can be adaptable to continuous production and can lend itself to automation as the parts are charged and withdrawn intermittently.
• Quenching (and subsequent tempering) of the parts directly after this treatment is possible.
• Low operating cost (due to reduced processing time and energy consumption) for mass production of boronized parts.

An important disadvantage lies in the continuous flushing of the boriding agent within the retort by the inert gas. The exhaust gases containing enriched fluorine compounds must be cleaned absolutely, for example, in an absorber filled with dry CaCO₃ chips to avoid environmental problems.

2.5.2.3.5. Liquid (salt bath) Boriding

**Liquid boriding** is grouped into two types;
1. Electroless
2. Electrolytic

*These processes have several disadvantages:*
• Removal of excess salt and unreacted boron is essential after the treatment; this step may prove to be expensive and time consuming.
• To achieve boronizing reproducibility, bath viscosity is not allowed to increase. This is done by recharging with salt, which involves high maintenance costs.
• In some situations protection from corrosive fumes may be required.

2.5.2.3.5.1. Electroless Liquid Boriding

Electroless salt bath boriding of ferrous materials is carried out in a borax-based melt at about 900 to 950 °C (1650 to 1750 °F), to which about 30 wt% B₄C is added. The boronizing action can be further improved by replacing up to 20 wt% B₄C with ferroaluminum because it is a more effective reductant. However, superior
results have been found by using a salt bath mixture containing 55% borax, 40 to 50% ferroboron, and 4 to 5% ferroaluminum. It has also been shown that 75:25 KBF₄-KF salt bath can be used at temperature below 670 °C (1240 °F) for boronizing nickel alloys, and at higher temperatures for ferrous alloys, to develop the desired boride layer thickness.

2.5.2.3.5.2. Electrolytic Liquid Boriding

In this process, the ferrous part acting as the cathode and a graphite anode are immersed in the electrolytic molten borax at 940 °C (1720 °F) for 4 h using a current density of about 0.15 A/cm². The parts are then air cooled. In general, the parts are rotated during the treatment to obtain a uniform layer. A high current density produces a thin coating on low-alloy steels in a short time. For high-alloy steels of greater thickness, lower current densities are required for a longer time.

In the fused state tetraborate decomposes into boric acid and nascent oxygen.

\[
B_4O_7 + 2e = 2B_2O_3 + O \quad \text{Eq. 2.5.2.3.5.2.1}
\]

Simultaneously, sodium ions, after being neutralized in the vicinity of cathode, react with boric acid to liberate boron.

\[
6 \text{Na} + B_2O_3 = 3 \text{Na}_2O + 2\text{B} \quad \text{Eq. 2.5.2.3.5.2.2}
\]

In this manner, a high boriding potential is established near the cathode region. Other satisfactory electrolytic salt bath compositions include:

- KBF₄-LiF-NaF-KF mixture for parts to be treated at 600 to 900 °C (1100 to 1650 °F).
- 20KF-30NaF-50LiF-0.7BF₂ mixture (by mole %) at 800 to 900 °C (1470 to 1650 °F) in 90N₂-10H₂ atmosphere
- 9:1 (KF-LiF)-KBF₄ mixture under argon atmosphere.
- KBF₄-NaCl mixture at 650 °C (1200 °F).
- 90(30LiF + 70KF)-10KBF₄ mixture at 700 to 850 °C (1300 to 1560 °F)
- 80Na₂B₄O₇-20NaCl at 800 to 900 °C (1470 to 1650 °F).
2.5.2.3.6. Plasma Boriding

Both mixtures of B$_2$H$_6$-H$_2$ and BCl$_3$-H$_2$-Ar may be used successfully in plasma boronizing. However, the former gas mixture can be applied to produce boride layer on various steels at relatively low temperatures such as 600 °C (1100 °F), which is impossible with a pack or liquid boronizing process. It has been claimed that plasma boriding in a mixture of BCl$_3$-H$_2$-Ar gases shows good features such as better control of BCl$_3$ concentration, reduction of the discharge voltage, and higher microhardness of the boride films. Figure 2.5.2.3.6.1 shows a schematic layout of a plasma boriding facility.

![Diagram of plasma boriding facility](image)

Figure 2.5.2.3.6.1: Layout of plasma boronizing facility.

The dual-phase layer is characterized by visible porosity, occasionally associated with a black boron deposit. This porosity, however, can be minimized by increasing the BCl$_3$ concentration. Boride layers up to 200 µm in thickness can be produced in steels after 6 h treatment at a temperature of 700 to 850 °C (1300 to 1560 °F) and a pressure of 270 to 800 Pa (2 to 6 torr).
Advantages of this process are:

- Control of composition and depth of the borided layer
- Increased boron potential compared to conventional pack boronizing
- Finer plasma-treated boride layers
- Reduction in temperature and duration of treatment
- Elimination of high-temperature furnaces and their accessories
- Savings in energy and gas consumption

The only disadvantage of the process is the extreme toxicity of the atmosphere employed. As a result, this process has not gained commercial acceptance. To avoid the above shortcoming, boriding from paste (containing a mixture of 60% amorphous boron and 40% liquid borax) in a glow discharge at the impregnating temperature has been recently developed, which is found to greatly increase the formation of the surface boride layer. [11]
PART 3. SCOPE OF EXPERIMENTAL WORK

This part consists of four sections which are:
1. Workpiece Preparation
2. Boriding Agent Preparation
3. Heat Treatment (Boriding)
4. Measurements After Boriding

3.1. WORKPIECE PREPARATION

The steel specimen was obtained from Asil Çelik San. Ve Tic. A.Ş. and the chemical composition is given below at Table 3.1.1.

<table>
<thead>
<tr>
<th>C %</th>
<th>Si %</th>
<th>Mn %</th>
<th>P %</th>
<th>S %</th>
<th>Fe %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.41</td>
<td>0.23</td>
<td>0.74</td>
<td>0.008</td>
<td>0.002</td>
<td>Retained</td>
</tr>
</tbody>
</table>

The specimens are prepared to use in the boriding process. For different temperature treatment totally six specimens are used. Their dimensions are given below at Figure 3.1.1.

![Figure 3.1.1: Dimensions of test specimen](image)

Before boriding process surface treatments are applied to obtain a smooth surface. Then the metallographic processes which are cutting, grinding, polishing and etching are applied to take photographs of microstructures. For the metallographic processes the devices used are given below Table 3.1.2.
### Table 3.1.2: Used devices during the metallographic processes.

<table>
<thead>
<tr>
<th>Device’s name</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Struers Discotom-5</td>
<td>Cutting</td>
</tr>
<tr>
<td>Struers Pronto Pres-10</td>
<td>Bakalite Coating</td>
</tr>
<tr>
<td>Struers Labopol-21</td>
<td>Grinding</td>
</tr>
<tr>
<td>Struers Dap-7</td>
<td>Diamond Polishing</td>
</tr>
<tr>
<td>Olympus B061</td>
<td>Photographing</td>
</tr>
</tbody>
</table>

### 3.2. BORIDING AGENT PREPERATION

During the liquid boriding process we use water free borax and Ferro-Silicon. The compositions of boridig agent are 70% wt Borax and 30% wt Fe-Si. To obtain water free borax we use Borax pentahydrate (Na₂B₄O₇·10H₂O). The crystalline water of Borax pentahydrate should be removed as much as possible against overflow of liquid mixture during the boriding heat treatment process. Because the borax can damage the refractory lining of the inerside of the furnace. For that process the temperature changes and time distributions are given at table 3.2.1

### Table 3.2.1: Temperature and Time distribution of borax pentahydrate.

<table>
<thead>
<tr>
<th>Temperature Interval (°C)</th>
<th>Time (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 -150</td>
<td>20</td>
</tr>
<tr>
<td>150 – 150</td>
<td>60</td>
</tr>
<tr>
<td>150 – 250</td>
<td>20</td>
</tr>
<tr>
<td>250 – 250</td>
<td>60</td>
</tr>
<tr>
<td>250 – 600</td>
<td>60</td>
</tr>
<tr>
<td>600 – 600</td>
<td>120</td>
</tr>
<tr>
<td>600 - 20</td>
<td>60</td>
</tr>
</tbody>
</table>

After calcination we take a TGA analysis for our water free borax. The graph has formed as seen at Figure 3.2.1. It tells us there is a bit crystalline water inside of borax. That can be happen because of the trapping air moisture during handling.
Other part of the boriding agent is Fe-Si. The preparation of ferro silicon consists of only crushing. Because of the coarse particles we need to get fine ferro silicon. So the powder mixture can be more homogeneous when we use fine particles. The devices for this part are given at table 3.2.2. The furnace which is shown at Figure 3.2.2, is also used during the boriding process.

Table 3.2.2: Used devices during the boriding agent preparation.

<table>
<thead>
<tr>
<th>Device's name</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nabertherm Supertherm HT 40/17</td>
<td>Heating</td>
</tr>
<tr>
<td>Fritsch Jaw Crusher</td>
<td>Crushing</td>
</tr>
<tr>
<td>Precisa XB 320 Max.</td>
<td>Weighting</td>
</tr>
<tr>
<td>Netzsch STA 409 CD</td>
<td>DTA/TGA</td>
</tr>
</tbody>
</table>
3.3. HEAT TREATMENT (BORIDING)

The prepared powder mixture has poured into the stainless steel box which is shown at Figure 3.3.1 rather than graphite laddle. First boriding agent is put in then the two specimen is put and finally boriding agent is put again. We use two specimen for each test because of precaution. All the system is set in the furnace and the boriding procedure is started. The heating time and temperatures are given at table 3.3.1.

Table 3.3.1: Temperature and Time distribution of boriding.

<table>
<thead>
<tr>
<th># of Boriding</th>
<th>Temperature Interval (°C)</th>
<th>Time (hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 -850</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>850 – 850</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>20 -900</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td>900 – 900</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>20 -950</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>950 – 950</td>
<td>6</td>
</tr>
</tbody>
</table>
Figure 3.3.1: Dimensions of the Stainless steel box.

After heat treatment about six hours the specimen should be taken out stainless steel box because solidification of liquid borax is rapid and the viscosity of the liquid increases with decreasing temperature. Then the specimens are normalized in air.

### 3.4. MEASUREMENTS AFTER BORIDING

After boriding the specimens are applied metallographic processes to take microstructural photos again. Then they are examined by SEM. Finally hardness values are obtained for all specimens with the Instron Hardness device which is shown at Figure 3.4.1 and the equipments which are used at that step are given table 3.4.1.

<table>
<thead>
<tr>
<th>Device's name</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instron Wolpert Testor 930/250</td>
<td>Hardness</td>
</tr>
<tr>
<td>Joel Low Vacuum</td>
<td>SEM</td>
</tr>
</tbody>
</table>

Table 3.4.1: Used devices during the measurements after boriding.
Figure 3.4.1: Instron Hardness Measurement Device.
PART 4. RESULTS

During the experimental steps we obtained some results which we will talk in that part. The steps should be as same as the part 3. The metallographic photographs before boriding and after boriding are seen at Figure 4.1, 4.2, 4.3.

Figure 4.1: Microstructures before boriding process. a) 200x, b)500x, c)800x.
Figure 4.2: Microstructures of boriding layer at 200x for different temperatures.

a) 850 °C, b) 900 °C, c) 950 °C
Figure 4.3: Microstructures of boriding layer at 800x for different temperatures.
   a) 850 °C, b) 900 °C, c) 950 °C.
The next process after metallography SEM is used to get photos of crystalline structure of boriding layer. Figure 4.4. shows the SEM photos and table 4.1. gives the chemical analysis of the boriding layer.

Figure 4.4: Crystalline structures of boring layer for different temperatures.

a) 10000x at 850°C, b) 5000x at 900°C, c) 5000x at 950°C.
Table 4.1: Chemical analysis of boriding layer at 900°C and 950°C.

<table>
<thead>
<tr>
<th>Boriding Temperature</th>
<th>B%</th>
<th>C%</th>
<th>Na%</th>
<th>Fe%</th>
<th>Total%</th>
</tr>
</thead>
<tbody>
<tr>
<td>900°C</td>
<td>24.21</td>
<td>52.63</td>
<td>5.83</td>
<td>17.34</td>
<td>100.00</td>
</tr>
<tr>
<td>950°C</td>
<td>28.34</td>
<td>58.16</td>
<td>7.12</td>
<td>6.38</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Final part of the measurements are hardness tests at above and below of borided layer and surface of initial state. Micro hardness values are obtained with using Instron hardness device as I told before. The dwell time for testing is 10 seconds and testing load is 30 kg. The results are given at table 4.2 and figure 4.5 shows the distributon.

Table 4.2: Data obtained from the measurements.

<table>
<thead>
<tr>
<th>Initial surface</th>
<th>Below the boriding layer</th>
<th>Borided Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>850 °C</td>
<td>900 °C</td>
</tr>
<tr>
<td>201 HV</td>
<td>222 HV</td>
<td>241 HV</td>
</tr>
<tr>
<td>205 HV</td>
<td>223 HV</td>
<td>244 HV</td>
</tr>
<tr>
<td>205 HV</td>
<td>223 HV</td>
<td>244 HV</td>
</tr>
<tr>
<td>206 HV</td>
<td>225 HV</td>
<td>246 HV</td>
</tr>
<tr>
<td>207 HV</td>
<td>225 HV</td>
<td>249 HV</td>
</tr>
</tbody>
</table>
Figure 4.5: The distribution of results according to the temperature and process condition.
PART 5. DISCUSSIONS AND EVALUATIONS

In this part we will discuss about the results which we obtained and mentioned at part 4. Before boriding process we have took photos to understand the specimen’s microstructure. As seen at Figure 4.1 the microstructure consist of mainly ferrite and pearlite. At 800x the pearlite lamellas are easily seen near the ferrite matrix.

After boriding process we can observe the boriding layer and the diffusion zones as shown at Figure 4.2 and 4.3. Because of the normalizing in air after the heat treatment, the microstructure becomes ferrite matrix and pearlite lamellas. Although we increase the temperature at the austenite region that does not affect the microstructure because of the normalizing process. At Figure 4.3 the microstructures and the boriding layer are shown obviously. Boriding layer consists of two regions which are FeB and Fe₂B. The upper and the brighter part is the FeB layer. The darker part which is in sawtooth shape is the Fe₂B. As I mentioned before at part 2.5.2.3. Fe₂B layer is more desirable than the FeB. In our experiment The process temperature like 850°C and 900°C affects the formation of the layer characteristics. Another reasen we an talk about the formation of FeB layer can be the boriding agent source during the experiment. The minority of the source can be affect that result.

The Figure 4.4. shows us the boriding layers at greater magnifications. The layer thickness directly affects the hardness because of the diffusion rules. The data are given at table 4.2. According to this table the micro hardness values increases with increasing temperature. The initial specimen’s hardness values are the lowest ones. Below the boriding layer the hardness values takes second because this part is also heat treated. That means the microstructure may be same as initials state but the hardness increases because of the removal of the residual stresses.

The plot is constructed with using table 4.2. and there is an obvious increase with respect to increasing temperature. Hardness values of boriding layer and the place just below the boriding layer varies.
According to the later investigations about boriding process about the wear resistance gives interesting results. During the compressional forces the boriding layer preserves its form but the longitudinal loadings such as cutting of the cross sectional area that damages the boriding layer.

We can clearly say that the boriding process can be easily applied for industrial applications except the conditions which I talk above. One disadvantage of liquid boriding is the difficulty of handling during the removal from the furnace. Because in liquid state it can be easily shaken and splashed on to the researcher.
PART 6. REFERENCES


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10. Etimaden entry on Properties of Boron, website; http://www.etimaden.gov.tr