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Boron induced surface modification of transition metals

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ABSTRACT

BORON INDUCED SURFACE MODIFICATION OF TRANSITION METALS

by
Raghasudha Vangaveti

Boronizing is a thermo-chemical surface treatment of metals in which boron atoms diffuse into the metal substrate and form hard metallic borides. As a result of boronizing, several properties such as hardness, wear resistance, corrosion resistance, and high temperature oxidation resistance improve which make the metal substrate more suitable for industrial applications. These boronized parts are used in many industrial applications like ingot moulds, crucibles, biomedical implants, die-casting moulds, magnetic head applications, drawing dies etc.

The objective of this work was to investigate the influence of boronizing on the properties of transition metals. Three transition metals, tantalum, niobium and tungsten were considered in this research. After boronizing, tantalum, niobium and tungsten exhibited a coating thickness of 3 μm, 10 μm and 10 μm respectively. The obtained coating exhibited a columnar structure showing a good adhesion with the substrate. The presence of boron was confirmed by the X-Ray analysis. The coating has a microhardness of 3200 HV, 3300 HV and 3200 HV for tantalum, niobium and tungsten respectively. Potentiodynamic corrosion resistance testing was performed in 4% NaCl for the three metals. The boronized transition metals exhibited better resistance to polarization than the unboronized transition metals indicating better corrosion resistance for the boronized metals than the unboronized metals.

BORON INDUCED SURFACE MODIFICATION OF TRANSITION METALS

by
Raghasudha Vangaveti

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BORON INDUCED SURFACE MODIFICATION OF TRANSITION METALS

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This work is dedicated to my mom and dad from bringing me up to this stage and giving me the liberty to attain my goals.

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CHAPTER 1

INTRODUCTION

1.1 Objective

The purpose of this research was to investigate the influence of thermo chemical heat treatment of boron coatings on transition metals. Boronizing was done on three transition metals – tantalum, niobium, tungsten. Tantalum and niobium are recently being used as implant materials in the biomedical industry. Tungsten is a very hard metal used in the materials and aerospace industry. These three transition metals were selected to study the influence of boronizing on the properties of these materials. After boronizing, the surface properties of these metals were investigated.

1.2 Background

Coating on materials is one way of improving the mechanical properties and other surface properties such as wear, corrosion, fatigue etc. There are various kinds of coatings used in the materials industry. Boronizing is one of the prominent techniques used today.

Boronizing is a thermochemical surface treatment in which boron atoms diffuse into the surface of the base metal and form hard borides [1-9]. Boronizing is the primary choice for control of wear [10-11]. In addition to wear, the other properties that are improved by boronizing are mechanical strength, corrosion resistance in acids and high temperature oxidation resistance. This technique is applied to a wide variety of metals and alloys including, carbon steels, low alloy steels, tool steel, stainless steel, nickel based alloys and transition metals. Boronizing fills the gap between the conventional heat treatment and physical/chemical vapor deposition techniques as it produces high quality products at low production cost.

Boronizing can be further classified into different types depending upon the state in which boron is added to the base metal. This classification includes the most commonly used techniques such as pack boronizing (the technique considered in this research), paste boronizing. Liquid and gas boronizing are the less popular due to the toxicity problems related to the boron in liquid and gas phase.

1.3 Surface Treatment of Transition Metals

Surface hardening of steels by boronizing has been successfully practiced for many years. However, in the past decade, this technology has been extended to transition metals, where the scope for research is enormous. Transition metal borides have numerous useful chemical and physical properties which make them important materials from a research point of view. Prominent among these characteristics are wear resistance, high mechanical strength, high melting points, corrosion resistance in acids and high temperature electrical resistance. They are used for high temperature applications like crucibles, ingot molds for precision metallurgy, aerospace etc [12]. As such, transition metals have high melting points and high hardness.

Refractory metals such as niobium, cobalt-chromium alloys, tantalum, titanium and its alloys are used as implant materials by the biomedical industry for their excellent corrosion resistance [13-14]. Tantalum and niobium show good electrochemical properties and equally good biocompatibility when compared to titanium, which is the most widely used material for implant applications. The disadvantage with tantalum and niobium is that they donot have good mechanical strength as compared to titanium and its alloys [15-16]. Though there are many ways of increasing the strength like alloying and cold working they might adversely affect the biocompatibility of these metals. Therefore boronizing can be applied in order to improve the mechanical strength of these metals. High temperature applications of these transition metals always require high strength and high melting points apart from high temperature oxidation resistance. All these properties can be achieved by boronizing. The strong covalent bonding in most of the transition metal borides is largely responsible for their melting points, high mechanical strengths and chemical inertness [17-18].

1.4 Boronizing vs. Other Coating Techniques

Coatings used for surface hardening of materials also improve many surface properties in addition to hardness. There are many coating techniques which are applied to metals other than boronizing. These include carburizing, nitriding, carbonitriding etc.

Carburizing: This is one of the most widely used surface hardening processes. The process involves diffusing carbon into a low carbon steel alloy to form a high carbon steel surface. It increases the hardness of steels

Nitriding: It is a process of diffusion of nitrogen into the surface layers of low carbon steel at elevated temperatures. It increases the hardness of steel.

Chromizing: This process is a surface treatment performed at elevated temperatures. It is generally carried out in pack, vapor, or salt bath, in which an alloy is formed by the inward diffusion of chromium into the base metal.

Aluminizing: This is a thermochemical heat treatment process by which aluminum atoms diffuse into metal and form coating. It is Very good against corrosion.

Carbo-Nitriding: This process is a thermochemical treatment involving the incorporation of both carbon and nitrogen into the surface of the component simultaneously. Using this process one can achieve higher hardness than carburizing and nitriding.

The advantage of boronizing over these coating techniques is that the borides obtained are heat resistant and are also resistant to many chemical environments.

Boronizing is a cost effective process when compared to other coating techniques. The hard borides obtained have very good wear resistance when compared to the other coating techniques.

CHAPTER 2

BORONIZING

2.1 Boronizing/Boriding

Boronizing is thermochemical surfaces treatment process in which boron atoms diffuse into the surface of the base metal and form hard borides. This process can be applied to a wide variety of ferrous, nonferrous and cermet materials. In this process, the metal which needs to be boronized is well cleaned and thermochemically treated to temperatures between 700^0C to 1200^0C. Usually the time of boronizing varies from 1 hour to 12 hours producing a boride layer of thickness as a function of time and temperature of boronizing. Boronizing can be carried out with boron in different states such as solid powder, paste, liquid and gas. In addition to the state in which boron powder is added to the base metal also boronizing can be performed using different techniques like plasma boronizing, boronizing in a fluidized bed reactor etc.

As a result of boronizing, properties such as wear resistance, corrosion resistance, mechanical strength and high temperature oxidation resistance are improved this will be discussed in detail in the next section.

2.2 Characteristics of Boride Layer

The boride layer produced has numerical characteristic features which make them different from the conventional heat treatments. The main advantage is that the boride layer has very high hardness (from 1500 HV to 5000 HV) with high melting point.

Table 2.2 shows the microhardness and the melting of various metal borides that are formed by this process.

Table 2.1 Melting Point and Microhardness of Various Boride Phases Formed During Boronizing [19-21]

Substrate	**Constituent phases in the boride layer**	**Melting points**		**Microhardness of layer, HV or kg/mm^2**
		°C	**°F**	
Fe	FeB	1390	2535	1900-2100
	Fe_2B			1800-2000
Co	CoB			1850
	Co_2B			1500-1600
Co-27.5 Cr	CoB			2200 (100 g)
	Co_2B			~1550 (100 g)
Ni	Ni_4B_3			1600
	Ni_2B			1500
	Ni_3B			900
Inco 100	. . .			1700 (200 g)
Mo	Mo_2B	2000	3630	1660
	MoB_2	2100	3810	2400-2700
	Mo_2B_5	2100	3810	
W	W_2B	2300	4170	~2700 (overall hardness)
	WB			
	W_2B_5			
Ti	TiB	1900	3450	2500
	TiB_2	2980	5395	3370
Ti-6Al-4V	TiB			3000 (100 g) (overall hardness)
	TiB_2			
Nb	Nb_2B_2	3050	5520	2600-3000 (overall hardness)
	NbB_4			
Ta	Ta_2B	3200-	5790-	3200-3500
	TaB_2	3500	6330	2500
		3200	5790	
Zr	ZrB_2	3040	5500	2300-2600 (overall hardness)
	Zr_2B			
Re	ReB	2100	3801	2700-2900

The combination of high surface hardness and a low coefficient of friction of the borided layer also make a significant contribution in combating wear mechanism [22-23]. Therefore the advantages of boronizing can be summarized as follow

Advantages of boronizing:

- Boronized metals can produce high hardness and high melting points
- Boronizing can enhance the corrosion resistance in alkaline and acidic media which is an advantage for many industrial applications.
- Borided surfaces have moderate oxidation resistance (up to 850^0C) and are quite resistant to attack by molten metals.
- Borided parts have increased fatigue life and service performance under oxidizing and corrosive environments.
- Boronizing increases wear resistance and can be applied to a wide variety of metals and alloys.

There are also certain disadvantages of boronizing which can be summarized as follows

Disadvantages of boronizing:

- The technique is labor intensive making the method less cost effective than other thermochemical surface hardening processes.
- 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

Overall boronizing can be considered to be one of the primary coating processes to obtain good surface properties for metals and alloys. The boronized metal parts have many applications in industry which will be further discussed.

2.3 Mechanisms of Boronizing

Boronizing is a diffusion process. Diffusion coatings are the most promising among protective coatings, because the strength of the cohesion between them and the matrix metal exceeds that of bonding of other kinds of coatings due to the penetration of the diffusing agent into the crystal lattice of the latter [24]. During boronizing, the boron atoms diffuse and are subsequently absorbed into the metallic substrate. Thus boron gets into the interstices of the metal lattice forming an interstitial boron compound with a single-phase or a poly-phase boride layer.

The boronizing process can be divided into two steps as there are two main reactions which are taking place during the diffusion of boron atoms into the base metal.

In the first step, the nuclei are formed as a function of time and temperature of Boronizing and are followed by the growth of the boride layer [25]. The metal borides that are formed in this process occupy the interstices of the metal and slowly the boride layer grows at these defect points. The type of metal boride that is formed depends on the process paramenters. If the boron medium is in excess, then there is a possibility that the boride layer may contain two or more intermetallics (for example, TaB, Ta_2B both can be present in the coating).

The second step is a diffusion controlled process where the thickness of the boride layer varies with respect to the parabolic time law,

$$X^2 = kt$$

In the above expression, x is the thickness of the boride layer, k is a constant depending of boronizing temperature and t is boronizing time [25]. Therefore, from the above expression, boronizing can be called as a time and temperature controlled process. The thickness of the boride layer depends upon the two factors- time and temperature. The boride layer thickness varies exponentially with temperature, and, with time, it shows a parabolic behavior.

2.4 Boronizing of Nonferrous Materials

Boride coatings on ferrous materials have been reported to sxhibit an excellent combination of corrosion and wear properties [26-27]. The boride coatings on nonferrous materials are well known for their high hardness including wear and corrosion properties [28-29]. Titanium and its alloys, especially, are attracting considerable attention because of their potential use as low density and high temperature structural materials. The high temperature oxidation resistance of titanium and its alloys can be improved by boronizing.

Nickel and its alloys are known for their usage as high temperature corrosion resistant materials however, they lack in the wear resistance which can be improved by boronizing. Similarly, for tantalum and niobium which have a potential demand as implant materials in the biomedical industry. Their mechanical strength can be improved by boronizing.

In the case of transition metals as discussed in the first chapter many properties such as mechanical strength, wear resistance and high temperature oxidation resistance can be improved by boronizing. This process needs to be performed at a higher temperature for ferrous materials. The typical boronizing temperature for transition metals ranges between 900^0C-1400^0C. Unlike for ferrous materials where the boron coating appears as a saw-tooth structure, for non ferrous materials, it looks more like a columnar structure. The saw tooth or the columnar structure helps in improving the mechanical adherence between the coating and the substrate.

Figure 2.1 shows boron coating on titanium where the combination of both saw tooth and columnar structure can be seen.

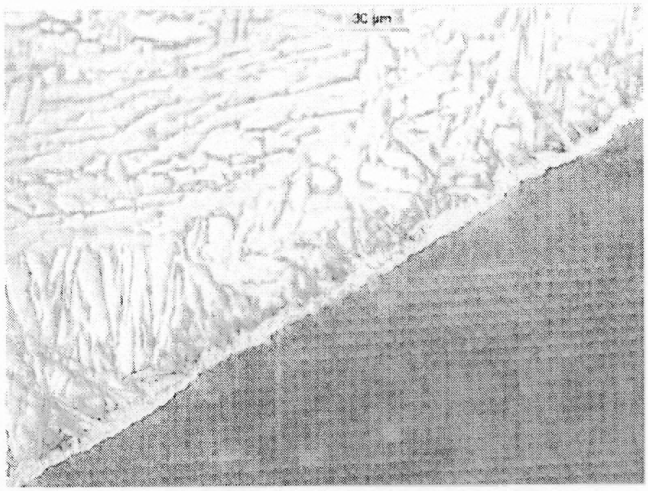


Figure 2.1 A combination of saw tooth and columnar structure of boron coating on 99.5% pure Ti [30] .

2.5 Application of Borided Parts

Boronized parts have several industrial applications due to their enhanced properties. Applications are being developed that take advantage of the hardness and corrosion resistance properties of boronized metals.

Diesel engine oil pump gears made from 4140 steel are boronized, hardened and tempered. The treated gears resist the adhesive wear due to the environment [31].

Type 316 stainless steel pipe-bends that transport vinyl chloride have a service life of half a year in a plant manufacturing PVC. Premature wear is developed, due to hydrochloric acid that is mixed with steam. After boronizing, the pipe-bends remained in service for over two years with no damage to the grain structure.

Boronizing has been applied to Ti-6Al-4V for parts such as rotor blade cladding for helicopter applications. Borided parts find applications in die-casting moulds, bending blocks, wire draw blocks, pipe clips, pressing, shaping rollers etc.

Boronized Permalloy is used for magnetic head applications. Boronized cemented carbides are used as drawing dies, guiding parts and dimensional measurement parts.

The hardness of tantalum and niobium are improved by boronizing without affecting their bio compatibility. Boronized tantalum and niobium are used as implant materials for bio medical applications [11].

Boronized tungsten is used in high temperature applications such as crucibles and ingot molds for precision metallurgy [10].

CHAPTER 3

PROCESS OF BORONIZING

3.1 Types of Boronizing

Boronizing process can be divided into different types based on the mode in which boron is added along with other elements. These are,

- Pack boronizing
- Paste boronizing
- Liquid boronizing
- Gas boronizing
- Plasma boronizing
- Fluidized bed boronizing
- Multi component boronizing

3.2 Pack Boronizing

Pack boronizing is the most widely used process of all the types due to various reasons. Pack boronizing is a type where boron is added to the substrate in the solid state. Boron powder is used as the coating medium in pack boronizing. This technique is the most preferred due to safety, the possibility to change the composition of the powder mixture, the need for limited equipment, the resultant economic savings and the relative ease of handling.

This process involves the embedding of the metallic sample into the boron powder mixture that is made up of three constituents [31]

The solid boron yielding constituent can be boron carbide, ferrous boron, amorphous boron etc.

- The activator usually activates the boron atoms at high temperature and allows them to diffuse in to the metal. The most commonly used activators are $NaBF_4$, KBF_4, $(NH_4)_3BF_4$, NH_4Cl, Na_2CO_3 and BaF_2.

- The third is the dilutent which usually does not participate in the reaction but prevents the caking of the boronizing agent, The most commonly used diluters are silicon carbide and alumina.

The sample or the work piece is packed along with the boron powder mixture in a crucible and is sealed with a lid. It is heated to the boronizing temperature in a furnace for a specific time. The heat treatment should be usually carried out in an atmosphere which is inert or vacuum or both in order to avoid high temperature oxidation.

Following the above procedure the powder mixture can be reused up to 5-6 times by blending it with 20%-50% with the new powder mixture.

3.3 Paste Boronizing

Paste boronizing can be considered to be a commercial process, while powder boronizing is not a manufacturable process. Large components or their selective parts can be boronized using this technique. In this process, a boronizing paste of 55% B_4C(grain size 200-240μm) and 45% cryolite [32], is applied over the entire or selected portions, after drying, a layer of about 1-2 μm thick is obtained. Then, these parts are placed in the furnace and heat treated in inert or vacuum atmosphere. After the heat treatment is done the paste is separated from the components by blast cleaning, brushing or washing.

3.4 Liquid Boronizing

Liquid boronizing is divided into electroless salt bath boriding and electrolytic salt bath boronizing processes. There are several disadvantages of these processes:

- Removal of excess salt and untreated boron is essential after the treatment. This step may prove expensive and time consuming.
- To achieve boronizing reproducibility, bath viscosity is not allowed to increase. This is done by recharging with salt which requires significant maintenance.
- In some situations protection from corrosion fumes may be required.

This process is very commonly applied for ferrous alloys and nickel based alloys at high temperatures. This is a simple, inexpensive process that offers capability to rapidly create a wide range of metal structures and propertie modifications on various parts and components.

3.5 Gas Boronizing

Gas boronizing is another type of boronizing in which the boron source is in the gaseous phase. At high temperature boron gas diffuses into the metal and hard borides are formed. The boron source which is commonly used in gas boronizing are boron chloride (BCl_3), diborane (B_2H_6) etc. This is not one of the common and most widely used techniques of boronizing because of toxicity. The problems with the explosion of the gas and the toxicity of boron limit the usage of gas boronizing technique. The BCl_3-H_2 gas mixture has previously been attempted to boronize steel, but the high concentration of BCl_3 causes the corrosion of the substrate and results in poor adherent layers. To improve the technique, the dilute (1:15) BCl_3-H_2 gas mixture is commonly used at 700- 900 °C and under the pressure of about 67 kPa [33]. This process can be used with titanium and its alloys.

3.6 Plasma Boronizing

Many efforts were made to develop the gas boronizing technique. This could not be achieved successfully only due to toxicity of materials (diborane and boron chloride) used as the gaseous medium for boronizing. However, trimethyl borate ($B(OCH_3)_3$) was introduced as an alternative for the precursors. Therefore, by using trimethyl borate as a medium, plasma assisted boronizing technique was developed for steels and a dense boride layer on the steel substrate was successfully formed in a plasma assisted boronizing process [34].

There are several advantages of plasma assisted boronizing technique:

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

3.7 Fluidized Bed Boronizing

Heat treatment of alloys in a fluidized bed reactor has been carried out for over twenty five years. This technique has been recently innovated for boronizing. Boronizing is performed in an oxygen free environment with the coarse grained silicon carbide as the bed material. Faster heating rates at shorter time periods can be achieved in this method. The main disadvantage of this process is the continuous flushing of the boronizing agent within the retort by the inert gas. Otherwise, fluidized bed boronizing has many advantages such as:

- High rates of heat flow, as well as direct withdrawal of parts, provide shorter operation cycles time.
- Temperature uniformity with low capital cost and flexibility is ensured
- Usually the fluidized bed furnace is very tightly packed due to the upward pressure of gases. This will ensure the inert atmosphere in the furnace.
- Using this process continuous production of boronized parts can be obtained.

The boride coating that were obtained using the fluidized bed boronizing have been reported to have excellent combination of properties such as high fatigue strength and wear resistance [35].

3.8 Multi-component Boronizing

Boronizing with a combination of other coating techniques are referred to as multi-component boronizing. There are many other surface coating techniques such as carburizing, nitriding, chromizing, aluminizing etc. If one of the coating elements in these multi-component coatings is boron, then it is called as multi component boronizing. This process may involve coating both the elements at the same time or coating one element after the other. Some of the metals which can be compatible with boron in these multi component coatings are aluminum, chromium, vanadium, silicon etc. Some of these multi component boronizing processes are illustrated in Table 3.1.

Table 3.1 Multi-Component Boronizing

Reference	Multi-component boronizing technique	Media type	Media composition, wt%	Process steps investigated*	Substrate(s) treated	Temperature, °C (°F)
36	Boroaluminizing	Electrolytic salt bath	3-20% Al_2O_3 in borax	S	Plain carbon steels	900 (1650)
37	Boroaluminizing	Pack	(A) 84% B_4C + 16%borax (B) 97%ferroaluminium + 3% NH_4Cl	S B-Al Al-B	Plain carbon steels	1050 (1920)
26	Borochromizing	Pack	(A) 5% B_4C + 5%KBF_4 + 90% SiC (Ekabor II) (B) 78% ferrochrome + 20% Al_2O_3 + 2% NH_4Cl	S B-Cr Cr-B	Plain carbon steels	Borided at 900 (1650) Chromized at 1000 (1830)
26	Borosiliconizing	Pack	(A) 5% B_4C + 5% KBF_4 + 90% SiC (Ekabor II) (B) 100% Si	B-Si Si-B	0.4% C steel	900-1000 (1650-1830)
26	Borovanadizing	Pack	(A) 5% B_4C + 5% KBF_4 + 90% SIC (Ekabor II) (B) 60% ferrovanadium + 37% Al_2O_3 + 3% NH_4Cl	B-V	1.0% C steel	Borided at 900 (1650) Vanadized at 1000 (1830)

* S = simultaneous boronizing and metallizing,
B-Al = boronized and then aluminized, Al-B= aluminized and then boronized.

CHAPTER 4

DESCRIPTION OF EXPERIMENT

4.1 Procedure of Experiment

In this section, a brief description of the experiment is given. Tantalum, niobium and tungsten were boronized at 950^0C for 4 hours. This temperature was chosen on the basis of the literature survey and also to be able to compare the results of all three metals as they would be boronized at the same temperature and time. Tantalum was boronized at temperatures 950^0C, 1050^0C for 2,4,6,8 hours respectively to investigate the kinetics of the boronizing reaction. This was mainly done in order to gain information on change in thickness of the coating with time and temperature. Thus the kinetics of the process can be investigated.

Boronizing basically includes series of steps in the experiment like cleaning the sample surface, packing the sample in the boron powder mixture and heat treatment. The obtained sample after heat treatment is characterized for phase identification (XRD), thickness of the coating and microhardness of the coating. Then the boronized samples and the plain samples are subjected to corrosion testing and the results are compared.

This procedure can be summarized in the flow chart shown in Figure 4.1.

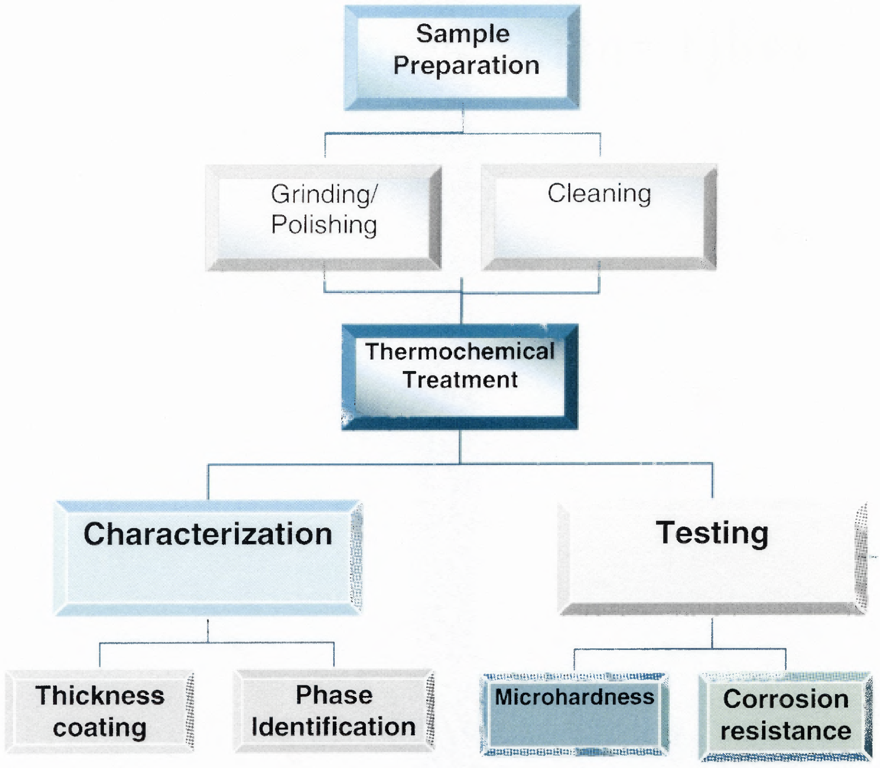


Figure 4.1 Flow chart showing the steps involved in boronizing process, characterization and properties evaluation.

4.2 Experimental Setup/Process Variables

Each in the flow chart has certain process variables and standards which will be discussed in this section.

4.2.1 Sample Preparation

Sample preparation can be subdivided into two steps- grinding/polishing and cleaning. 99.9% pure Tungsten, tantalum and niobium are cut into 8 X 8 X 2 mm dimensions using a diamond blade. These samples are then grinded on silicon carbide sand paper form grit size 120 to 600. Starting from grit size 120,220,400 and 600, the sample is ground until all the scratches on the surface were inclined in one direction. Grit size 120 and 220 are the coarser sizes where the sample gets ground. 400 and 600 are the finer grit sizes used for polishing of the sample. This will comprise the grinding/polishing step of the sample preparation. Samples are then cleaned in ultrasonic bath with acetone for upto 5 minutes.

4.2.2 Boronizing

The initial step of boronizing was preparation of the boron powder mixture for heat treatment. The boron powder mixture comprises of the following compounds

- 90% – 95% w/w boron carbide (B_4C)[240 grit, technical grade from Electro Abrasive Corporation]
- 5% – 9% w/w Aluminum oxide (Al_2O_3)[Atlantic Equipment Engineers]
- 0.5% – 2% w/w potassium tetraflouroborate (KBF_4) [99.5% (assay) of Alfa Aesar]

The above powders were measured according to the percentage composition on an electronic balance. Initially, alumina and potassium tetraflouroborate are mixed together in order to have a fine mixture and also to eliminate any bit of clusters present in the mixture. Then, gradually, boron carbide is added to this mixture and ground well in order to have a homogeneous mixture of the three compounds. Finally, this mixture is mixed in the blender.

The crucible containing the sample embedded in the boron powder mixture is covered by the lid and is placed in the furnace at 950^0C. An inert atmosphere is maintained in the furnace by pumping argon gas (Grade 5, 99.99% pure from SOS Gases). After the time is reached the furnace is cooled by reducing the temperature.

The crucible lid was removed and the sample is extracted from the powder mixture. The samples are then cleaned in the ultrasonic bath.

4.2.3 Characterization Techniques

The sample was then subjected to various characterization techniques as summerized in the flow chart in Figure 4.1. The first of these is phase identification

Phase identification is done using the X-ray diffraction technique [XRD Philips (PW3040 MPD DY715]. Using this technique, the boronized and unboronized samples are analyzed. The process parameters are as follows: the wavelength of the X-rays used are Cu K-α 1 at 45 kV and 40 mA. 1/4" diverging slit and 1/4" anti scattering slits are used for the divergence and scattering of X-rays. The scan range for 2θ is from 5 to 100^0. The phases of the specimen were determined by the software called X'Pert high score.

The surface of the boronized sample and the unboronized samples are observed under the Axio Tech Microscope from Carl Ziess with 10x eyepiece lens and a magnification of 20x, 50x and 100x objective lens. The surface images are taken from the microscope using the digital camera [Pixelink PL-A662] which is connected to the computer.

In order to observe the crossection image and the coating thickness, the boronized samples are mounted in an epoxy resin from Allied High Tech products Inc. The mounting mixture contained epoxy and hardener which are mixed in the ration of 10:3 by weight. This mixture is stirred well to obtain a homogeneous mixture. This mounting mixture is poured into a mould with the sample placed at the center of the mould. The mount is then placed in vacuum for 10 minutes in order to eliminate air bubbles. The mount is left at room temperature for a minimum of nine hours and there after the sample mount is taken out of the mould. This was then subjected to grinding and polishing.

Met Prep 3 from Allied High Tech Products Inc is used for grinding and polishing the mounted samples. The samples are ground on silicon carbide paper of 180, 320 and 600 grit size for about 8 minutes with a head pressure of 8 LB with the extender being water (H_2O). The polishing is done on diamond compound of 6,3,1 microns and finally on a colloidal silica suspension of 0.05 microns. The polishing time for each of these steps was 4 minutes. The extenders used are red lube and blue lube respectively.

The samples after grinding and polishing are cleaned with a cleaning solution which is mixed in according to 100:2 ratio with water (100 parts) and then finally the samples are cleaned with water. The samples are then allowed to dry. The echants used for each of the metals are listed in Table 4.2. Etching is done in order to observe the microstructure and the coating thickness.

Table 4.2 Etchants used for the Transition Metals

Metal/sample	Etchant	Time of etching
Tantalum	50 ml H_2SO_4 (98%) 20 ml HNO_3 (65%) 20 ml HF (48%)	10 -20 seconds Rinse with De Ionized water
Niobium	50 ml distilled water 20 ml HF (40%) 10 ml HNO_3 (65%) 15 ml H_2SO_4 (98%)	15 seconds
Tungsten	100 ml distilled water 1 ml H_2O_2 (30%)	Boiling for 30-90 seconds

The etched samples after drying are observed under the microscope for surface morphology of the coating. The adherence between the coating and the substrate materials is observed. The thickness of the coating is measured using the Axio Vision software version 4.1 of Carl Zeiss. The coating thickness is measured at various places and an average coating thickness is considered.

4.2.4 Microhardness Testing

The microhardness of the transition metal samples is determined using the LM700 Microhardness Tester with the Knoop indenter from Leco. The indentations are taken from the substrate surface to the coating. Indentations were taken along the coating in order to have a proper estimate of the microhardness of the coating at different places. The obtained depth of the indentations are observed with respect to the microhardness values and a graph is plotted between microhardness Vs distance from surface to the interior of the substrate.

4.2.5 Corrosion Resistance Testing

The corrosion resistance testing of the samples is done using PARSTAT 2263 from Princeton Applied Research. These are the potentiodynamic corrosion measurement techniques. The sample is placed in a flat cell containing 4 % NaCl solution as shown in the Figure 4.2

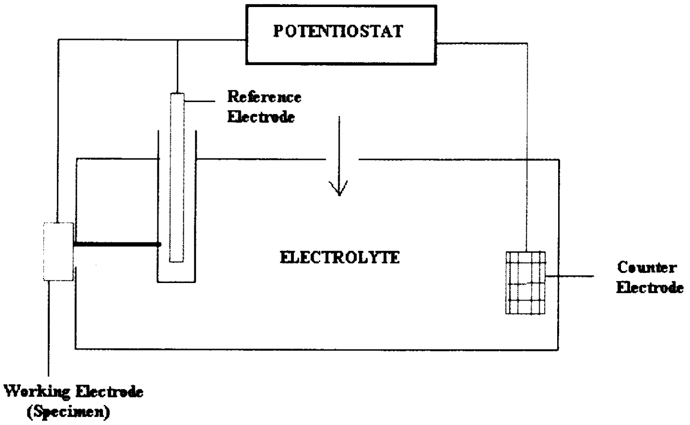


Figure 4.2 Flat cell used for corrosion resistance measurements.

The sample (which was the working electrode) is placed at one end of the flat cell with one of its surface exposed to the 4% NaCl solution. The other end is the counter electrode. This flat cell is connected to the potentiostat and this whole setup is connected to the computer. When the current is passed with the help of the software Power Corr from Princeton Applied Research the linear polarization graphs (potential Vs Current density) and the Tafel plots (potential Vs log current density) are developed. Using the resistance to polarization value provided by the software the corrosion resistance of the boronized and the unboronized samples are compared and analyzed.

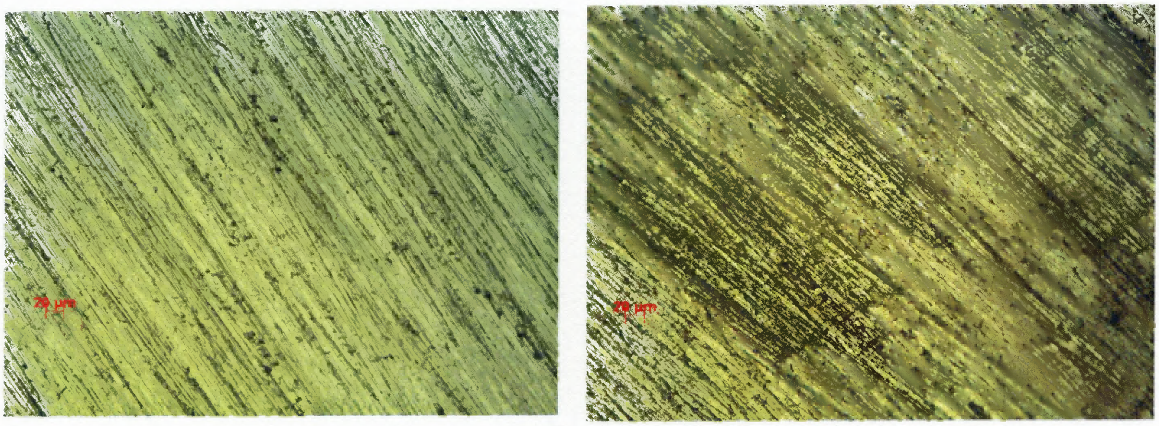
CHAPTER 5

RESULTS AND DISCUSSION

5.1 Characteristics of Boride Layer on Tantalum

5.1.1 Surface Morphology

Tantalum before boronizing is a grey metal with lusture. After boronizing, tantalum changes its color to a brown lusture metal. The surface of tantalum before and after boronizing can be seen in Figures 5.1 (a) and (b) respectively. From the figure, it could be concluded that the presence of the boride layer is the reason for this change. The surface roughness is increased after boronizing when compared to the sample before boronizing.



(a) Surface before boronizing

(b) Surface after boronizing

Figure 5.1 Surface Images of Tantalum before and after boronizing at 950^0C for 4hours.

5.1.2 Investigation of Kinetics

The kinetics of the boronizing reaction is investigated for tantalum. Tantalum is boronized at two temperatures 950^{0}C and 1050^{0}C each at four different boronizing times 2 hours, 4 hours, 6 hours and 8 hours respectively. This is done to investigate the variation of the thickness of the coating with boronizing time and temperature.

Table 5.1 shows the thickness obtained on boronizing tantalum at the above mentioned temperatures and times.

Table 5.1 Thickness of Boron Coating Obtained for Tantalum

Temperature/Time	**2hrs**	**4hrs**	**6hrs**	**8hrs**
950°C	1.5-2.7 μm	3-4 μm	5-6.5 μm	7-8 μm
1050°C	10-12 μm	13-15 μm	18-20 μm	20-22 μm

As discussed earlier in Section 2.3, thickness of the coating increases exponentially with temperature of boronizing and it increases parabolically with boronizing time. This is observed in Figures 5.2 and 5.3 respectively.

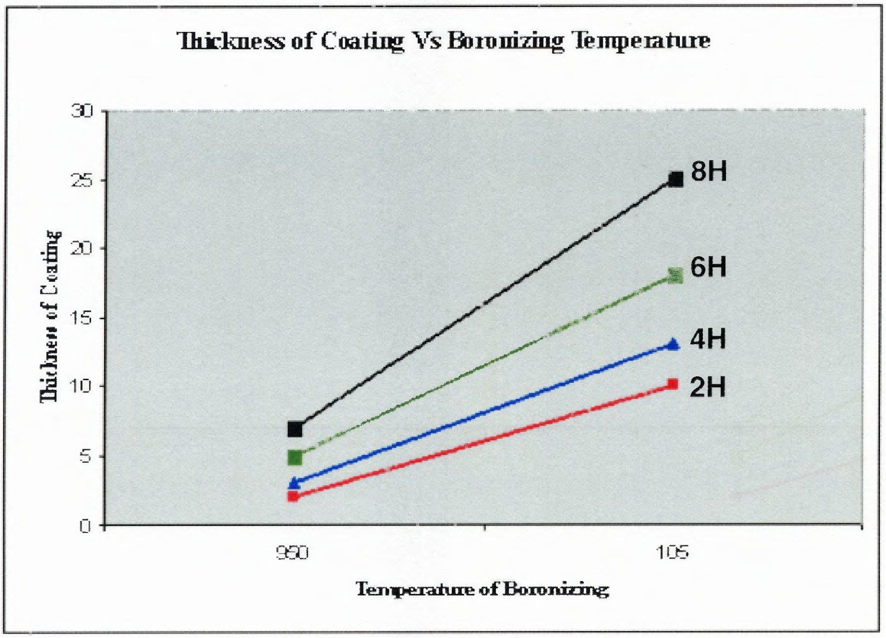


Figure 5.2 Effect of Temperature on the thickness of Boron coating on Tantalum.

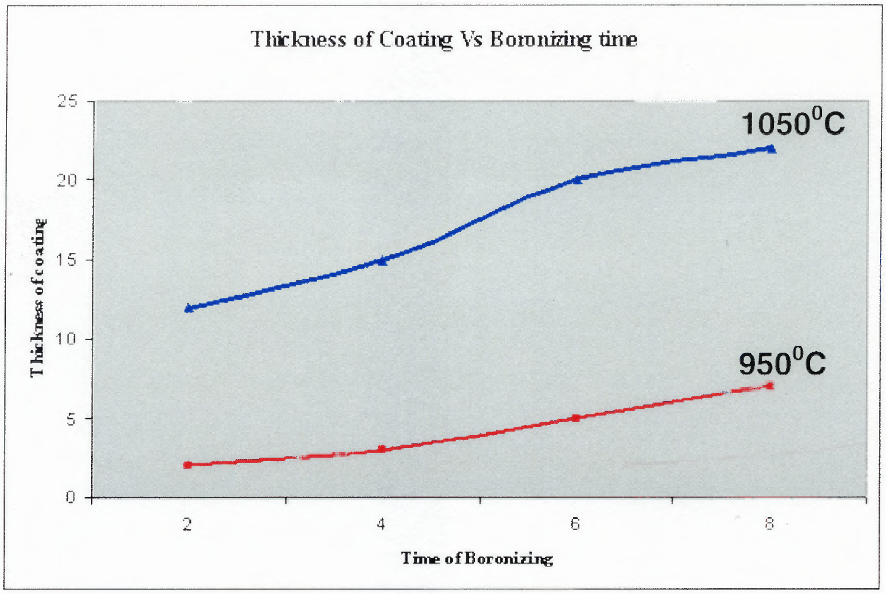


Figure 5.3 Effect of time on the thickness of boron coating on Tantalum.

5.1.3 Phase Identification

The presence of boron is confirmed by the X-ray diffraction method. The peaks obtained after boronizing are compared to the peaks of tantalum before boronizing. By doing this, and also by comparing the peaks with some standard tantalum boride peaks, the presence of tantalum boride is observed.

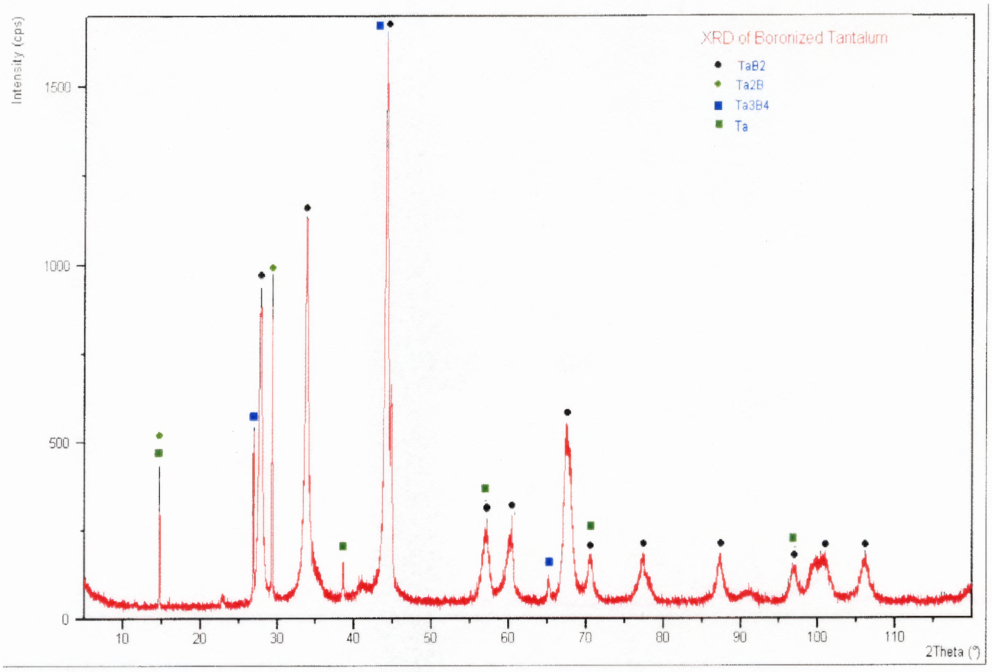


Figure 5.4 The XRD pattern of boronized tantalum.

The phases in boronized tantalum are determined to be Ta_2B, TaB_2 and Ta_3B_4. This is obtained from the analysis of the phase diagram of boron and tantalum and comparing the peaks with the peaks of the tantalum boride phases.

5.1.4 Thickness of Boron Coating

The coating obtained on tantalum when boronized at 950^{0}C for 4 hours is approximately 3-4 μm thick. A columnar structure of the coating showing a good adhesion with the substrate is observed form the microstructure.

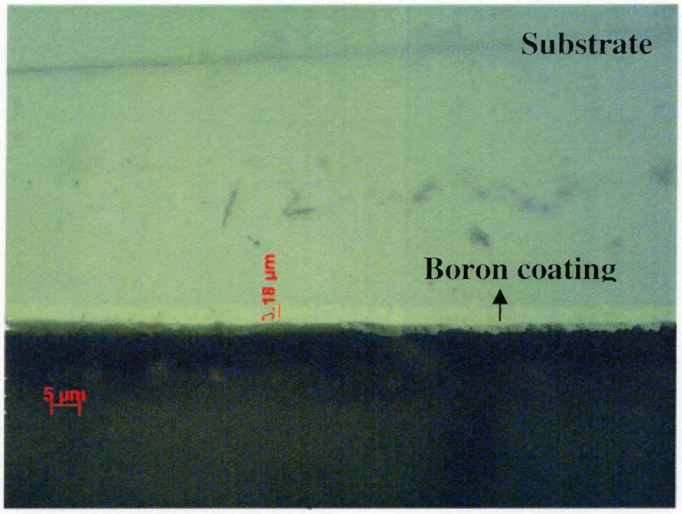


Figure 5.5 Boride coating on tantalum substrate after boronizing at 950^{0}C for 4 hours.

From the microstructure in Figure 5.5 it can be observed that the coating is uniform through out the surface. The coating layer has three phases Ta_2B, Ta_3B_4 and TaB_2. Further, this coating is investigated for microhardness testing.

5.1.5 Microhardness Measurements

The microhardness measurements show a difference in the microhardness of the substrate to that of the coating. The coating has a higher microhardness when compared to the microhardness of the substrate material. Also it is observed from Figure 5.6 that the microhardness gradually decreased from the coating as it approaches the substrate. The microhardness measurements are made across the coating to test the uniformity of the microhardness along the coating and it is found that the microhardness of the coating was uniform through out the surface.

The microhardness of the obtained coating ranges from 3200-3300 on the Knoop scale whereas the microhardness of the substrate is about 10 times less than that was on the coating

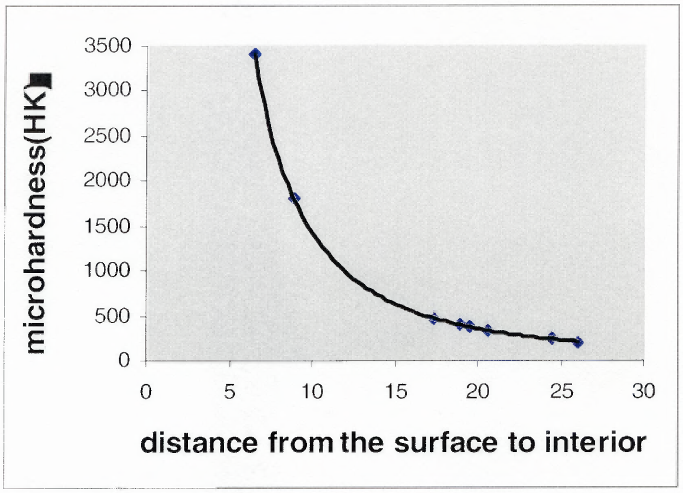
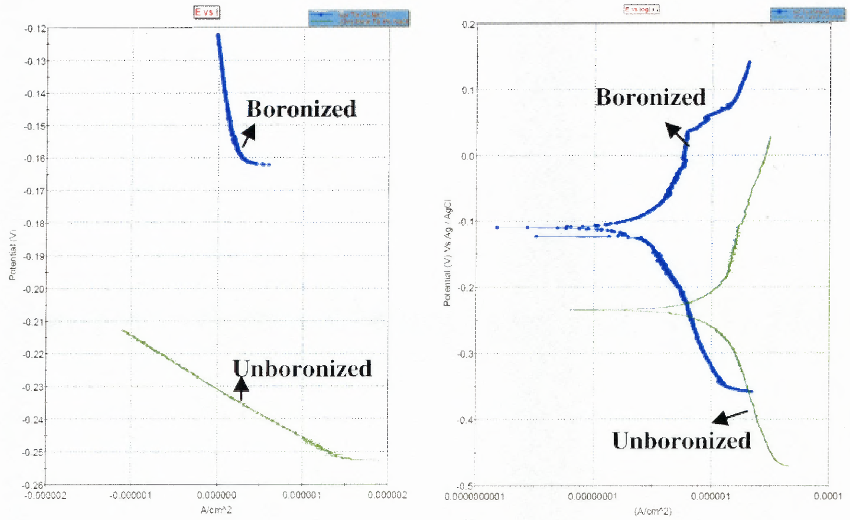


Figure 5.6 The microhardness plot of boronized tantalum.

5.1.6 Corrosion Resistance Testing

The corrosion resistance testing for both boronized and unboronized is done in 4 % w/v NaCl solution. Figures 5.4 (a) and (b) show the plots of linear polarization and Tafel plots.



(a) Linear polarization plot (b) Tafel Plot

Figure 5.7 Comparative graphs of linear polarization and Tafel plots for boronized and unboronized tantalum.

From the linear polarization plot two main points can be concluded.

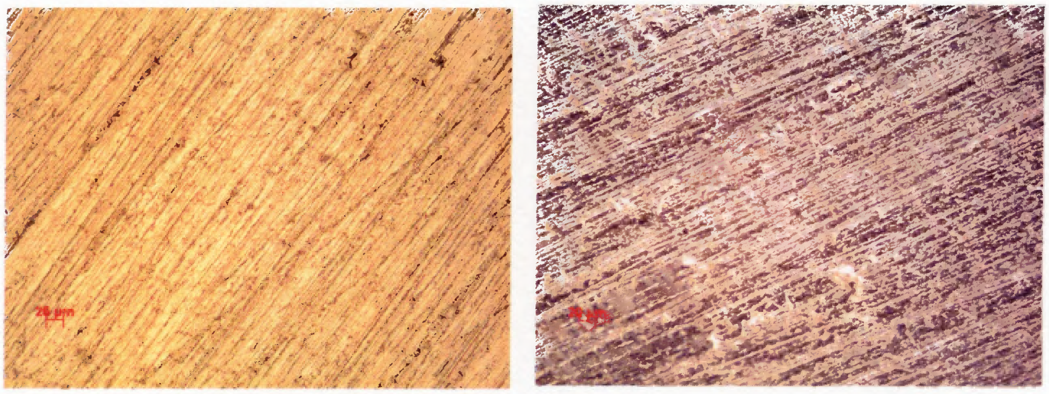
- The boronized sample shows more positive potential when compared to the unboronized sample
- The resistance to polarization of boronized tantalum is 1.29 X 10^5 Ω when compared to that of the unboronized tantalum is 1.5 X 10^3 Ω

From the Tafel plots, one can observe that the boronized sample has more noble open circuit potential when compared to the unboronized sample. In the anodic region of the graph, the boronized sample shows a more stable behavior or resistance to corrosion than the unboronized sample. The improved corrosion resistance of boronized Tantalum 4% NaCl is also discussed in the work done R. Petrova et.al[38]

5.2 Characteristics of Boride Layer on Niobium

5.2.1 Surface Morphology

The outer surface of niobium before and after boronizing is shown in Figures 5.8 (a) and (b), respectively. Even in the case of niobium, it is observed that boronizing increased the surface roughness.



(a) Before Boronizing

(b) After Boronizing

Figure 5.8 Surface morphology of niobium before and after boronizing.

5.2.2 Phase Identification

The XRD data of boronized niobium is compared with the XRD peaks of unboronized niobium and the presence of the boron phase is determined. The peaks in the XRD graph of boronized niobium corresponded to niobium borides Nb_2B and NbB_2 apart from niobium. This is in agreement with the results obtained by Metin Usta obtained on boronizing niobium at 940^0C for four hours [11].

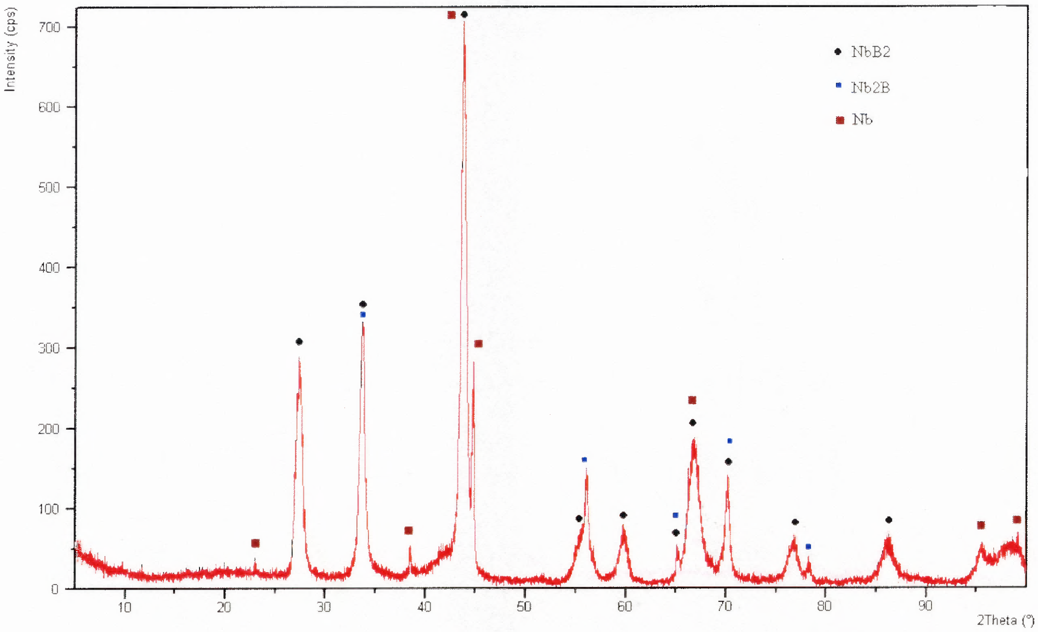


Figure 5.9 XRD pattern of niobium boronized at 950^0C for 4 hours.

5.2.3 Thickness of Coating

The boron coating on niobium also has a columnar structure showing good adhesion between the coating and the substrate. The obtained coating is 10-12 μm thick which is much thicker when compared to tantalum. By this, one can observe that boron is forming a thicker coating than tantalum at the same temperature. One can conclude that boron is more compatible with niobium and has a tendency of penetrating more into niobium. Figure 5.10 shows the coating on niobium

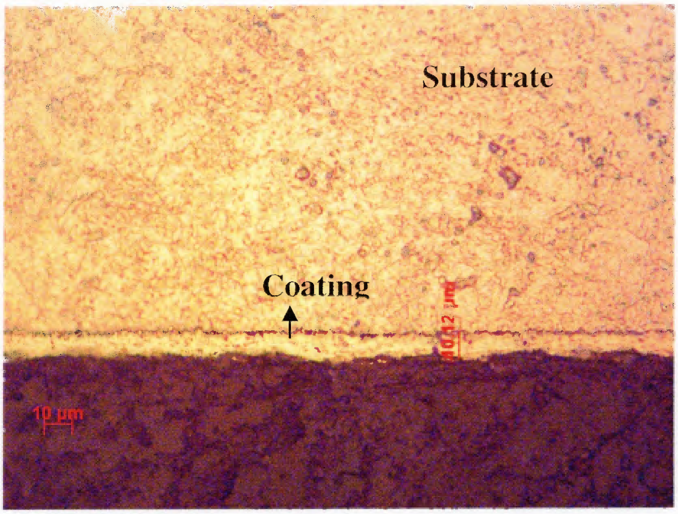


Figure 5.10 Microstructure of boron coating on niobium boronized at 950^0C for 4 hours.

5.2.3 Microhardness Measurements

The microhardness of the obtained coating is measured and is found to range between 3100-3200 HK. The microhardness is uniform throughout the coating. As in the case of tantalum, niobium shows a gradual decrease in the microhardness from the coating to the substrate surface.

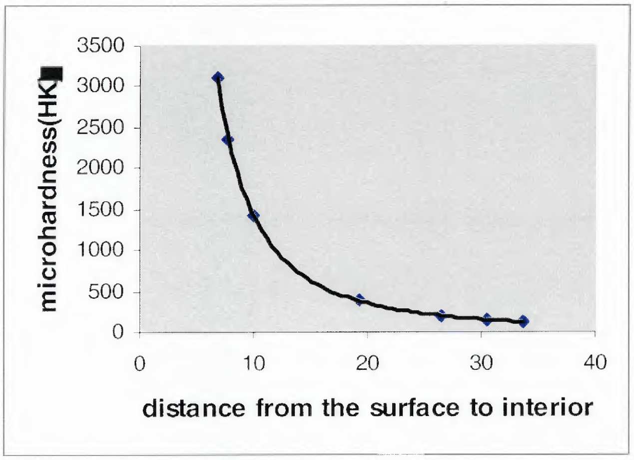
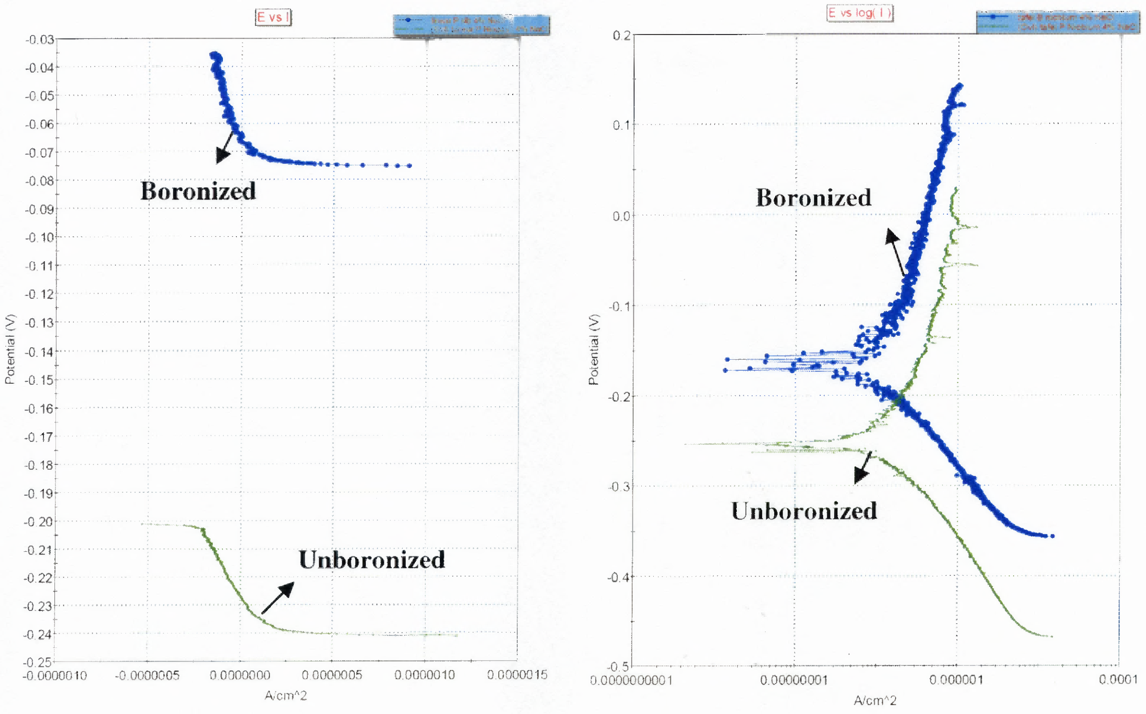


Figure 5.11 Microhardness Vs distance plot for boronized niobium.

5.2.4 Corrosion Resistance Testing

The corrosion resistance testing for niobium is done in 4% w/v NaCl. The obtained linear polarization graph and the Tafel comparative graphs have been analyzed. The open circuit potential is nobler for boronized niobium than that for unboronized niobium. From the linear polarization graph, one can observe that the boronized sample shows a more positive potential than the unboronized sample. Figures 5.12 (a) and (b) show the comparative graphs of both boronized and un boronized samples.



(a) Linear Polarization

(b) Tafel Plot

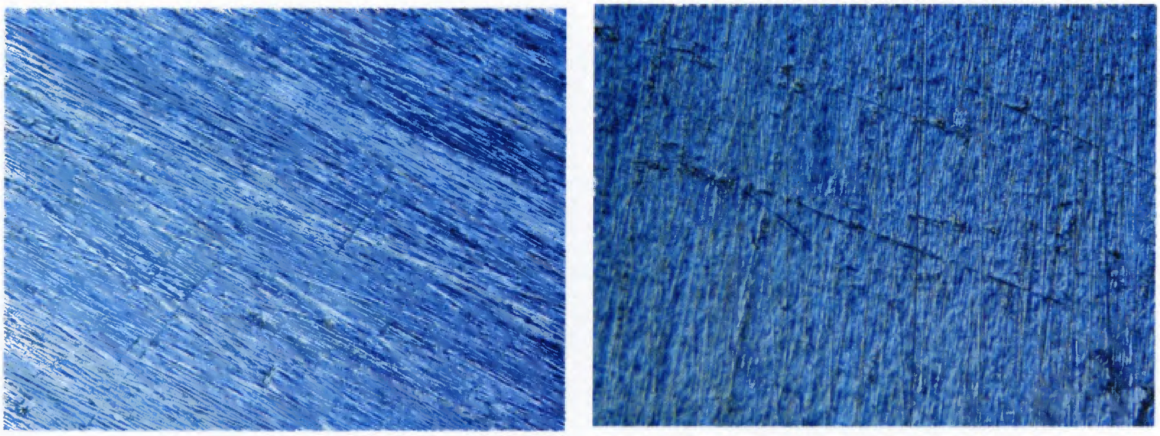
Figure 5.12 Comparative Tafel and polarization graphs for boronized and plain niobium.

The resistance to polarization (R_p) for the boronized sample is 1.01 X 10^5 Ω, and is very high when compared to the unboronized sample which showed a resistance of 1.05 X 10^3 Ω.

5.3 Characteristics of Boride Layer on Tungsten

5.3.1 Surface Morphology

Tungsten is boronized at 950^0C for four hours. The surface morphology observed in tungsten is similar to what is observed in the case of tantalum and niobium. The presence of borides changes the outer color of the tungsten samples. The surface roughness increased after boronizing. Figures 5.13 (a) and (b) show the surface roughness of tungsten before and after boronizing respectively.



(a) Before Boronizing (b) After Boronizing

Figure 5.13 Surface images of tungsten before and after boronizing at 950^0C for 4 hours.

5.3.2 Phase Identification

The XRD analysis reveales the presence of tungsten boride (WB) and tungsten diboride (W_2B) as shown in Figure 5.14. From the tungsten boron phase diagram one can observe that low order borides interstitials formed at lower temperatures. The experimental studies carried out by M.Usta et al. [39] of the boronizing of tungsten (940^0C for 4 hours) confirmes the above two phases in the XRD analysis.

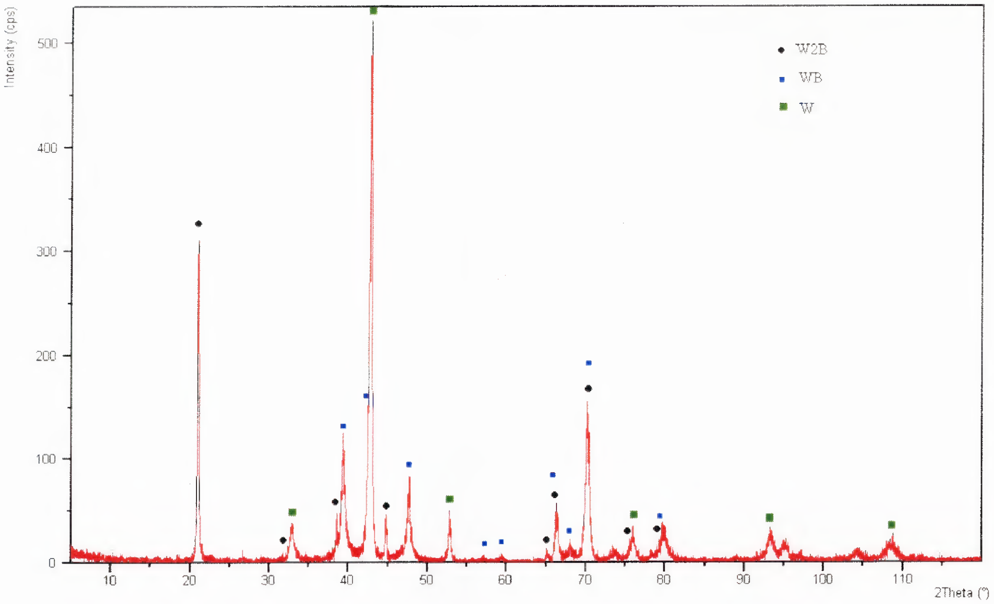


Figure 5.14 XRD peaks for tungsten boronized at 950^0C for 4 hours.

5.3.3 Microstructure Analysis

The coating obtained on tungsten is 11-12 μm thick. Figure 5.15 shows the microstructure of the boron coating on tungsten.

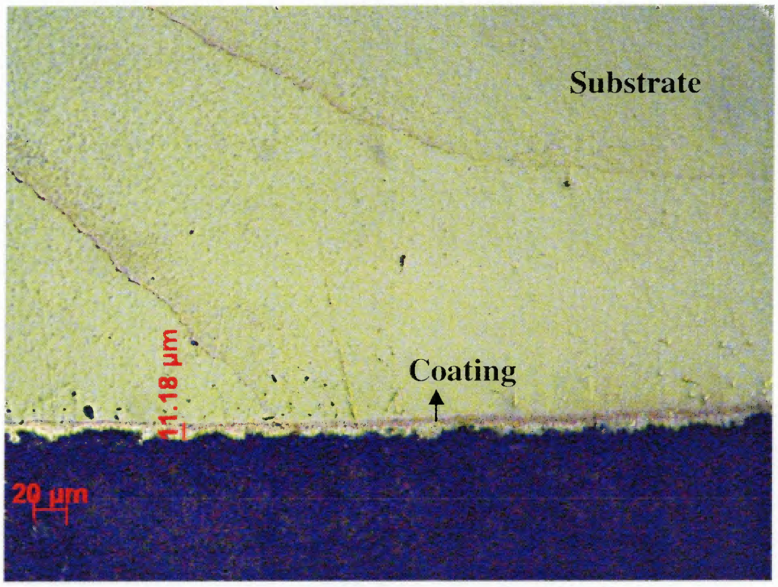


Figure 5.15 Boron coating on tungsten boronized at 950^0C for 4 hours.

Unlike for tantalum and niobium tungsten did not show a columnar structure but the coating was thick and uniform through out the surface. Further studies are needed to identify the difference in the phases that are present in the coating.

5.3.4 Microhardness Measurements

The microhardness on the coating is obtained to be 3200 HK and the microhardness on the substrate is 700 HK. The microhardness gradually decreased but is not as gradual as it is for tantalum and niobium. Figure 5.16 shows the microhardness values from the substrate to the coating.

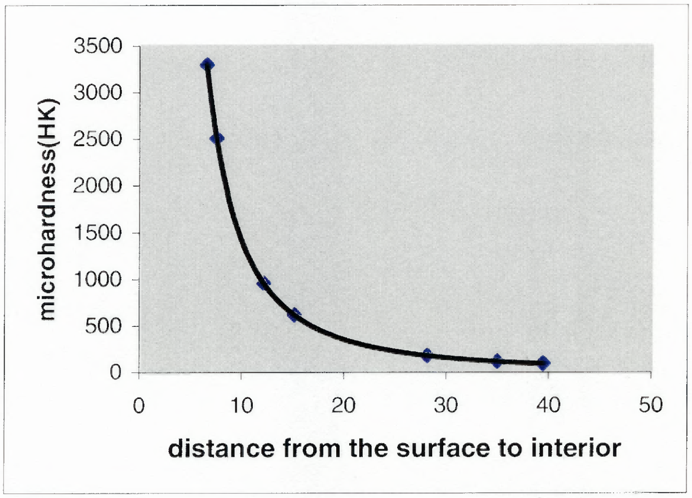
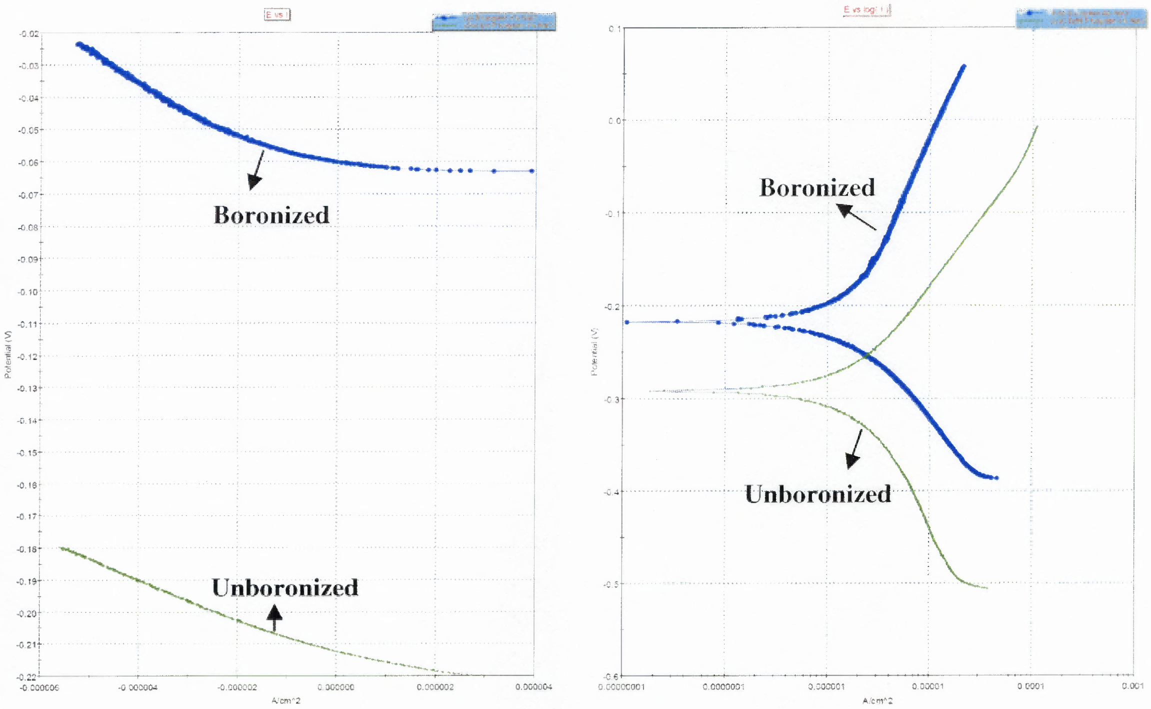


Figure 5.16 Microhardness Vs distance plot for boronized tungsten.

5.3.5 Corrosion Resistance Testing

The corrosion testing of tungsten is done in 4% NaCl and the linear polarization curves and the Tafel curves are obtained. Figure 5.17 show the comparative linear polarization and the Tafel plots for both boronized and unboronized samples



(a) Linear polarization

(b) Tafel plot

Figure 5.17 Comparative Tafel and polarization graphs for boronized and plain tungsten

From Figure 5.17 (a), it can be observed that the boronized sample shows a much positive potential than the unboronized sample. The resistance to polarization for the boronized sample is higher than the unboronized sample.

The comparative Tafel plots shown in Figure 5.17 (b) proves that the boronized sample exhibits a more noble open circuit potential than the unboronized sample. In the anodic region of the graph the pull back tendency for the boronized sample is more than the unboronized sample.

The R_p for unboronized sample is 6.69X 10^3 Ω. The boronized sample resisted the corrosion very well with the R_p value of 1.04 X 10^4 Ω.

CHAPTER 6

CONCLUSIONS

The boronizing technique applied to Tantalum, Niobium and Tungsten was successful. The investigation of the surface properties revealed the following conclusions for the metals:

1. A uniform coating of 3 μm was obtained on Tantalum with a columnar structure. During the investigation of kinetics it was observed that the coating thickness increased exponentially with temperature and it increased parabolically with time. The obtained coating was very hard with a microhardness of 3300 HK. After boronizing, the resistance to polarization of tantalum increased by 8 times in 4% NaCl. Hence, it could be concluded that the corrosion rate for boronized tantalum decreased by 8 times (Corr. Rate $\alpha \frac{1}{R_p}$).
2. Unlike tantalum, a much thicker coating of 10 μm was obtained on niobium and it a show a columnar structure. The microhardness of the coating was 3200 HK which was almost 10 times harder than the substrate. The resistance to polarization of niobium was improved by 9 times after boronizing. This concludes a 9 time decrease in the corrosion rate of niobium.
3. A thick coating of 11 μm was observed on tungsten and the coating was uniform through out the surface. The microhardness of the coating obtained was 3200 HK. The corrosion resistance of tungsten in 4% NaCl was improved by 2 times after boronizing.

Further studies need to be conducted on the boride phase composition. The evaluation of different borides in the coating needs to be done. The oxidation resistance testing and wear resistance testing of these boronized transition metals need to be performed as these properties are expected to improve after boronizing. Further experiments like cyclic polarization and electrochemical impedance spectroscopy need to be conducted to explore the mechanism of corrosion in these metals.

APPENDIX – A

BORON – TANTALUM PHASE DIAGRAM

This is the phase diagram between boron and tantalum which shows the different intermetallics formed between tantalum and boron.

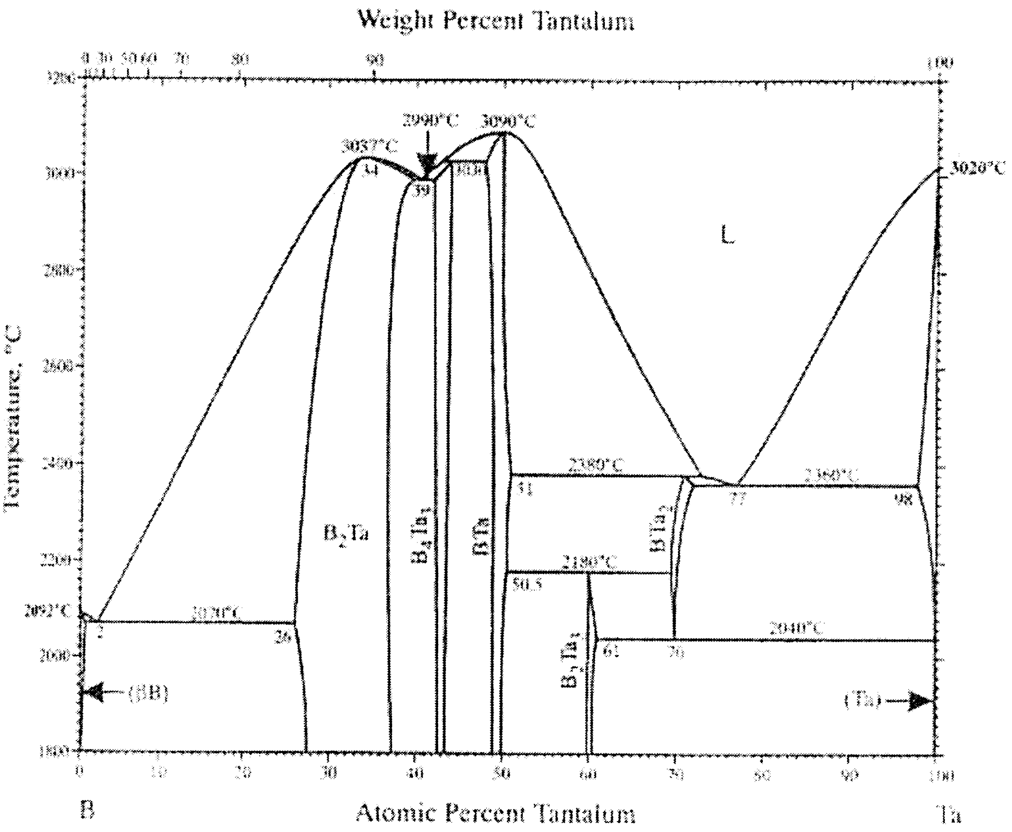


Figure A-1 Tantalum-Boron phase diagram.

APPENDIX – B

BORON-NIOBIUM PHASE DIAGRAM

The different intermetallics formed between boron and niobium at high temperature can be observed in the phase diagram.

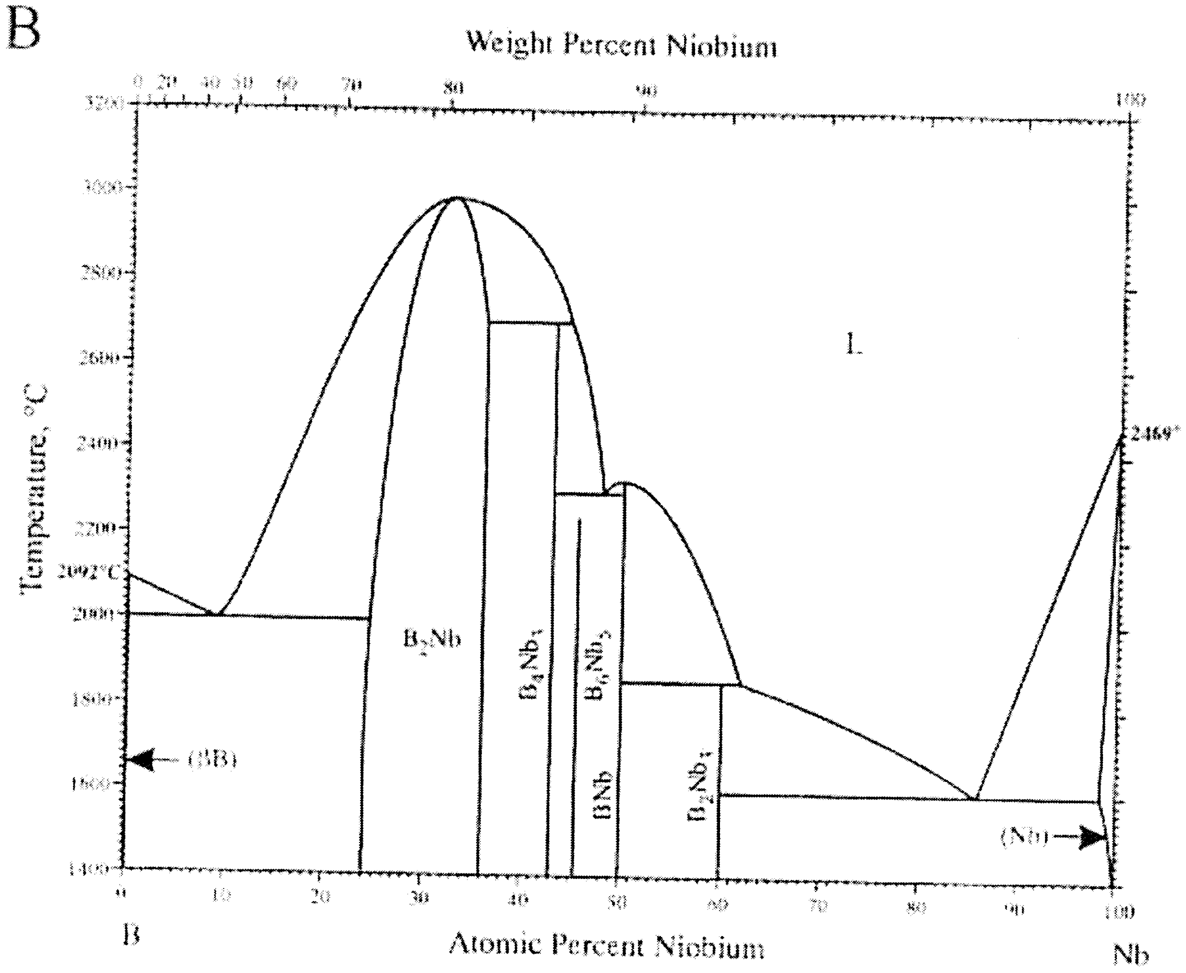


Figure A-2 Niobium-Boron Phase diagram

APPENDIX – C

BORON – TUNGSTEN PHASE DIAGRAM

This is the phase diagram between tungsten and boron. With this phase diagram the phases obtained while boronizing can be predicted.

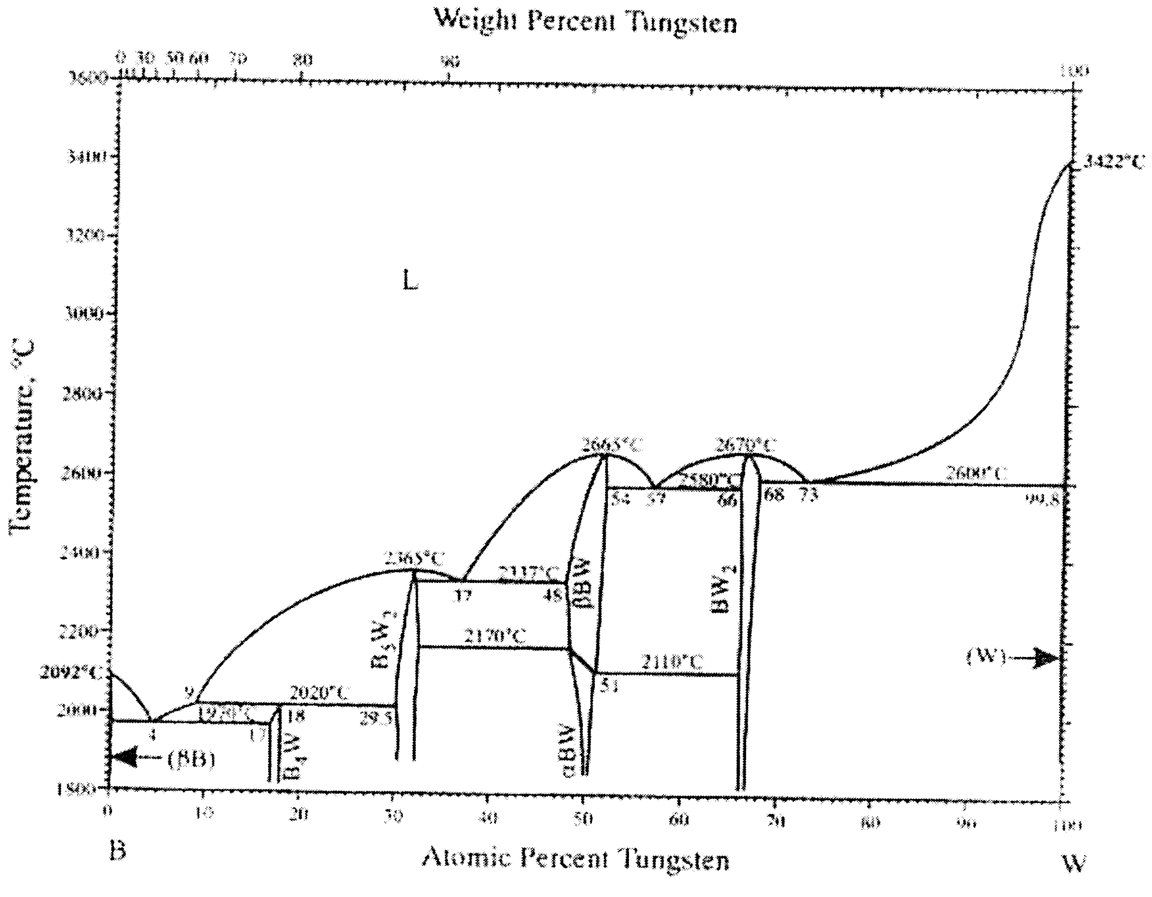


Figure A-3 Tungsten-Boron phase diagram

REFERENCES

1. H.J. Hunger, G.Trute, materials Science Forum, Vol. 163 165 (1994), pp. 341-346.
2. A.K. Sinha, Boronizing, Heat treatment – ASM Internatinoal Handbook –Vol. 4 (1991), pp. 437-447.
3. R.H.Biddulph, Thin Solid Films, Vol. 45, (1977), pp. 341-347.
4. M.Carbucicchio, L.Bardani, G.P.Polambarini, Journal Of Material Science (1980), pp. 711-719.
5. M.Carbucicchio, G.P.Polambarini, Journal of Materials Science (1987), pp. 1147-1149.
6. I. Ozbek,H. Akbulut, Surface Coatings & Technology, Vol. 126, (2000), pp. 166-170.
7. N. Suwattananont, Surface Treatment Of Ferrous Alloys With Boron, NJIT (2004), pp. 1-7.
8. Z.Zakhariev, M.Marinov, R. Petrova, C.Christov, Journal of Surface and Coating Technology, Vol. 31(3), (1987), pp. 265-271.
9. R. Petrova, N. Suwattananont, Journal of Electronic Materials, Vol. 34, (2005), pp. 575-582.
10. A.Erdemir, C.Bindal, Surface Coatings and Technology Vol. 77, (1995), pp. 443-449.
11. C.Bindal, A.H.Ucisik, J.Aust, Ceramics Society, Vol. 34(2), (1998), pp. 287-292.
12. S.Stadler, R.P.Winarski, J.M. MacLaren, Journal of Electronic spectroscope related phenomenon, Vol. 110, (2000), pp. 75-86.
13. M. Usta, Surface coatings and Technology, Vol. 194(2-3),(2005), pp. 251-255.
14. H. Matsuna, A. Yokoyama, F. Eatari, Biomaterials, Vol. 22,(2001), pp. 1253-1262.
15. M.Papakyriacou, H. Mayer, C. Pypen, S. Stanzl, Internatinoal Journal of fatigue, Vol. 22, (2000), pp. 873-886.
16. H. Zitter, H. Plenk, Journal of biomedical materials research, Vol. 21, (1987), pp. 881-896.
17. A.H.Ucisik, C.Bindal, Surface and Coatings Technology, Vol. 94 , (1997), pp. 561-565.

18. S.Otani, M.M. Korsukova, T. Mitsuhashi, Journal of crystal growth, Vol. 194, (1998), pp. 430-433.

19. P. Dearnley, T. Bell, Surface engineering, Vol. 1, (1985), pp. 203-217.

20. S. Motojima, K. Maeda, K. Sugiyama, Journal of Less-Comman Metals, Vol. 81, (1981), pp. 267-272.

21. O. Knotek, E. Lugscheider, K. Leuschan, Thin Solid Films, Vol. 45, (1977), pp. 331-339.

22. W.J.G. Fichtl, Hear Treatment Of Materials, (1983), pp. 79-80.

23. K.H. Habig and R. Chatterjee-Fischer, Tribiology Internatinoal, Vol. 14, (1981), pp. 209-215.

24. A.M. Mokrova, Yu.V. Burtseva, Metal Science and Heat treatment, Vol. 44, (2002), pp. 443-444.

25. Chatterjee- Fischer, Boriding and Diffusion Metallizing - Surface Modification Technologies, (1989), pp. 567-609.

26. A. Graft, Matsuchka, Boronizing, (1980), Philadelphia, PA, Heyden & Son Inc.

27. J. Cataldo, F. Galligani, D. Harraden, Advanced Materials processes, (2000), Vol. 157 (4), pp. 35-38.

28. D.N. Tsipas, G.K. Triantfyllidis, J. Jipkemoi, Y. Flitris, Materials Manufacturing Process, Vol. 14(5), (1999), pp. 697-712.

29. N. Ueda, T. Mizukoshi, K. Demizu, T. Sone, A. Ikenanga, Surface and Coatings technology, Vol. 126(1), (2000), pp. 23-30.

30. K.G. Anthymidis, G. Stergioudis, D. Rouddod, P. Zinviadis, D. N. Tsipas, Surface Engineering, Vol .18(4), (2002), pp. 255-259.

31. P. A. Dearnley, T. Bell, Surface Engineering, Vol. 1(3), pp. 203-217.

32. R. Petrova, Z.T. Zahariev, Bulg Chem Comm, Vol. 26(1), (1985), pp. 82-89.

33. L.P. Skugorova, V.I. Shylkov, A.I. Netschaev, Metalloved term. Obra. Met., Vol. 5, (1972), pp. 61-62.

34. Dr. I. Arnim Kuper, Advanced Materials & Processes, Vol. 161(3), (2003), pp. 20-22.

35. P. Agrianidis, K.G. Anthymidis, K. David, D.N. Tsipas, Computer Methods and Experimental Measurments for Surface Effects and Contact mechanics, Vol. 6, pp. 195-196.

36. S.Y. Pasechnik st al,. Protective coatings on Metals, Vol. 4, (1972), pp. 37-40.

37. N.G. Kaidash, Protective Coatings on Metals, Vol. 4, (1972), pp. 149-155.

38. R. Petrova, N. Suwattananont, K. Pallegar, R. Vangaveti, Conference Proceedings, First World Congress on Corrosion for Military, 2005..

39. M. Usta, I. Ozbek ,M. Ipek, C. Bindal, A.H. Ucisik, Surface & Coatings technology, Vol. 194(2-3), (2005), p.p 330-334.