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NbC COATING ON STEELS .

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SUMMARY

NbC layers were formed on DIN115CrV3 steel substrates at temperatures between 850-1000°C by dipping into molten borax bath containing 20% Fe-Nb powder additions, for 2-4-6 hours time periods. The composition of bath was kept constant while, the treatment temperature and time were varied systematically.

The thickness and microstructure of coated specimens were investigated by optical microscopy and the characterization of bath and coated layers were made by XRD analysis. Hardness of coated layers and substrate were measured by microhardness tester.

It was seen by optical microscopy that the layers were smooth, uniform and pore free and the thickness range was between 2-17 microns. The hardness of layers were measured between 3000-4200 Hv. The process was found to be diffusion controlled and the activation energy of carbide formation was calculated as $\sim$ 30 Kcal/mol. XRD analysis of bath revealed NbO_2 as the oxide which causes the bath to become active.

ÇELİKLER ÜZERİNE NbC KAPLAMA

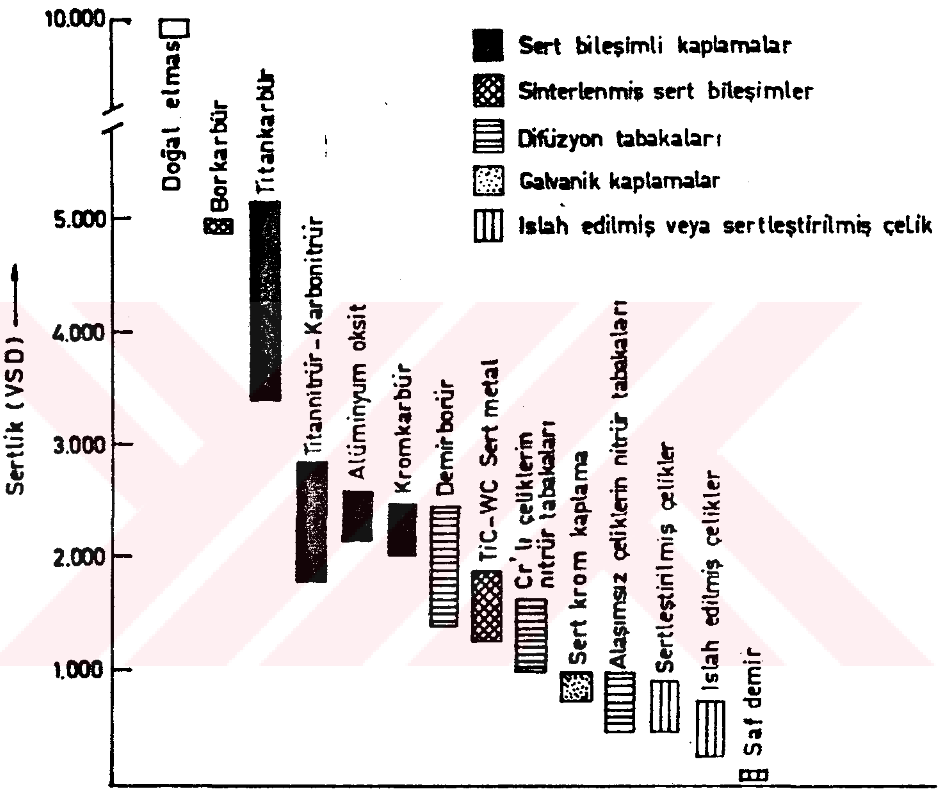
ÖZET

Teknolojideki hızlı gelişme, malzemelerden daha üstün nitelikler istemekte, yüksek sıcaklıklara, darbelere, gerilmelere, aşınmaya, korozyona dayanım gibi bir çok özelliğin birarada bulunmasını gerektirmektedir. Özellikle gittikçe artan ve konvansiyonel alaşımların, refrakter metallerin ergime noktalarına yakınlaşan kullanım sıcaklıkları, tüm özellikleri bir malzemede bulmayı imkansızlaştırmış ve karbür, borür, nitrürlere dayalı seramik kaplamaların gelişmesine yol açmıştır. Bu sınıf malzemeler,ergime noktalarının, sertliklerinin yüksek oluşu, yeterli mukavemet ve kimyasal pasiflikleri dolayısıyla aşınma şartlarının en umut verici bileşikleri durumuna gelmişlerdir. Özellikle karbürler, ilk insan yapısı refrakterler olmaları sebebiyle en ilgi çekici bileşikler sınıfını oluşturmaktadırlar.

Karakteristik olarak karbürler, sertlikleri, elektrik termal iletkenlikleri ve kararlılıkları yüksek bileşiklerdir. Bununla beraber, kırılgan olmaları karbürlerin özellikle aşınma koşullarında ve yapısal uygulamalarda tek malzeme olarak kullanımlarını engellemiş ve karbür kaplamaların gelişimine sebep olmuştur. İlk karbür tabaka L.E. Campbell tarafından 1949'da oluşturulmuş fakat endüstriyel talebin azlığı dolayısıyla dikkat çekmemiştir. Sert karbür yüzeyleri oluşturmaya ilgi 1960'larda artmıştır.

Zamanla, özellikle demir grubu metallerin karbür kaplama suretiyle aşınma dayanımlarını arttırmak amacıyla, sementasyon, püskürtme, buhar fazında kaplama gibi karmaşık teknikler geliştirilmiştir. Çeşitli metodlar kullanılarak elde edilen kaplama sertlikleri tablo 1' de gösterilmiştir.

TABLO: 1. Çeşitli Metotlarla Elde Edilen Kaplama Sertliklerinin Karşılaştırması.



Sementasyon işleminde kaplanan tabaka karbür ve anametal karışımı ikili bir yapı içerdiğinden, tamamen karbür kaplı tabakaya göre daha düşük sertlik ve aşınma performansı göstermektedir.

Püskürtme işleminde hernekadar aşınma ve sıcak gaz korozyonuna karşı mükemmel sonuçlar alınsada, hem kaplama malzemesi çok pahalıdır hem de kaplanacak malzemeye yüzeyde pürüzlük oluşturucu ek işlemler gerekmektedir.

Buhar fazında kaplamada ise, kaplama malzemesi kaynağı olarak halojenler kullanıldığından; atmosfer kontrollü, karmaşık yapılı ve çok pahalı fırınlar gerekmektedir.

Karbür veya nitrür kaplamak suretiyle mükemmel aşınma dayanımı sağlamak amacıyla en son geliştirilen buhar fazı kaplama yöntemleri, kimyasal buhar çöktürme (CVD) ile fiziksel buhar çöktürme (PVD) teknikleridir. W. Ruppert tarafından 70'lerde geliştirilen CVD ile TiC kaplama; kaplama teknolojisinde büyük ilerlemeye yol açmıştır. Fakat tüm buhar fazı kaplama işlemleri pahalı, karmaşık aletler içerdiğinden ve üretim hızları düşük olduğundan endüstriyel uygulamalarda pratik değillerdir.

Yine 70'li yıllarda daha pratik bir yöntem olarak ergimiş boraks banyosu ile açık atmosferde bor kaplama geliştirilmiştir. Bu işlem, buhar fazı tekniklerinin tersine çok basit ve ucuz aletler gerektirmekte fakat elde edilen bor tabakaları özellikle metal şekillendirme kalıp ve takımlarında kullanım sağlayacak kadar tok olmamaktadır. Bu yüzden araştırmalar CVD ile karbür kaplamanın mükemmel performansı ile borlamanın basitliğini birleştirmek için yoğunlaşmış ve Japonya'da Toyota Merkezi Araştırma ve Geliştirme Labratuarlarında T. Arai ve arkadaşları tarafından yeni ve çok pratik bir karbür kaplama yöntemi teknolojik dünyaya sunulmuştur. Toyota difüzyon (TD) işlemi olarak adlandırılan bu yöntem karbür yapıcı elementleri içeren ergimiş boraks banyosu kullanarak, difüzyonla karbür kaplama işlemidir.

TD işlemi ile karbon içeren metal yüzeylerine yoğun, düzgün, gözeneksiz, ince film şeklinde VC, NbC, Cr_7C_3 gibi tranzisyon elementlerin karbürleri, ergimiş boraks banyosu içine Fe-V, Fe-Nb, FeCr alaşım tozları ilave edilerek, koruyucu gaz atmosferi kullanılmaksızın kaplanabilmektedir. Bu yolla, sertliği yüksek, aşınmaya, korozyona, oksidasyona dayanıklı, yeterli toklukta, sürtünme katsayısı düşük ve anametale sıkı bağlı tabakalar elde edilmektedir.

TD işleminin avantajları şu şekilde sıralanabilir:

* Kalıp ve takım ömründe uzama
* Daha ucuz malzemelerle daha uzun ömür
* Yağlayıcı kullanımından tasarruf
* Onarım-bakım süresinde azalma
* Bakım masraflarında azalma
* Üretimde artış
* Ürün kalitesinde artış
* Hava kirliliğine yol açmama
* Kalite kontrol maliyetlerinde azalma

TD işlemi kısa zamanda Japon endüstrisinin otomobil elektrik, kimya, tekstil, döküm, dövme, soğuk-sıcak çekme gibi birçok sektörüne girmiştir. Toyota grubu ve rakipleri de dahil olmak üzere birçok Japon otomobil ve parça üreticileri bu işlemden faydalanmışlardır.

TD işlemi, Japonya'daki yaygın kullanımı yanında, Avustralya, Fransa, Italya, Tayvan, ABD ve İngiltere gibi ülkelerde de kullanılmaktadır.

Çok ucuz aletlerle, mükemmel özellikte karbür kaplamaların oluşturulmasını sağlayan bu işlem Türkiye gibi gelişmekte olan ve otomobil üretiminde de pay sahibi olmak isteyen bir ülke için çok uygundur. Fakat, işlemin geliştiricisi özel bir şirket olduğundan, pratik teknoloji hakkında bilgi alabilmek oldukça zordur. Bu yüzden bu çalışmanın hedefi, bu tür bir karbür kaplama için kendi teknolojimizi kurabilmek, geliştirmektir. Bu amaçla, DIN 115 CrV3 çeliği üzerine, boraks ve Fe-Nb alaşım tozları içeren ergimiş banyo kullanarak, NbC tabakası oluşturulmuştur.

NbC yüksek ergime noktası ve sertilğe sahip,yüksek sıcaklıkta korozyona ve aşınmaya dayanıklı, elektrik iletkenliği yüksek bir karbür bileşiğidir. Bu nedenle özellikle, koruyucu ve aşınmaya dayanıklı kaplamalarda kullanılmaktadır.

Deneysel çalışmalarda önce, optimum bir kaplama banyosu elde edilmeye çalışılmış ve sonuçta % 80 boraks % 20 Fe-Nb alaşım tozu içeren karışım tesbit edilmiştir. Elde edilen bu banyoda, 850-1000^{o}C arasında değişen sıcaklıklarda 2-4-6 saat peryotlarda, grafit pota içerisinde deneyler ile , çeşitli kalınlıklarda kaplamalar elde edilmiştir. İncelenen kaplamaların gözeneksiz, yoğun ve anametale difüzyon nedeniyle sıkı bağlı olduğu, sertliklerinin 3000-42000 Hv arasında değiştiği görülmüştür. Ayrıca işlemin kinetiği ve banyonun aktivasyonu üzerinde çalışılmış, karbon atomlarının yayınması sonucu oluşan karbür tabakasının oluşum aktivasyon enerjisi 30 K.Kal/mol. olarak bulunmuştur. Aktif banyo oluşumuna sebep olarak literatürde gösterilen Nb_2O_3 yerine bu çalışmada NbO_2 bileşiği tesbit edilmiştir.

CHAPTER 1. INTRODUCTION

High technology today demands combinations of diverse properties from a material. Definite limits are being approached or have been reached in single materials development. At present there exist no single material which can withstand all the extreme working conditions.

In the material-environment configuration, the surface of a component is a vital parameter in determining its optimum useefulness. This is the basis for the development of coating technology [1].

Operation of materials at progressively higher temperatures close to the melting points of conventional alloys or refractory metals has led to the development of ceramic coatings based an refractory compounds namely borides, carbides and nitrides. Because their ratio of melting point to the melting point of the corresponding metals is graeater than unity (Table 1.1)[2]. Also their great hardness, adequate strength and chemical passivity makes them the most promising compounds under conditions of wear.

TABLE: 1.1. Ratio of Melting Point of High Temperature Compounds to Melting Point of the Corresponding Metals [2].

Metal	Carbide	Boride	Nitride
Nb	1.52	1.23	0.94
V	1.62	1.39	1.37
Ti	1.86	1.76	1.89
Cr	0.98	1.14	-

In particular, carbides constitute an interesting family of compounds in that they were the first man made refractories. Characteristically, most of carbides have high hardness, good electrical and thermal conductivity and high stability [3].

The brittleness of carbides, however, has prevented their use as single-phase materials in wear and structural applications and has led to the development of carbide coatings.

First carbide layer was formed by L.E Campbell in 1949 [4]. However, this didn't bear fruit perhaps for a lack of industrial demand. The attraction for producing hard carbide surfaces increased in the early 1960's.

Sophisticated techniques have been developed over the years. The vapor phase coating, the cementation, the spraying and the like processes have been employed for the formation of carbide coatings on the ferrous products so as to improve its wear resisting characteristics.

In the case of the cementation process, the surface of the material to be coated is likely to become rather rough and the coated layer consists of a mixed structure of the carbide and the substrate material, representing thus a lower grade of surface hardness and wearing performance than a layer exclusively composed of carbide [5].

In the spraying process, although excellent results are obtained against wear and hot gas corrosion, the coating material is very high in price and the material to be coated needs special surface preparation such as grit blasting and the bonding or the coated layer with the substrate is frequently inferior [6].

For carrying out the vapor phase coating, halides are employed as the coating material source, which necessitates the use of a specifically selected atmosphere furnace of rather complicated design [5].

Among the recently developed vapor phase techniques of surface treatment the basic techniques are the chemical vapor deposition (CVD) and physical vapor deposition (PVD) processes for depositing carbides or nitrides to provide superior wear resistance.

The CVD-TiC coating process which was developed by W.Ruppert [7] in West Germany has led to a great advance in coating technology.

CVD produces a thin solid coating on a heated substrate by means of a chemical reaction between geseous reactants passing over the substrate. Reaction temperatures can be any where between about 200°C and 2220°C but are mostly between 500-1100°C [8].

As the coating procedure is carried out at elevated temperatures, good adherence of the coating to the substrate results. At these temperatures, a thin diffusion zone between the base metal and the coating is formed providing a metallurgical bond [9].

The PVD process takes place at temperatures below 500^{o}C. There are three methods, namely evaporation, ion plating and sputtering [10]. All three PVD processes are very rapid and considerable benefit is gained by their applications.

But all these vapor deposition processes requires complicated equipment and is low in productivity. Besides, simultaneous core hardening during cooling also, is not possible. On the other hand, a boriding process by use of molten borax bath under ambient atmosphere has been developed. The equipment for this process is simple and the chemicals are low in cost while the obtained boride layers are not tough enough to be widely used for metal forming dies and tools [11]. Therefore researchers undertook studies to develop a coating process which combines excellent performance of the carbide coating by CVD with the simplicity of the boriding process [12]. These attempts have succeeded in the development and a new carbide coating method have been introduced into technological world by T.Arai at Toyota Central Research and Development labs in 1970 [13]. The process referred to (TD) process which is a diffusion coating process using molten borax bath.

The TD process is a worlds unique and truly practical process to form on a metal substrate a dense, smooth and thin carbide layer of mainly VC, NbC and Cr_7C_3 having extrene hardness and high resistance to wear, seizure and oxidation [14].

This simplicity and good quality that can be achieved resulted in the TD process prevailing in various fields of Japanese Industry (automobile, electric applience, metallurgical and chemical industry) [15]. A great number of Japanese automobile makers and component makers, including, Toyota group companies and their competitors, have been benefited by this process [16].

As well as being widely used in Japan, the process has spread to Australia, France, Italy, Taiwan, USA and UK [17].

As this process can lead to the coating having extreme properties only by very cheap equipment, is best suited for Turkey which has been getting an important position in automobile production. But the developer of this process is a privately owned company. Therefore obtaining the khow-how or knowledge on the practical technologies is too difficult.

The aim in this study is to evaluate our know-how about the the carbide coating process. For that purpose NbC layers were formed en steel substrates by using Fe-Nb powders and molten borax bath.

The principal properties characteristic of NbC are a high melting point and hardness, a high resistance to the action of molten metals and metal vapors, reasonable strength at elevated temperatures, low vapor pressure, high electrical conductivity and good emissivity. These properties determine the field of application of NbC, namely for the manufacture of heating elements for high temperature furnaces and of evaporating plants for aluminum, for protective and wear resistant coatings [18].

Experimental study has been carried out on the determination of optimum bath in which dense NbC coatings that adhere well to the substrate forms, the hardness and the thickness measurements of layers over a wide range of temperatures and times, the kinetics of diffusion and the activation of bath.

CHAPTER 2. PRINCIPLES OF APPLYING COATINGS BY DIFFUSION

Diffusion coating processes enable the surface of a metal article to be changed in chemical composition by diffusing into it another metal or a nonmetallic element. Alloying between the substrate and the coating metals occurs at the diffused surface, but little or no change of the dimensions of the diffused article takes place. Diffusion coatings can be applied to a range of metals and alloys including copper, molybdenum, nickel, niobium, tantalum, titanium and tungsten but the widest use of these coatings is on ferrous materials [19].

The most widely used metals in diffusion coatings are chromium, aluminium and zinc although other metals, notably tin, may be subjected to diffusional treatments. Carbon and nitrogen are probably the classical examples of diffusional coatings which improve surface mechanical properties [20].

The diffusion of the coating metal in substrate is on an atomic scale, and atomic and molecular bonding occurs so that total adhesion is obtained and the distortion of the crystal that occurs leads to an increase in the hardness of the metal surface. Coating thichnesses applied are generally in the range 5-15 μ [19].

2.1. Theory of Diffusion

Diffusion processes play an important practical part in chemicothermal treatment, phase transformations, sintering, graphitization and decarburization, creep rupture and solid state relaxation processes [21].

In the process, the atoms must acquire sufficient energy to permit their displacement at an appreciable rate. In the case of metal lattices, this energy can be provided by a suitable rise in temperature.

In the application of coatings the diffusion process is arrested at a suitable stage when there is a considerable solute concentration gradient between the surface and the required depth of penetration.

In metals, the distance between the individual atoms in the lattice is of the order of 0.4 nm and only atoms of very small size are able to penetrate interstitially. This takes places for instance, in the diffusion of hydrogen into iron, and of carbon into austenite, etc. This type of interstitial diffusion is usually rapid, since the inward movement of the solute atoms is relatively unhampered.

Interstitial diffusion is rarely possible when two metals interdiffuse, since their atomic radii are usually of the same order. Several mechanisms have been proposed, but it is now generally accepted that interdiffusion is due to the motion of vacant sites within the lattice, solvent and solute atoms moving as the vacant sites migrate. The diffusion process is thus dependent upon the state of imperfection of the solvent metal and the alloy being formed [22].

The theory of diffusion may be divided into three major fields:

Diffusion mechanism and kinetics
Thermodynamics of diffusion
The influence of structure on diffusion [21]

The kinetics of the diffusion process can be expressed by Fick's equation in the form of [22].

$$\frac{dc}{dt} = D \frac{d^2C}{dx^2} \qquad (2.1)$$

Where D is the diffusion coefficient, c is the concentration, x is the distance and t is the time.Equation (2.1) expresses the rate of increase of concentration at any point [23].

This differential equation has been solved for the appropriate boundary conditions of the experimental data available, but for the law to be applicable certain basic features must be maintained. These include a constant temperature, an isotropic solvent metal, that a suitable referance plane must be available and that diffusion must be by bulk or volume diffusion mechanisms: Any departure from these conditions will necessiarily lead to uncertainity in the analysis.
For a simple diffusion couple, equation (2.1) may be shown that:

$$X^2 = 2\ Dt \qquad (2.2)$$

Where X is the distance of diffusion, D is the diffusion coefficient and t is the time [24].

The temperature dependence of D is almost always accurately described by the Arrhenius law,

$$D = A \exp \left(- \frac{Q}{RT}\right) \qquad (2.3)$$

It is generally found that the more carefully D is measured, the more accurately the law is obeyed, that is the more closely the points lie on a straight line when log D is plotted against 1/T. The terms Q which is activation energy and A which is frequency factor are independent of temperature [25].

2.2. Methods of Deposition by Diffusion

The results of investigations of diffuison obtained on the same systems but by different methods are often very contradictory. This makes it difficult to use these data for quantitative evaluation of technological processes connected with diffusion. In many cases, the results of calculations made with experimental data do not agree with the data of direct quantitative measurements. Therefore, the process in which diffusion takes place should be examined [21].

The diffusion process depends on an adequate supply of solute metal at the surface of the solvent. So long as such a supply is available, the diffusion will proceed at a rate which is largely determined by the temperature selected for the process.
Various methods of providing this supply may be employed All the methods can be divided into three major categories [22].

- Solid -solid deposition
- Gas phase deposition
- Molten bath deposition

2.2.1. Solid Solid Deposition

Coating treatment is similar to pack cementation. Process is carried out in a sealed container, with the cleaned metal articles packed in a powder containing the coating metal, activator and inner filler. The container is heated for several hours at a temperature near to but lower than the melting point of the coating metal.

The powders, although containing some metallic particles, are in fact poor thermal conductors and hence process times are long [5].

Chromising or aluminizing of iron base alloys which provide significant oxidation resistance are examples of this kind. Among the advantages of solid-solid diffusion are:

1)- Effective improvement of the surface without expensive equipment.

2)- Avoidance of annealing post treatments.

3)- Applicability to a wide variety of metals.

4)- Ability to coat pieces of moderate size and different shapes.

5)- Relative ease to control the coating composition and microstructure.

The reaction step at the surface may be extremely complex, involving adsorption, dissociation, surface diffusion, and a number of other steps. The deposited coating element diffuses into the substrate to form the desired diffusion coating. Solid state diffusion theory (Fick's second law) applies this step. In order to understand the reaction mechanism of the process and to control the coating composition and properties, the local thermodynamic equilibria in the powder and at the substrate surface, the gas-solid reactions at the interface, and the kinetics of gas diffusion and solid-state diffusion must be considered [26]. However, the technique is unsuitable for continuous operation so that it cannot attain high production moreover the protection against oxidation which it affords is inadequate [5].

2.2.2. Gas Phase Deposition

Rates of heating are faster than by solid-solid deposition and hence process times are shorter. Also it is sometimes possible to operate at lower temperatures. Method offers a valuable extention to the possible variations in the chemical composition of the gases used for coating.

With the gas process, there is always the problem of contact or support points where the coating may be deficient. This leads to some doubt as to its total applicability for corrosion resistant coatings, but for wear resistant coatings, it is a good method [5].

The vaporized halide of the coating metal is passed over the metal to be coated while it is being heated and maintained in either an inert or a reducing atmosphere. Three basic reactions occur:

1)- An exchange reaction between the two metals.

2)- A reduction of the coating halide to produce the metallic phase.

3)- Dissociation of the coating halide to produce the metallic phase.

These reactions are encouraged to proceed to completion by maintaining the concentration of available halide and by removing the reaction products from the reaction vessel [22].

Vapor phase plating is also suitable for continuous operation and requires complex and expensive equipment Figure 2.1.

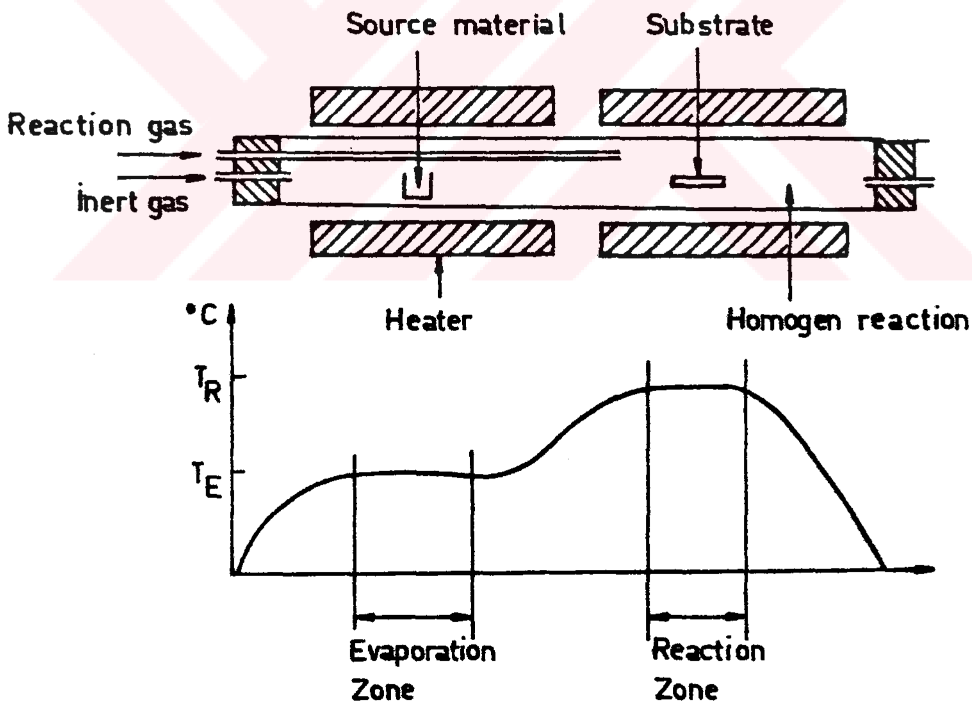


FIGURE: 2.1. Schematic Diagram of CVD Apparatus [22].

2.2.3. Molten Bath Deposition

Heating rates are likely to be highest with liquid metallizing baths but this many not always be an advantage. As with gas phase, all work must be jigged, wired or placed on racks, which again gives the problem of contact points, and thereby places some restrictions on use.

A further comment relating the salt baths is that, it is possible to move directly from the coating process into a heat treatment stage with direct quenching. In fact, this helps in the removal of the molten salt, and if allowed to solidify, is much more difficult to dissolve and can thereby expose a coated part to a corrosive environment [5].

Diffusion surface saturation of the coated metal can be easily and simply achieved in molten media. Molten mixtures of the chlorides of alkaline and alkaline earth metals as well as other elements are used as such media. Recently, molten borax has been used as salt bath by T.Arai as mentioned in chapter I. to coat carbide layers with the following compositions: [27-28].

67 % Borax + 33% Fe- Cr (67 % Cr)
95 % Borax + 5 % Fe- Cr (67 % Cr)
80 % B_2O_3 + 20% Fe- Cr (67 % Cr)
37.2% Borax+ 20% Fe- Cr+68% NaF
70 % Borax + 30% Fe-.Cr (67% Cr)
50 % Borax + 50% Fe-Nb (59 % Nb)
50 % Borax + 50% Fe- C (52 % V)
70 % Borax + 30% Fe- Nb(59 % Nb)
95 % Borax + 5 % Fe- Nb(59 % Nb)
42 % Borax + 30% V powder+12% NaCl+16%KCl
70 % Borax + 30% V powder
50 % Borax + 30% V powder + 20% NaCN
70 % Borax + 30% Fe- V (52 % V).

Diffusion layers in liquid baths are formed at high temperatures, therefore in application, it is necessary to create conditions which eliminate the possibility of surface oxidation of the coated metal and of the coating element by the oxygen in air [29].

A serious drawback of the method of coatings formation in molten media is the rapid heating of the parts immersed in the molten mixture and their rather fast cooling after the coating; the cooling may result in an undesirable deformation and distortion of large parts.

CHAPTER 3. DIFFUSION CARBIDE COATING PROCESS

It is well known that the surfaces of materials coated with thin hard films consisting of carbide, nitride and carbonitride considerably improve resistance to wear. As the method of coatings, CVD, PVD and the salt bath immersion process, mentioned in chapter I, developed by T.Arai [30] have been applied in recent years.

The salt bath process involves immersion of materials to be coated in a molten borax bath that contains the relevant carbide forming element usually vanadium, niobium or chromium under ambient atmosphere. The temperature of the molten borax bath is generally adjusted to be around the hardening temperature of the substrate steel; so that coating and substrate hardening are performed in the one operation. Thus, the salt bath process can be said to be a kind of the salt bath heat treatment for steels [31].

The most remarkable advantage of the salt bath process is that the process operates much simpler and less equipment than the other two methods.

Unlike CVD and PVD, which are highly confined to die and tool application, the salt bath process has been used to small machine parts such as fasteners roller chains , pumps, as well as to dies and toolings [32]. Therefore in this chapter, the mechanism of carbide layer formation in molten borax salt bath, the properties of carbide coatings and their applications has been discussed.

3.1. Mechanism of Carbide Layer Formation

Carbide coatings are formed by the chemical combination of carbon atoms in the substrate and the carbide forming elements in the treating reagent, due to the small free energy of carbide formation [33].

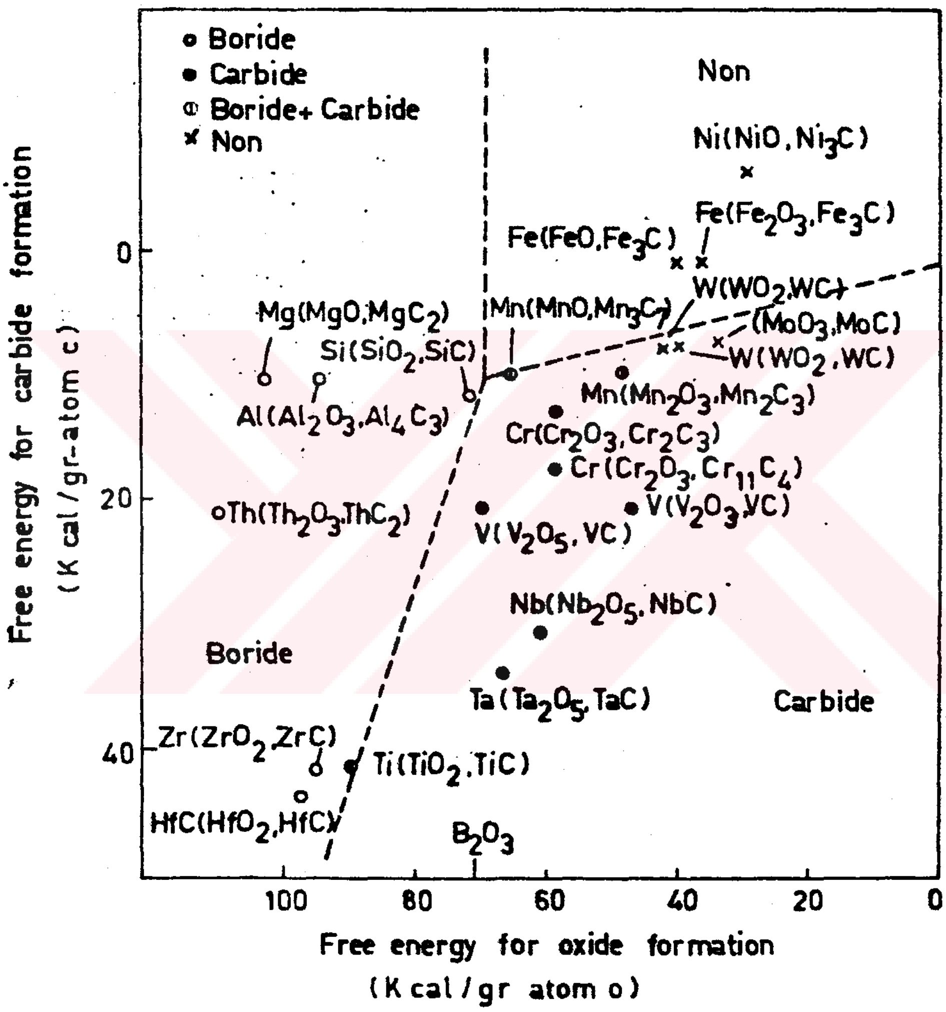


FIGURE: 3.1. Relationship between formation free energies of elements and kinds of layers formed on high carbon steel in the molten borax bath (950°C) [30].

Figure 3.1. shows in relation to free energy for oxide formation (ΔG_o) and free energy for carbide formation (ΔG_c) the kinds of the coating layers formed on high carbon steel dipped in a molten borax bath containing various elements. An element having a small ΔG_o, such Al or Mg, reduces B_2O_3 in the molten borax and the diffusion of the resulting active boron into steel forms a boriding layer composed of Fe_2B and FeB. The value of ΔG_c does not affect the formation of such boriding layer in any way [30,34].

An element having a ΔG_o value larger than that of B_2O_3 and a ΔG_c value smaller than that of Fe, such as V, Nb or Cr, combines with carbon in the steel to form a carbide layer composed of, for example, VC, NbC or a combination of Cr_7C_3 and $Cr_{23}C_6$, as it does not serve to reduce B_2O_3. An element having a large ΔG_o value and a large ΔG_c value, such as Ni or Co, does not reduce B_2O_3 or form any carbide. But in some experimental conditions, these elements diffuse into the steel to from a layer of Fe-Ni alloy or Fe-Co alloy [34]. Thus, the ΔG_o and ΔG_c values of the elements to be added to the molten borax make it possible to guess with a substantially perfect degree of accuracy the kinds of the layers formed by those elements.

Growing up of carbide coatings is maintained by the continuous supply of carbon atoms to the surface of coatings from the substrate, in this respect, the process can be called termo-reactive deposition and diffusion [33].

The ease of practical application is strongly influenced by a proper selection of the treating reagents. The salt, solid powders and gas can be used in various methods like as a molten salt bath, a fluidized bed, paste with binder packing in a box and a gas atmosphere [34]. The molten salt bath among them is most favourable for applications to toolings, dies and other many products for which hard substrate is indispensable, since steel substrates can be easily quench-hardened after discharging from the bath kept at high treating temperature [33].

Metals, oxides and halides containing carbide forming elements can be mixed into salt bath in the form of powder or flake in the following forms:

Metals: Fe-V,Fe-Nb,Fe-Cr, Cr,Fe-Ti, Fe-Mn,Fe-W etc.

Oxides: V_2O_5, Na_3VO_4, Nb_2O_5, Cr_2O_3, $K_2Cr_2O_7$ etc.

Reducing Agents: Fe-Si, Fe-Ti, Ti, Fe-Al,Al, Fe-Mn,Ca-Si, etc.

Halides: VCl_3, $NbCl_5$, $CrCl_3$, K_2TiF_6. etc. [4].

In the progress of carbide formation, although there is a distinct straight boundary between the substrate and the carbide layer, minor diffusion of iron and other elements from substrate into carbide layers, and carbide forming element into substrate occurs which provides metallurgically bonded structure [35].

The lower limit of C content in substrate materials which is allowable to make complete carbide layers is affected by the kinds of carbides to be formed and treating temperature. Figures 3.2, 3.3 [31].
NbC layers can be formed even on steels with less than 0.1 % C [36]. In the absence of sufficient carbon in substrate metals, solid solution layers may be produced instead of or accompanied with, carbide layers[37].

Two compounds are formed in the Nb-NbC system: Figure 3.4.

Nb_2C : Orthorhombic
NbC : Cubic

The lattice parameter of pure NbC varies with composition according to equation. Table 3.1.

$$a_o = 4.09 + 0.71 \left(\frac{C}{Nb}\right) + 0.34 \left(\frac{C}{Nb}\right)^2 \quad [38].$$

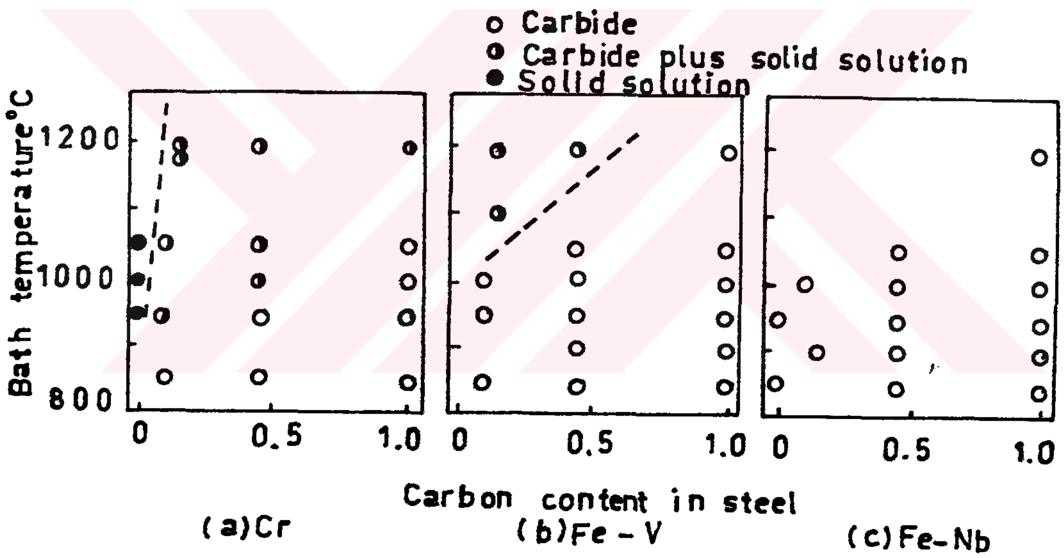


FIGURE: 3.2. Relationship between temperature of borax baths added with appreciable amount of Cr, Fe-V and Fe-Nb powders and layers carbon content, at 1273K. [31].

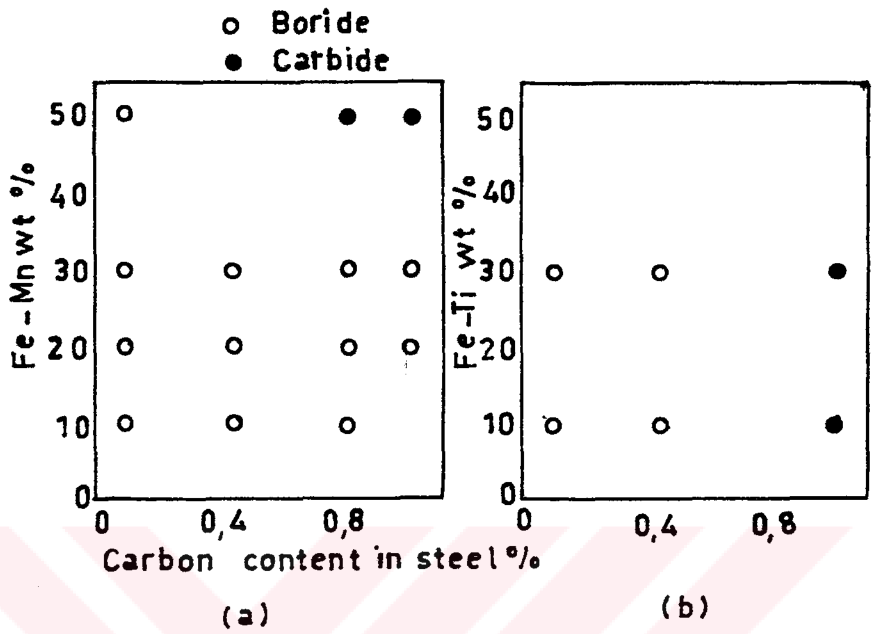


FIGURE: 3.3. Relationship between amount of Fe-Mn(a) and Fe-Ti(b) added in borax bath and Layers formed on plain carbon steels containing different carbon content at 1273K [31].

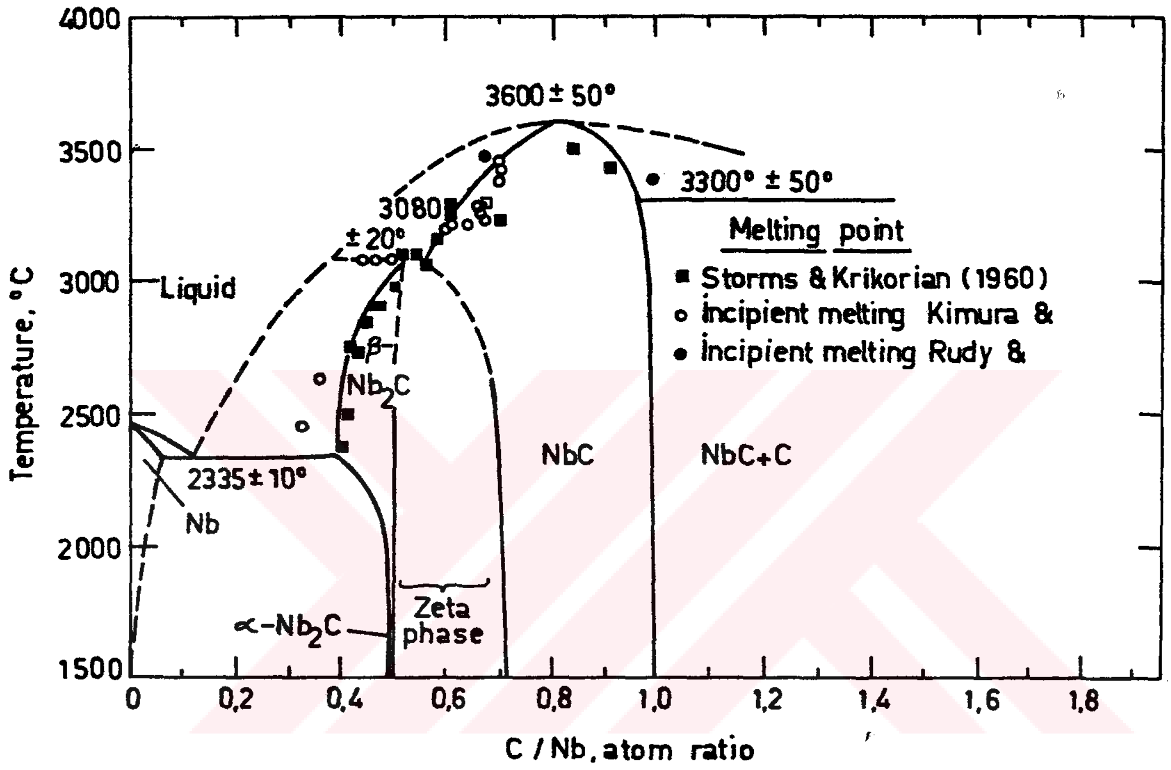


FIGURE: 3.4. Phase diagram of the Nb-NbC system. [38].

TABLE: 3.1. Structure and lattice-parameter of Nb- $+Nb_2C$ and NbC [38].

Phase in equilibrium	Composition of first phase	Structuretype	Lattice paremeter (A)	Investigator
Nb	Pure	bcc(A2)	a=3.3000 = 00003	Seybelt (1954)
$Nb+Nb_2C$	Carbon-saturated quenched from 2000^0		a=3.3012	Brauer and Lesser(1959a)
$z-Nb_2C+Nb$	NbC_{o40}	Basedon	a=3.127 = 0001	Storms and Krikoran (1960)
		L3indexing	e=4.965 = 0001	
$z-Nb_2C-NbC$	NbC_{050}	BasedenL3	a=3.127 = 0001	Storms and Krikoran (1960)
		indexing	c=4.972 = 0001	
$z-Nb_2C-Nb$	NbC_{040}	Orthorhombic	a=10.9042= 00008 b=3.0958 = 00004 c=4.9700 = 00003	Storms (1060b)
$NbC - Nb_2C$	NbC_{070}	fcc(B1)	a=4.4318 = 00004	Kempter et al.(1960)
NbC - C	NbC_{099}	fcc(B1)	a=4.4707 = 00003	Kempter et al.(1060)

In this thermochemical process, carbide coatings are formed on the substrate surface like as in the case of CVD and PVD. Just after less than a few seconds carbide grains are observed on the substrate. Number of grains increases with elapsed time and finally, whole over surface is covered with carbide grains. Thereafter dense carbide layers can be observed. The minimum time needed for making the whole coverage and their thickness are determined by many factors, ranging from 5 seconds to 10 minutes and thinner than 1 micron.

Growth rate of coatings is affected by the following factors [33].

1)- Temperature
2)- Immersion time
3)- Substrate material
4)- Carbide type.

It has been confirmed that nitrogen in the substrate acts just like carbon to produce nitride or corbonitride coatings onto nitrogen containing materials like as silicon nitride and nitrided steels [13].

3.2. Properties of Carbide Coated Materials

This process provides the layers, consisting of carbide only, free from binder phase and scarcely reduces the toughness of substrate [39]. Thus, carbide coated materials are characterized by a proper combination of surface properties inherent in the carbides such as high hardness, excellent wear, seizure, oxidation, corrosion resistance and the strength inherent in the substrate materials [37] (Table 3.2).

TABLE: 3.2. Some Physical Properties of Refractory Carbides [37]

Property:	NbC	VC	TiC	B_4C
Lattice parameter, ^{o}A	4.466	4.182	4.33	a= 5.61 c= 12.07
Melting poingt, ^{o}C	3760	2830	3250	2450
Density, gr/cm^3	7.81	5.83	4.95	2.51
Coefficient of linear thermal expansion $10^{-6}/^{o}C$	6	7.2	5.5	4.5
Thermal conductuvity $cal/cm^{o}C$ sec.	0.034	0.058	0.041	0.07
Resistivity. $\mu\Omega$ cm	51.1	65	52.5	

Extensive research works have been made to evaluate various properties including resistance of wear, seizure, corrosion, oxidation, attacking by molten metals, toughness, fatigue strength, thermal shock resistance and adhesion strenght [33].

3.2.1. Hardness of Coatings

The metallic hard materieals in particular, the carbides have wide homogeneity ranges as shown in figure 3.5 for Nb-NbC system. This causes profound property changes, demonstrated here for hardness measured for different compositions. Figure 3.5 [39].

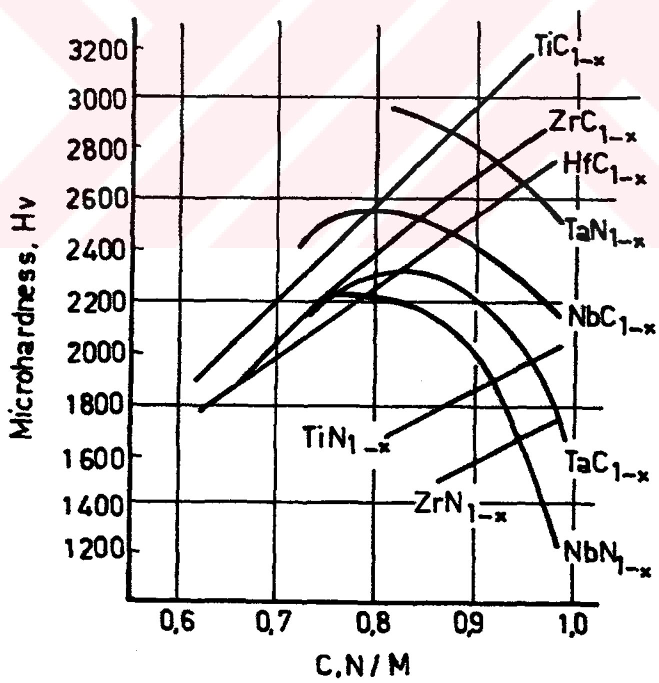


FIGURE: 3.5. Change of hardness with the nonmetal-to metal ratio. [39].

The adjustment of a fixed nonmetal-to-metal ratio allows one therefore to control many properties.

The hardness of the carbide coating is also a function of the carbide forming element. The layers have very high hardness not only at room temperature but also at high tmperatures Figure 3.6 [40].

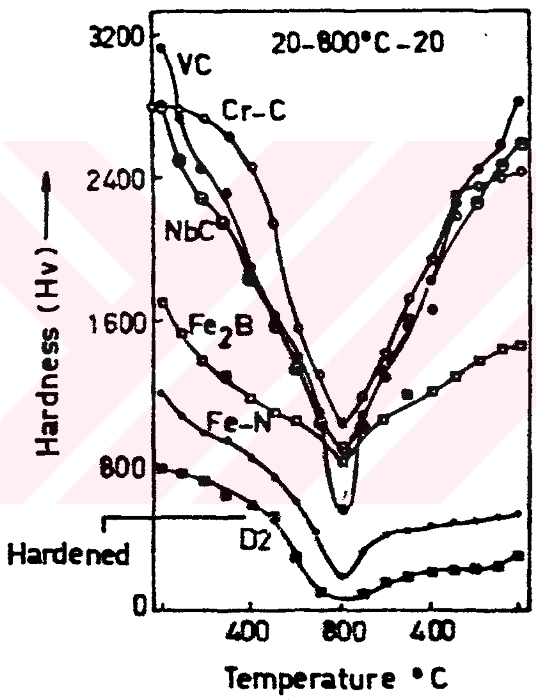


FIGURE: 3.6. Comparison of high temperature hardness. [40].

3.2.2. Wear Resistance

The excellent wear resistance was recognized against various materials including nonferrous metals, sand, glass, wood, etc. [41] Figure 3.7.

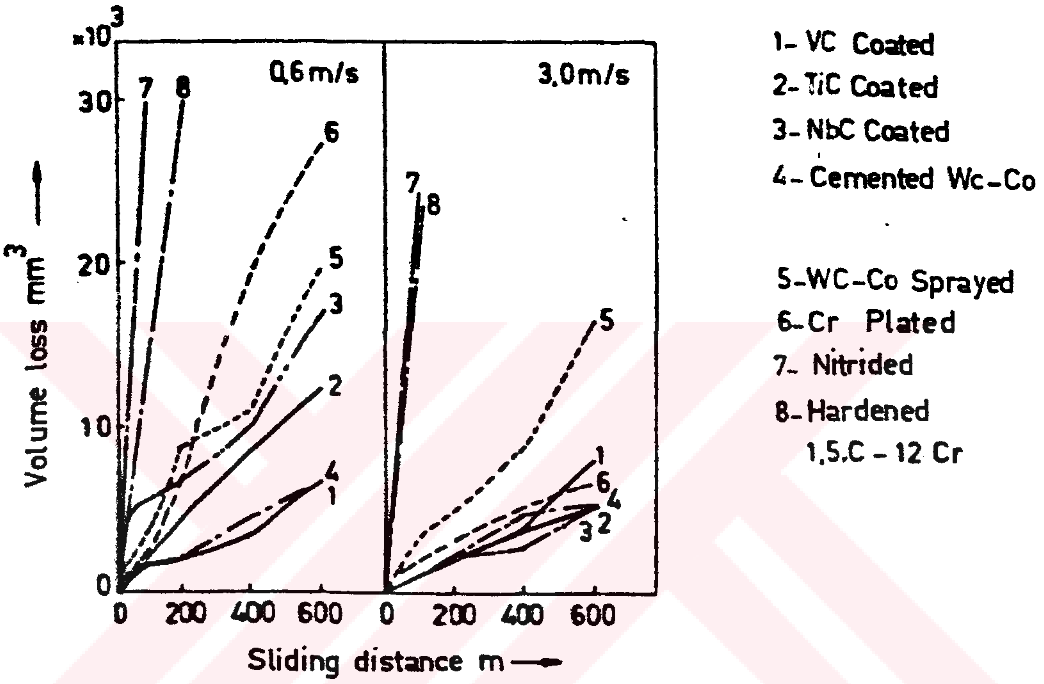


FIGURE: 3.7. Comparison of volume loss between carbide coated cold working die steel and other wear resistant material specimens in the dry wear test. (Final load:3.3 Kg, Sliding velocity:0.6 or 3.0 m/sec) [41].

Vanadium carbide and niobium carbide coated steels are comparable to Titanium carbide coated steels made by CVD.

3.2.3. Toughness

Carbide coating does not reduce rupture strength and energy absorption in static and dynamic bending tests. Figure 3.8, 3.9. Therefore, when steels with high toughness are used as substrates, very tough carbide coated steels can be obtained.

According to the results of industrial applications, decrease in toughness was not recognized also in the case, in which pre-hardening treatment had been employed on high speed steel to minimize the size change due to the change of crystal structure [40].

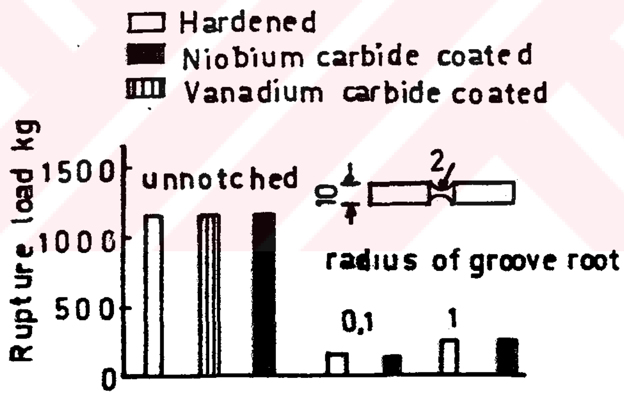


FIGURE: 3.8. Comparison of rupture load in the static bending test with grooved and unnotched D2 specimens.[41].

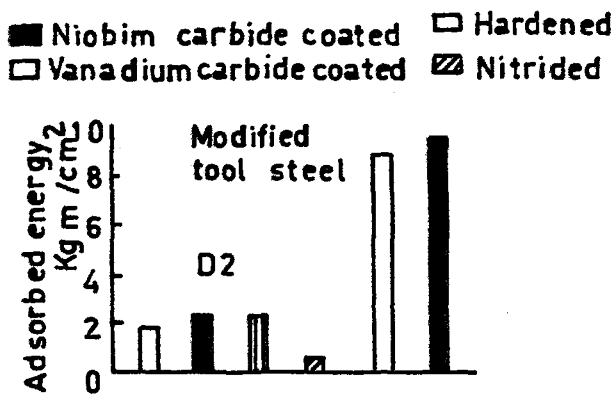


FIGURE: 3.9. Comparison of absorbed energy in the Izod type dynamic bending test with grooved tool steel specimens. (Specimen size: 14 x 103 Radius of groove root: 5R).[41]

3.2.4. Resistance to Cracking and Flaking

Deformation of substrate make cracks in the carbide layer. The measured critical strain to induce microcracks, invisible with maked eyes, was roughly 0.8 $\sim$ 14% under tensile stress, and 0.6$\sim$1% under compressive stress, depending on the kinds of carbide the thickness of layer and substrate composition. Figure 3.10 [40].

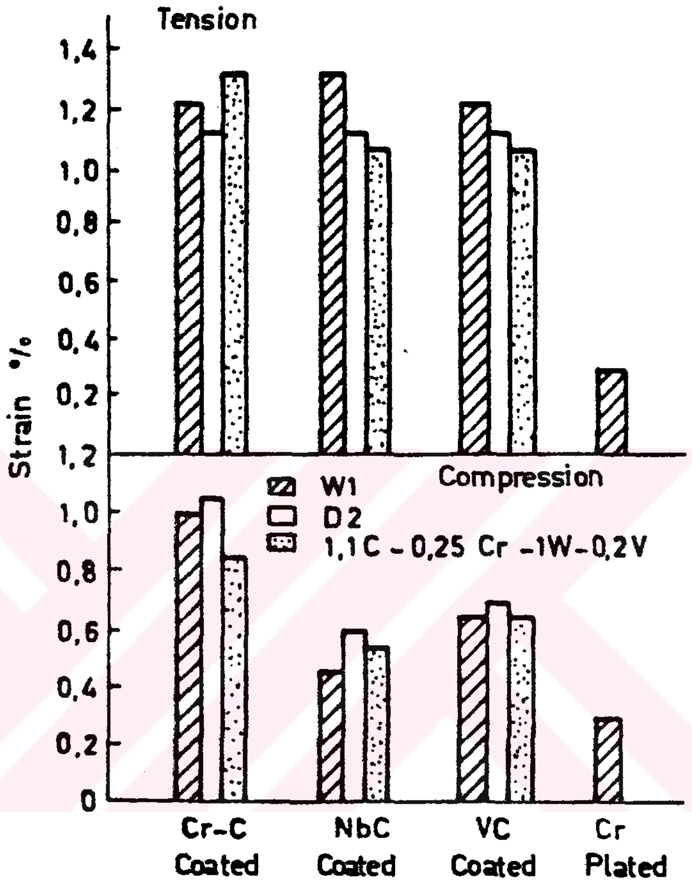


FIGURE: 3.10. Comparison of the critical strain to induce micro cracks in the static bending test. [40].

3.2.5. Resistance to Oxidation and Corrosion

When exposed to air for a long time at a temperature above 500^{0}C, vanadium and niobium carbide layers are oxidized significantly. However, application of such carbide coating to hot forging dies for steels would provide successful results, since the temperature of dies can exceed 500^{0}C only while the dies are in contact with heated blanks. Cr-C layer is hardly oxidized even at 800^{0}C providing no scale [41].

Carbide coated steels also have good corrosion resistance to various kinds of aqueous solutions Table 3.3. [40].

TABLE: 3.3. Comparison of Corrosion Resistance In Various Aqueous Solutions (Room Temperature, 50 hr) [40].

0 No corrosion - Not tested

X Severe corrosion

	Uncoated		Coated		
	W1	304	Cr-C	NbC	VC
5% NaCl	X	0	0	0	0
5% NaOH	0	0	0	0	0
10% H_3PO_4	X	0	0	0	0
10% HNO_3	X	0	0	0	0
10% H_2SO_4	X	X	0	0	0
50%	X	X	0	0	0
10%	X	X	0	0	0
20% HCl	X	X	-	0	-
36%	X	X	0	0	0

3.3. Application in Industries

Because of the effective elimination of wear and galling problem and resulting industrial benefits, like as improvement of life, saving of lubricant, saving of labor etc. carbide coatings have quite wide application, ranging from dies and toolings for metal forming, blades for cutting and cutting off, various wear jigs and parts used for processing, conveying and assembling.

Unlike CVD and PVD, which is largely confined to tools and dies application, salt bath process has been successfully applied to small machine parts made of constructional steel due to its low processing cost [4].

Aluminum die casting industry is one of the most benefited. Dissolution loss and scuffing are eliminated and bothersome labor for polishing of pins is significantly reduced.

Because of the excellent abrasive wear resistance of carbide coatings, the process is being increasingly used in nonmetallic material processing, such as injection molding and extrusion molding of plastics and rubber and compacting of ceramic compounds [36].

Substitution of materials to lower grade ones is widely realized in various fields. Typical substitutions are high speed steel or die steel for cemented carbides, die steel for high speed steel in cold forging dies. Plain carbon and low alloy structural steels are also performed well with this process, especially in cases where high core hardness is not required [36]. However, other profits rather than saving of die consumption are worth noting; these are:

A)- Improvement in product quality, especially surface roughness and dimensional accuracy and precision.

B)- A reduction in cost for inspection of products.

C)- Saving in cost of subsequent processing for products.

D)- Saving of lubricant.

E)- Reduction in maintenance labor.

F)- Decrease in shot down time.

CHAPTER 4. EXPERIMENTAL STUDIES

After preliminary runs of experiments first an optimum bath composition to be studied during the whole course of experimental work was fixed which contains mainly borax as mass transfer agent plus carbide forming element Fe-Nb powders. Because having prepared a reactive bath, it is possible to produce carbide layers on a wide range of steels, cast irons, cemented carbide and graphite.

Studies for utilizing chlorides and fluorides of alkali metals as the salt bath have been conducted but none resulted in useful. The main reasons for the selection of borax may be counted as follows:

* Borax acts as a kind of flux capable of keeping the specimen surface in its clean and fresh state and suppresses the formation of oxide thereon because it dissolves any oxide on the surface of substrate or the crucible [27]. Therefore the process doesn't need a nonoxidizing atmosphere.

* Turkey has large amount of boron minerals.

* Borax can fuse at a relatively low temperature, which is 741°C [42].

* Borax baths involve no emission of dangerous gas and generates no visible fumes unlike choride baths.

These are the reasons which lead to choose borax as the main component of the salt bath.

After the determination of bath reagents, experimental studies carried out during the process are as follows:

* Coating of specimens at various temperatures and times.
* Microexamination of coated specimens by optical microscopy.
* Examination of layer structure by X-ray diffactometry.
* Hardness measurements by microhardness indentatation tests.
* Examination of oxidation state of the bath by X-Ray diffractometry.
* Evaluation of the kinetics of diffusional process.

4.1. Equipments Used

Since no protective atmosphere is needed and agitation is unnecessary, during the operation a simple, externally heated electric resistant type furnace capable of heating up to 1200^{0}C with $\mp$ 5^{0}C tolerance was used.

Carbon containing graphite crucibles were used in order to supply carbon atoms to the salt bath. It has been found that part of the carbon will be dissolved out of the crucible material into the molten salt bath.

These crucibles were produced from the discards of electric are furnace electrodes which were taken from KROMAN A.Ş. and has dimensions of 100 mm in diameter and 65 mm in height.

4.2. Materials Used

Materials used during the process can be divided into three.

* Substrate material.
* Coating material.
* Bath reagent.

As substrate material DIN 115 CrV3 stell was chosen because of its high carbon centent which ease the diffusion process. The steel has the following cemposition:

C: 1.16 %	V: 0.058 %
S: 0.0065%	P: 0.025 %
Cr:0.25 %	Mn: 0.2 %
Si:0.26%	

Specimens were cut in 10x10x10 dimensions and a grinding scheme was developed to obtain a smooth coated surface after the treatment and to remove any existing natural oxide films, corrosion products etc. Grinding steps were performed with 400-600-1200 grit SiC emery paper sequentially.

As the coating material ferroniobium powders were added into the bath which were grinded under 200 mesh size for effective activation. They have the composition of:

Nb : 63-67 %
Si : 2 %
S : 0.15 %
The rest: Fe

As the bath transfer reagent borax which was taken from the ETİBANK and has the composition of $Na_2B_4O_7 10H_2O$ was used. A calcination procedure was applied to this constituent for the removal of crystalline water, as follows:

The chemical was first heated to 300°C and holded an hour at this temperature. Secondly the temperature was raised to 600°C and hept 3 hours at this temperature. After these runs, chemically bonded crystal water has been removed and calcined borax $-Na_2B_4O_7-$ was obtained.

4.3. Procedure For The Experiment

All the specimens produced in the manner described before, were dipped in a bath containing 80% borax and 20% Fe-Nb alloy powders and has a weight of 40 gr. for a definite duration and temperature for carbide formation

The growth rate or control of carbide layer thickness was affected only by the bath temperature and dipping time by keeping the substrate and bath compositions constant.

The bath temperature was selected around the hardening temperature of the steel substrate that in the range 850-1000°C so that quench hardening of the substrate can be performed during cooling after withdrawal from the bath without a reheating hardening porcess. This is the greatest advantage over the CVD process.

Immersion time can be changed between 1-10 hours depending on the required layer thichkness. In the experiment these periods were taken as 2-4-6 hours and in each experiment the bath was renewed.

The specimens taken out from the bath carries a thin glassy film of sticked borax salt. Since borax is water soluble this attached salt was easily removed by simply immersing into boiling water for 2-3 hours.

Hardening of substrate is one of the most important problems to provide successful application. It can be performed by cooling in water, oil, salt or air according to the required substrate hardness, size of material and hardenability of the substrate steel. But in the study all the specimens were air cooled.

4.4. Metallographic Examination

As coated specimens were grinded in order to remove the top of coated surface and to obtain a section part, then they were mounted in bakelite and mechanically polished. Etching was made by 3% Nital.

Microstructure of treated specimens were examined by optical microscope and micrographs showing the coated layers were presented in figures (5.3-5.6).

The average thickness of the coatings was measured by observing the coating cross section at 400 X magnification.

4.5. Microhardness Measurement

Microhardness, Hv, measurements on the coated specimens were used to estimate the hardness of the layers and of the substrate cross section. Therefore, as coated specimens were first polished to measure the layer hardness and then the layers were removed by grinding to measure substrate hardness adjacent to the layer, through the core of the specimen.

Because the coatings were thin a low indentation load of 100 gr was applied by diamond indentor. At least 10 indentation values have been taken for a coated specimen to minimize the experimental error that might happen during the observation of small surface indentations Microhardness values were presented in figure 5.8.

4.6. X-Ray Characterization

In this part, investigations of crystallinity were made on two constituents of process.

1)- The coated layers.
2)- The treatment bath.

Coated specimens were first cleaned thoroughly in boiling water to remove attached glassy layer for X-ray diffraction (XRD) tests.

Examination of X-Ray diffraction peaks of coated layers revealed NbC, as the coating layer figure 5.12.

In the second study, the crystallinity of the treatment bath was performed. For this aim, baths were sampled from various regions of crucible. Then these samples were put in boiling water for about 2-3 hours. After, they were filtrated and were dried in an oven. The XRD peaks were presented in figure 5.10.

CHAPTER 5. RESULTS AND DISCUSSION

As mentioned in chaper 4 , first finding on optimum bath was planned in the experimental study. For this aim, the bath composition was varied continually by keeping temperature and immersion time constant until a sufficient thickness and fluidity of bath was reached. Figure 5.1.

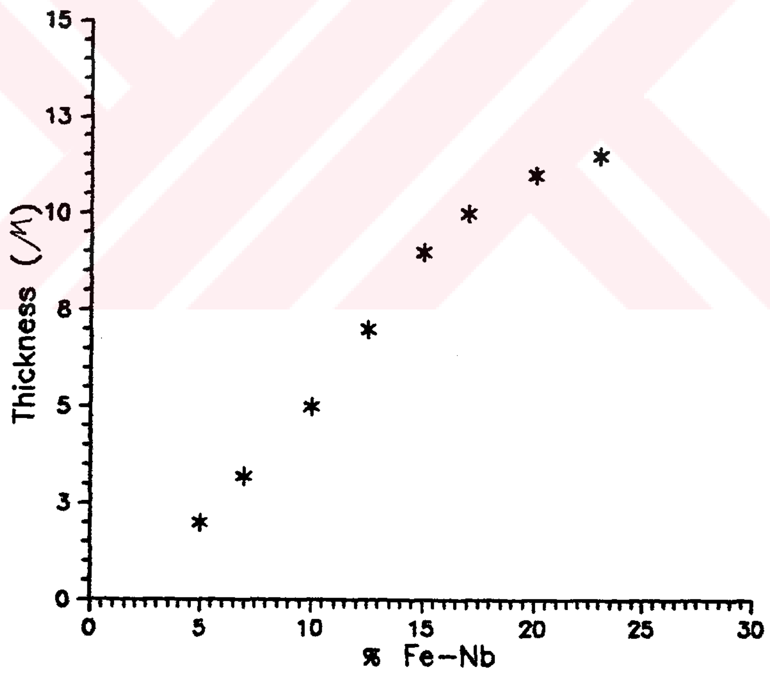


FİGURE: 5.1. Effect of Fe-Nb additions on the thickness of NbC layer.

It has been seen that additions of Fe-Nb powders increased the layer thickness fairly up to 20 %,further additions above that didn't provide an appreciable increase. However, increased the viscosity of the bath to such a value that the dipping of the specimens into the bath became impractical. Even when the immersion was possible with only difficulty, the resulting carbide layer became too much uneven. Therefore, 20% Fe-Nb and 80% borax composition was decided as an optimum and successive experiments were performed with this bath composition. Arai has used about 10-12% Fe-Nb additions containing 59 weight percent Nb to obtain 4-7 micron layer thichness which was considered enough for commercial practices [37].

5.1. The Effect of Temperature

The treating temperature may theoretically extend from the fusing point of the bath material to the melting point of the specimen to be treated upon. In the experiment, however, it was preferably selected in between 850-1000^{o}C taking the growing velocity of the carbide layer and embrittlement caused by excessive grain growth at temperatures above 1000^{o}C into account.

Figure 5.2 shows the effect of time and temperature on the thickness of NbC layers and the micrographs presented in figures (5.3, 5.6). show the microstructures.

Between 850-900^{o}C, the increase in thickness is high, after 900^{o}C this rate decreases. Figure 5.2.

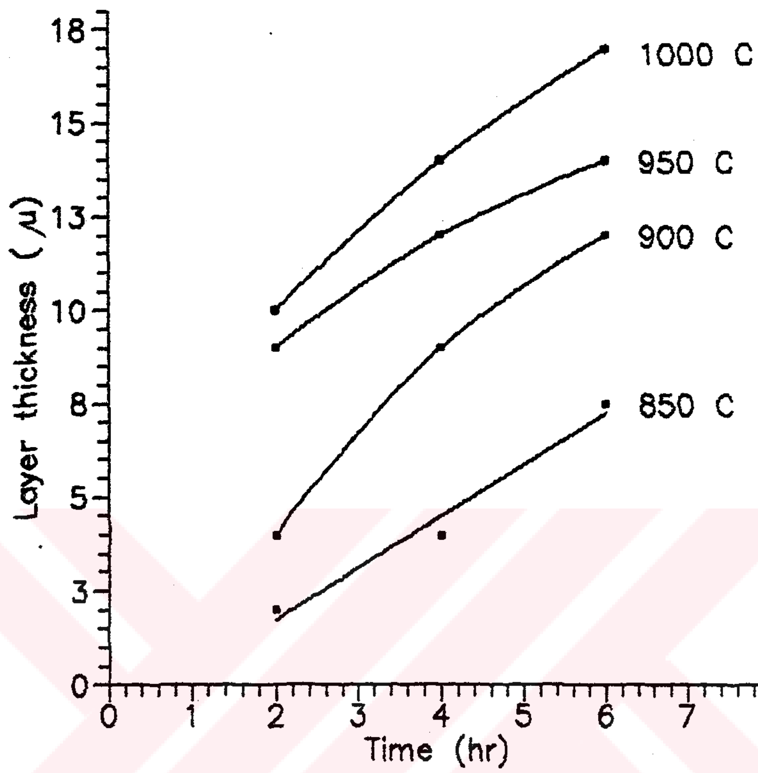
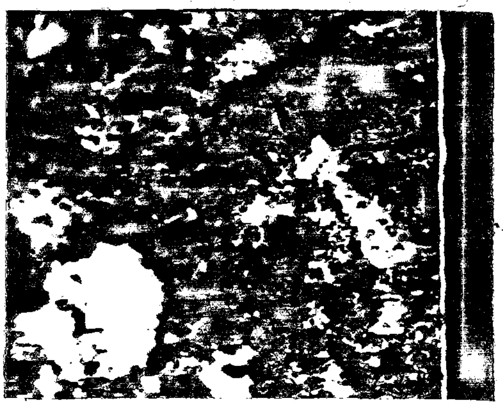
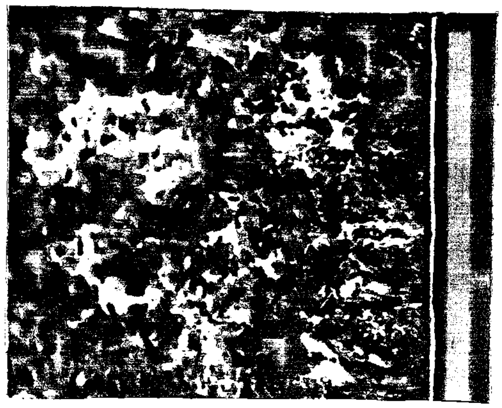


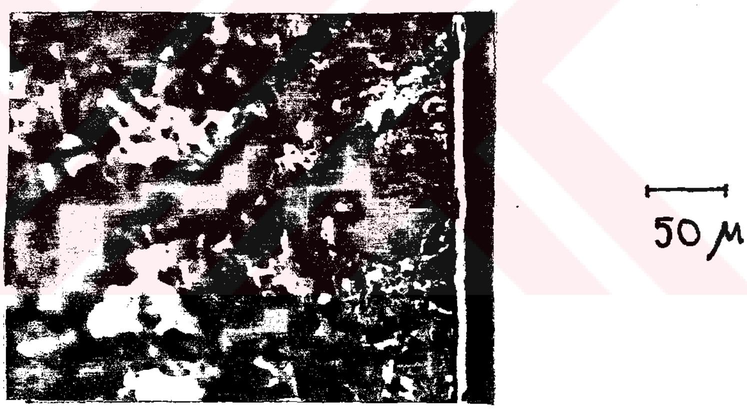
FIGURE: 5.2. The effect of time and temperature on the thickness of NbC layer.



A



B



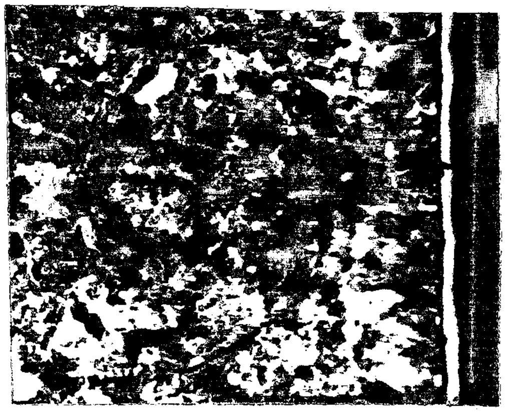
C

FIGURE: 5.3. Coated layers at 850°C

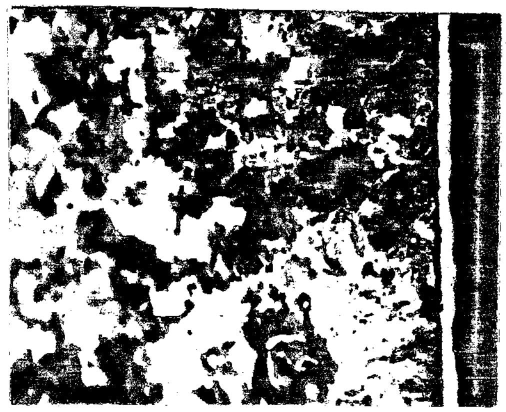
a)- 2 hour.

b)- 4 hour.

c)- 6 hour.



A



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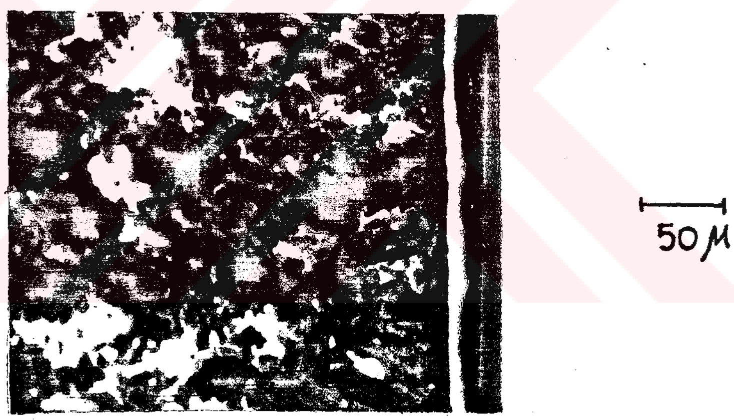


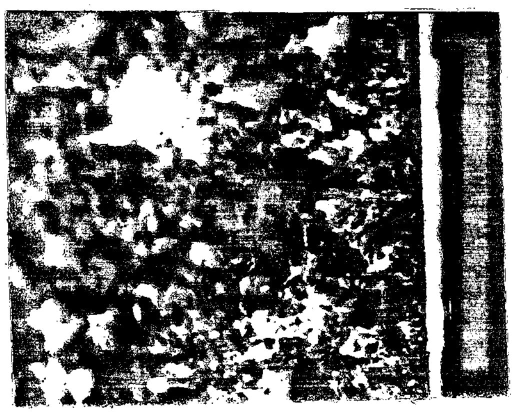
C

FIGURE: 5.4. Coated layers at 900^{o}C

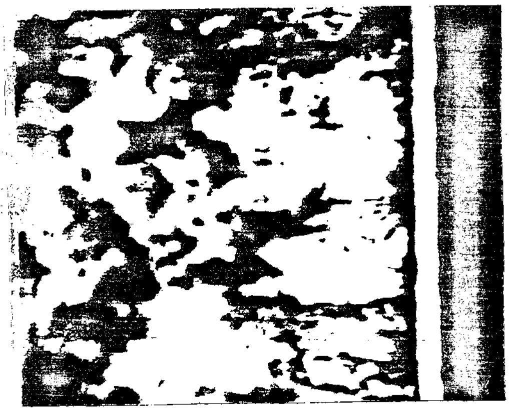
a)- 2 hour.

b)- 4 hour.

c)- 6 hour.



A



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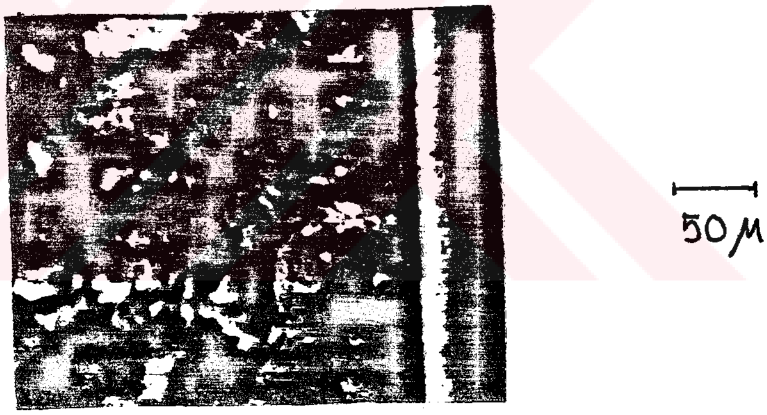


C

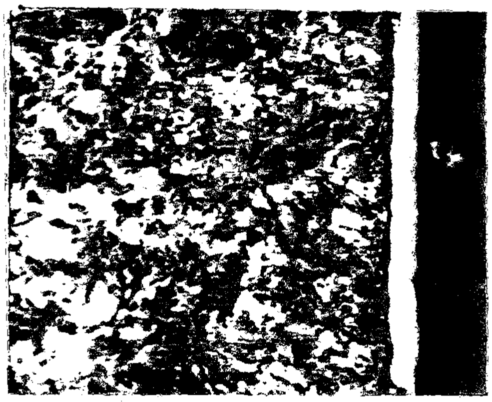
FIGURE: 5.5. Coated layers at 950^{o}C

a)- 2 hour.

b)- 4 hour.

c)- 6 hour.

A



B

C

FIGURE: 5.6. Coated layers at 1000^{o}C

a)- 2 hour.

b)- 4 hour.

c)- 6 hour.

5.2. The Effect of Immersion Time

The treating time period depends upon the thickness of the carbide layer to be formed. The treatment shorter than an hour, provided no practically acceptable formation of carbide layer although the final determination of the treating period depends upon the treating temperature.

Therefore during the experimental runs 2-4-6 hours were chobsen as time periods. As shown from figure(5.2) with increase in treating period, the growth of carbide layer first do show a linear increase, then a diminishing region appears in the rate. In practice, to obtain a sufficient wear resistant layer at least 3 hours was required. It is not necessary to prolong the treatment beyond 10 hours, since the desired thickness can usually be achieved within this period.

5.3. Hardness of Coated Specimens

Microhardness measurements were applied on:

- Coated layers
- Substrate cross section

The hardness of coated layers was found to increase with increase in treating temperature. Figure 5.7. This can be attributed to the higher solubility of carbon in the layer with increasing temperature. The measured hardness values was observed to change between 3000-4200 Hv, although in the literature it was reported as 2500-3200 Hv [14].

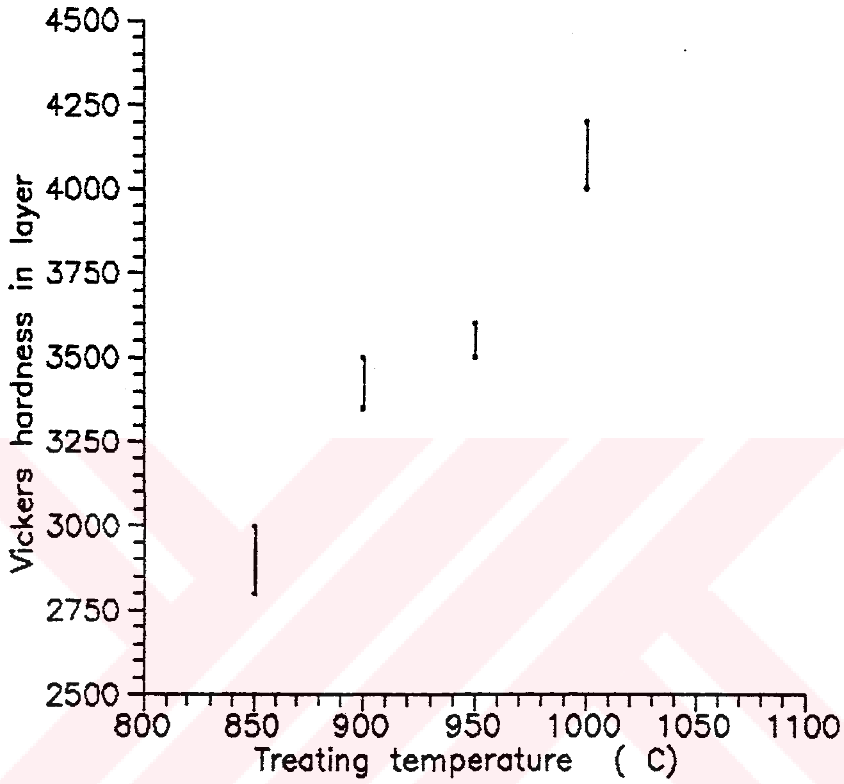


FIGURE: 5.7. Hardness of coatings with bath temperature.

The hardness distribution along the substrate cross section do show an increase and then reaches a limiting value depending on treatment temperature. Figure 5.8. This is a parallel result with the work of Arai [32].

The reason for the hardness decrease adjacent to the layer can be attributed to the deplation of carbon atoms from the substrate to the layer.

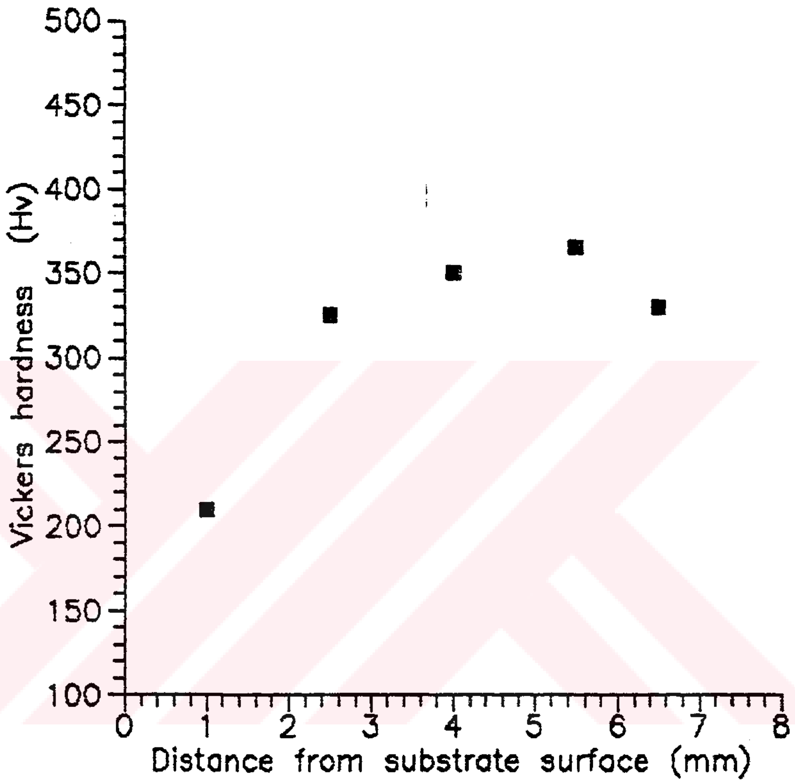


FIGURE: 5.8.a. Hardness distribution from the substrate-coating interface at A)- 850^{0}C

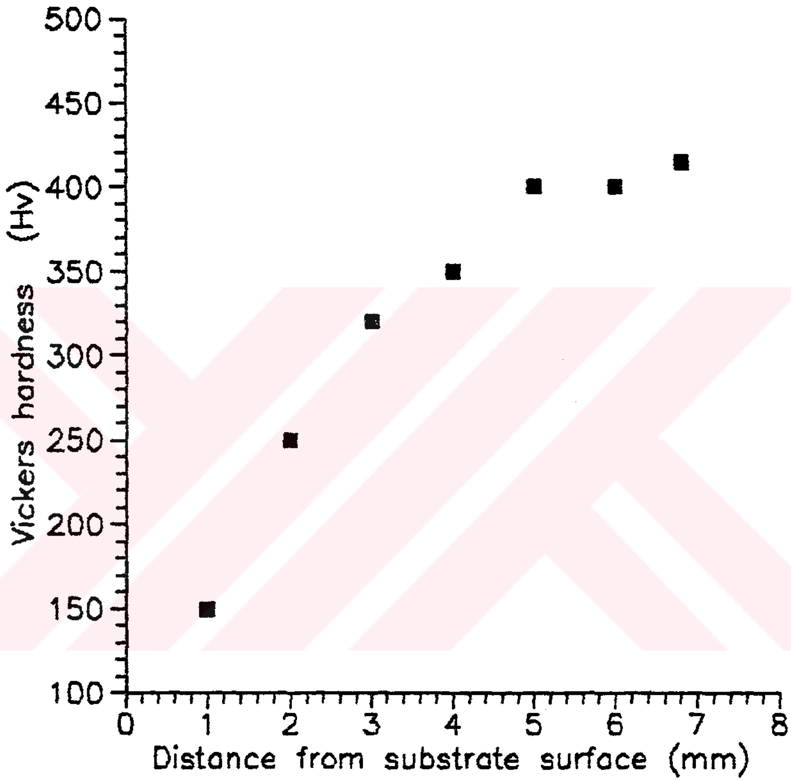


FIGURE: 5.8.b. Hardness distribution from the substrate-coating interface at B)- 900°C

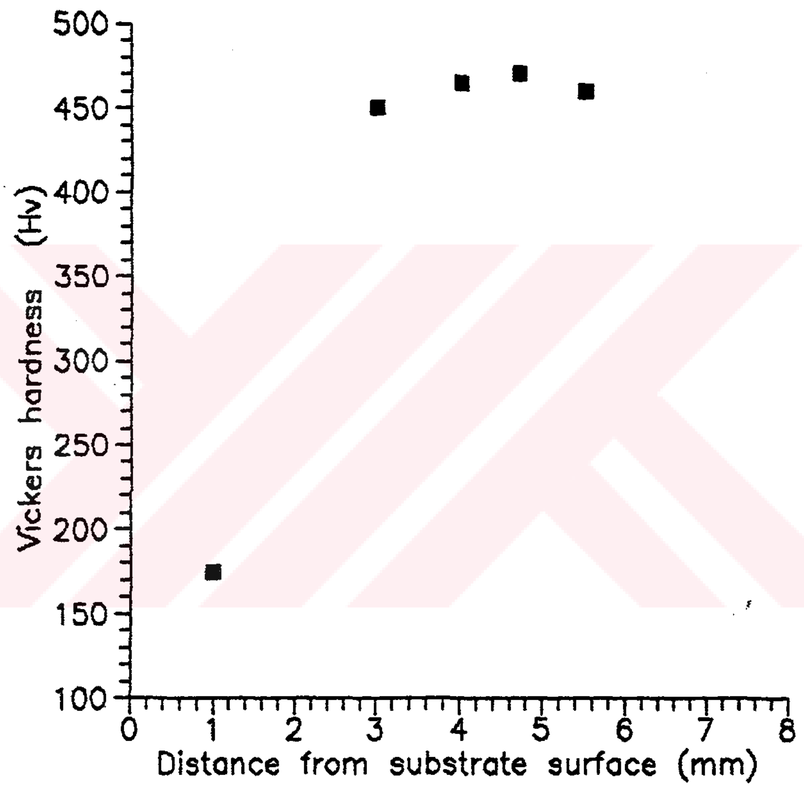


FIGURE: 5.8.c. Hardness distribution from the substrate-coating interface at C)- 950^{o}C

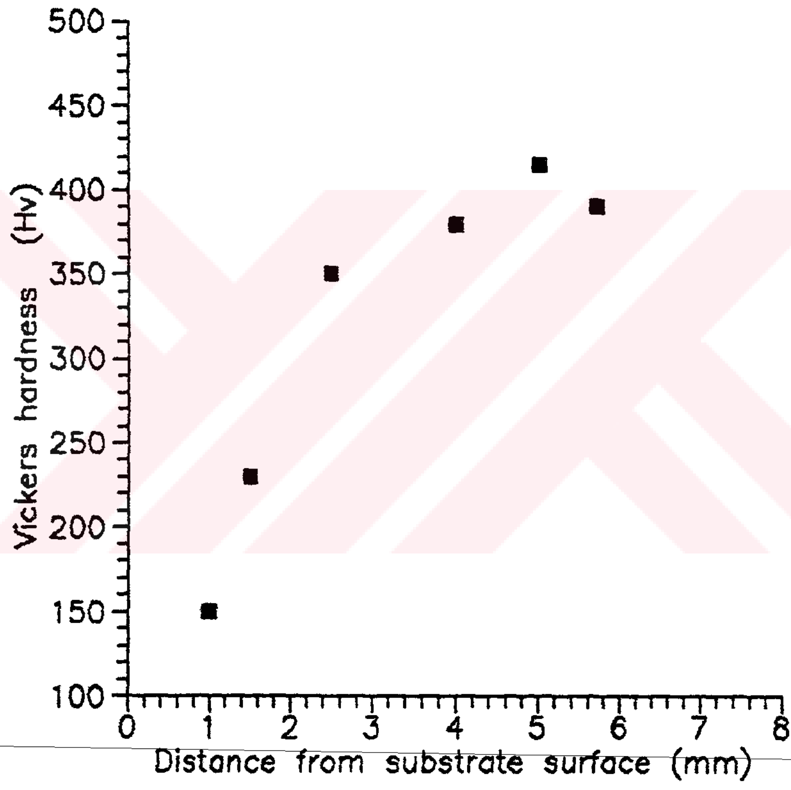


FIGURE: 5.8.d. Hardness distribution from the substrate-coating interface at D)- 1000^{o}C

5.4. Diffusion Kinetics of Carbide Layer Formation

The kinetics of carbide layer formation was investigated by taking the results shown in figure 5.2. into consideration for there is a confliction in the literature about the build up of the layer that whether it is proceeding at a given reaction rate or the process is diffusion controlled.

Linearity in the development of layer thichness with time explains a reaction rate controlled process. However if the development do show a parabolic relation, the process is diffusion controlled [43].

Arai shows a linear relation between layer thickness and time for NbC coating on tool steel [44]. On the other hand, Child attempts to resolve this problem have resulted in equally confusing evidence with both linear and parabolic relation [43].

Coming to this study, there seems a parabolic relationship as shown in figure (5.2) which suggests the process is diffusion controlled.

The diffusion coefficients of the carbide formation process was calculated by the equation for parabolic law:

$$d^2 = 2Dt$$

The slope of figure(5.9)gives the diffusion coefficients at treating temperatures which were tabulated in Table 5.1.

As can be understood from Table 5.1, while the bath temperature rises, the diffusion rate of carbon in the layer increases resulting in an increase in depth.

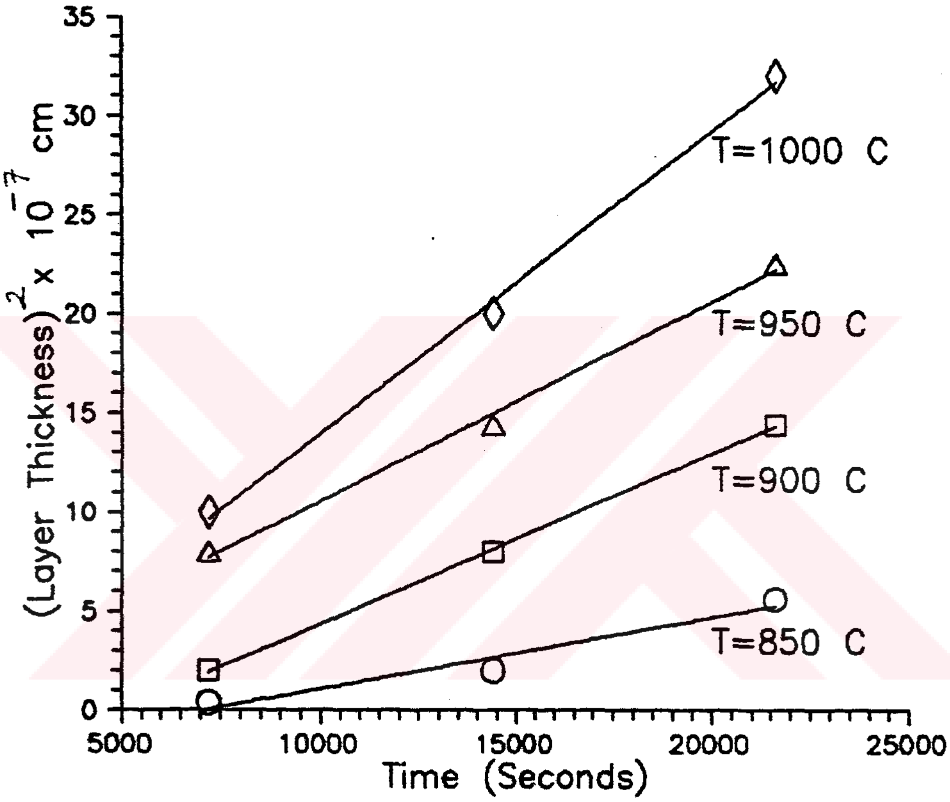


FIGURE: 5.9. Layer thickness square -time graph at various bath temperatures.

TABLE: 5.1. Diffusion Coefficient Values at Various Bath Temperatures.

Temperature	D(cm^2/sec.)	Correlation (K)
850	1.5×10^{-11}	096
900	4.4×10^{-11}	099
950	5×10^{-11}	098
1000	7.8×10^{-11}	099

The bath temperature affects the thickness of the layer by the equation.

$$\frac{d^2}{t} = D = A \exp\left(-\frac{Q}{RT}\right)$$

Where:

d : layer thickness (cm)
t : Immersion time (sec.)
D : Diffusion coefficient (cm^2/sec.)
A : Frequency factor (cm^2/sec.)
Q : Activation energy of carbon diffused in the carbide (K cal/mol ^{o}K)
R : Gas constant (cal/mol ^{o}K)
T : Absolute temperature ^{o}K

In order to find out the activation energy of carbon diffusion, the slope of Figure (5.10). has been calculated and this activation energy of carbon atoms to form NbC layer was found as $\sim$ 30 Kcal/mole for the optimum bath choosen.

This is a much lower value than the value found by Arai which is 50 Kcal/mole [37]. The reason for this difference may strongly be the higher carbide forming element Fe-Nb content of the bath.

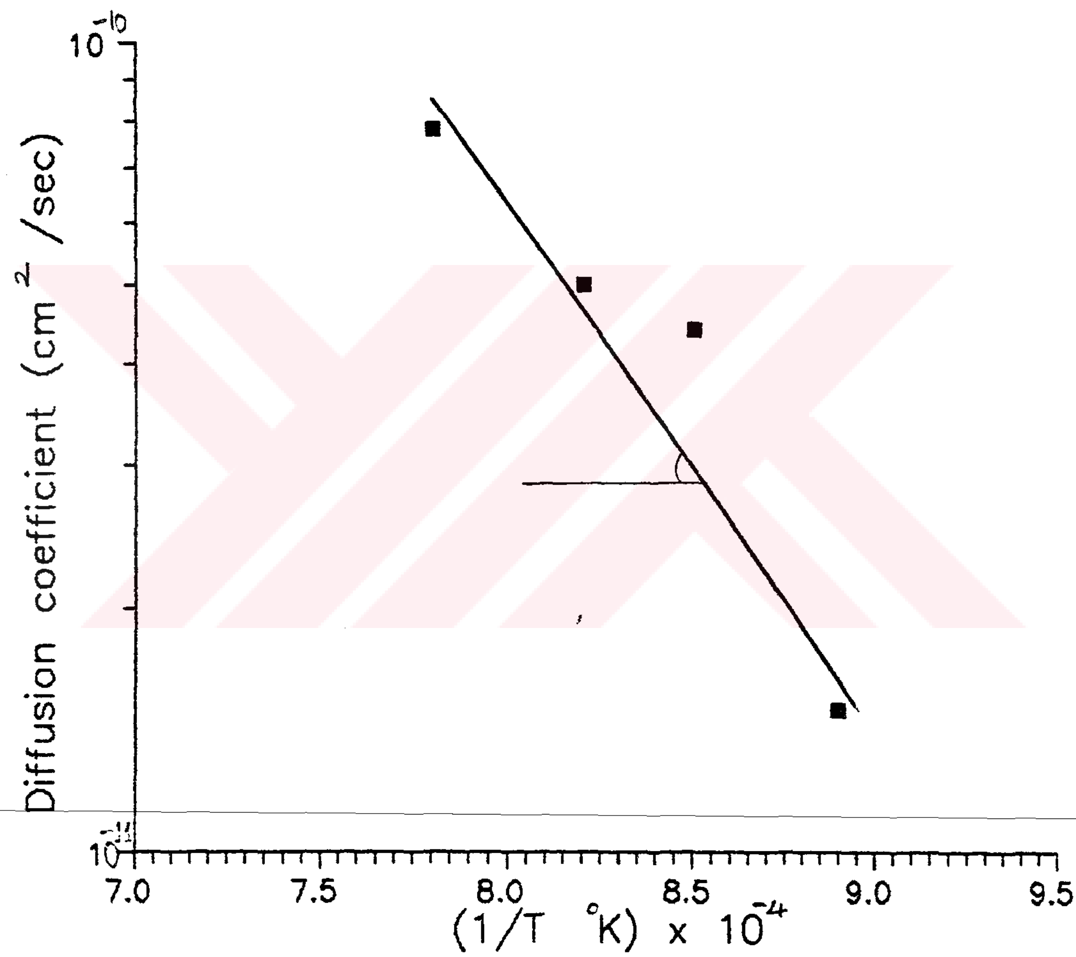


FIGURE: 5.10. Diffusion coefficient-temperature relationship.

5.5. Nature of Bath

The nature and behavior of fused borax bath suitable for producing carbide layers are investigated.

Understanding of reactions prevailing in the bath favorably controlling reactions is critical and formation of an active bath which cause build up of carbide layers depend upon these reactions.

Because the developer of the process is a technical firm, much of the study concerned with practical rather than theoretical concepts. Therefore some mystery still remains on the reduction reactions especially taking place between the bath and crucible material.

In this field the first academic paper was published by Child [43] about the oxidation and kinetics of reactions.

Initially it was thought that the process operated by reaction at the bath substrate interface between the solid ferroalloy and the carbon in the substrate [43]. But later it was found that oxidation of carbide forming elements under certain conditions determine the activity or passivity of the bath.

Oxidation may occur at the salt/air interface particularly if the bath is stirred. During melt down there is also opportunity for oxidation by entrapped air. These factors lead to strong oxidizing conditions and therefore unlike metals, ferroallys do not dissolve in fused borax but are first oxidized.

Sometimes excess or over oxidation may happen to occur which must be avoided for, it forms stable higher oxides of carbide forming elements such as V_2O_5,Nb_2O_5 etc. which are difficult to reduce into ions.

In the case of niobium, forming a pentaoxide Nb_2O_5 makes the bath passive ie uncapable of forming carbide layer.

In this study, the XRD examination of active bath samples taken from the middle and bottom section of crucible at 950^{0}C and 6 hour have revealed that: Figure 5.11 .

In the middle sections near the treated specimens NbO_2, cementite, iron and little iron oxide present.

At the bottom levels of bath, the amount of Fe-O and cementite increases whereas NbO_2 decreases.

The results show that; Fe-Nb powders dissociate and oxidizes ás NbO_2 although in the literature [43] it has been suggested as Nb_2O_3. As a result of interaction of bath and graphite crucible, the content of cementite is high at the bottom.

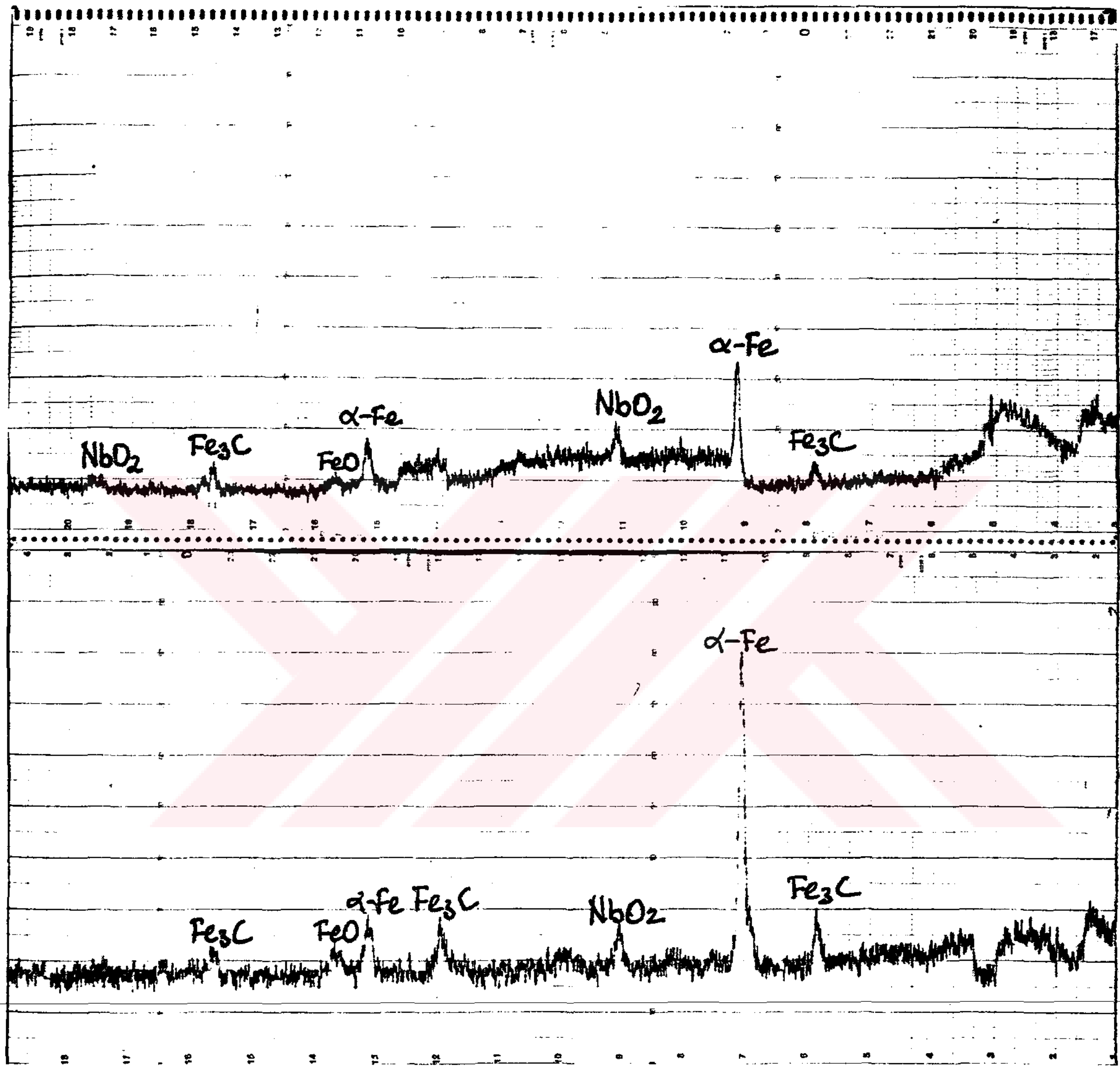


FIGURE: 5.11. XRD pattern of coating bath.

a)- Specimen surface.

b)- Bottom of bath.

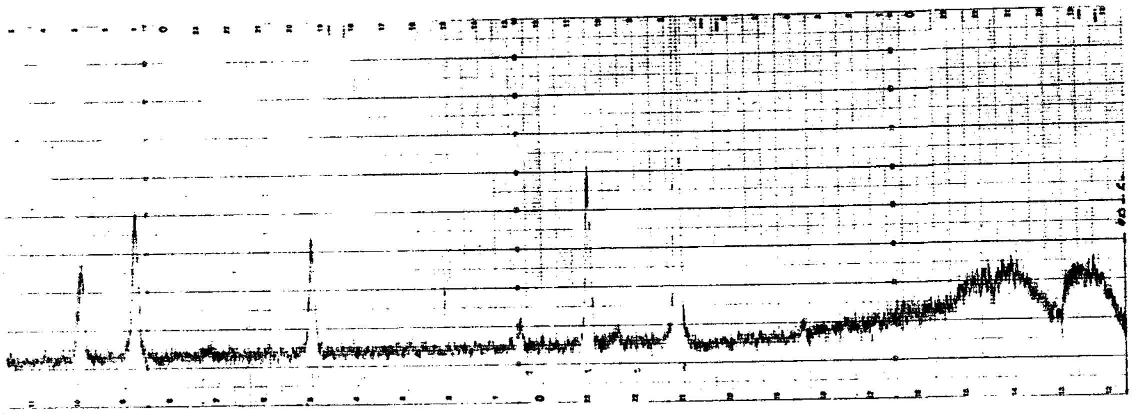


FIGURE: 5.12. XRD of NbC coated specimen.

CONCLUSIONS

From the experimental results and discussions the following conclusions can be drawn:

1)- Pore free NbC layers were formed on DIN115CrV_3 steel substrates by immersing in a bath containing borax solvent and 20% Fe-Nb powders.

2)- The hardness values of coatings were measured between 3000-4200 Hv.

3)- The maximum thickness coated was found as 17 micron. It was observed to be uniform even in small openings, in narrow recesses and at sharp edges.

4)- The hardness of substrate next to the layer has showed a decrease before attaining its normal quench hardening value because of decarburaziton.

5)- Neither cracks, spall or peel of carbide layers was observed even if they were quenched immediately after withrawal from the bath.

6)- Metallographic examinations have revealed that there is a sharp boundary between the substrate and the coating with no appreciable intermediate layer.

7)- The study made on kinetics of carbide formation showed that the process is diffusion controlled.

The activation energy of carbon atoms to form carbide layers was found as $\sim$30 Kcal/mole.

8)- The oxide which causes the active bath formation was found as NbO_2.

Finally, this work has proved that the process can be easily applied to Turkish Industry which heavily demands such an economic and practical process to produce excellent wear resistant coatings.

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