**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY**

# PASSIVE LAYERS FOR PREVENTING GAS NITRIDING

**M.Sc. THESIS**

**Ebru ÖZEL**

**Department of Advanced Technologies**

**Material Science and Engineering Programme**

**Thesis Advisor: Prof. Dr. Mustafa ÜRGEN**

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# GAZ NİTRÜRLEMEYİ ENGELLEYEN PASİF YÜZEYLER

**YÜKSEK LİSANS TEZİ**

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**TEMMUZ 2012**

**Name-surname**, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student 521101007, successfully defended the **thesis/dissertation** entitled "PASSIVE LAYERS FOR PREVENTING GAS NITRIDING ", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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|---|---|---|
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**Date of Submission : 29 June 2012**
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***To my parents,***

**FOREWORD**

I would like to thank to my supervisor Prof. Dr. Mustafa Ürgen for his guidance throughout the period of my thesis studies**.** I would like to thank to my supervisor in RBTR, Dr. Azra Martin, for problem solving supports through the project and valuable advices both in technical and personal development areas and I am very much thankful to Zühre Varol.
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June 2012

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**TABLE OF CONTENTS**

**Page**

**ABBREVIATIONS**

**RBTR** : Robert Bosch Turkey
**CR-Injector** : Common Rail injector
**$K_N$** : Nitriding Potential
**CL** : Compound Layer
**DL** : Diffusion Layer
**LM** : Light Microscope
**XRD** : X-Ray Diffraction
**T** : Temperature

## LIST OF TABLES

**Page**

**LIST OF FIGURE**

**Page**

## PASSIVE LAYERS FOR PREVENTING GAS NITRIDING

## SUMMARY

Fuel injection technology represents one of the main drivers towards improving current characteristics of diesel engines and identifying future enhancements aiming reduction of exhaust emission, combustion noise and fuel consumption. New generation injection systems should be resistant to high pressure to improve combustion and vaporization of the fuel. In order to increase the performance of injectors in terms of fatigue resistance, gas nitriding is one of the effective methods. Beside in the past corrosion resistance increase on nitrided injector bodies is experienced [1].

Cleaning is a very important process before heat treatment processes, since residual films from cleaning chemicals and also ineffective cleaning create local passivation and cloudy surfaces after gas nitriding. In the light of the results of former experiments, it is shown that some of cleaning chemicals create an undesired passivation on the sample surface. One of the aim of this project is to investigate different cleaning chemicals for their positive or negative effects on nitriding.

In some sensitive locations on components, nitriding is needed to be eliminated for avoiding premature failures. There is a clear need for totally/partially passive surfaces to prevent formation of nitrided layers on stress sensitive locations of the parts, namely threads and sealing surfaces. However, the complex geometry of injector parts, makes the applicaiton of passive surface layers on stress sensitive locations of the injector more important. Today's most preffered protective methods are nickel, copper electroplating and stop off masks. However the most preffered stop off masks, are difficult to handle and creates risk of particle formation after nitriding

The main aim of this project is to develop and investigate protective layers to prevent nitriding locally on CR injector parts with the help of chemical, electrochemical or Sol-Gel coating technologies. The developed methodology needs to be economically feasible and technically applicable in a serial production and easy to integrate into the production chain.

For this study, samples with two different geometries are used. These samples are made of 50CrMo4, since this material is a promising material for new generation CR-injector. The real CR components were not used in order to reduce cost and for the ease of analysis. All Samples were nitrided at 520°C for 10 hours at $K_N$ 2 nitriding potential and after nitriding the diffusion layer, compound layer thickness and hardness measurements were conducted .

In this project, the efficinecy of different cleaning chemicals on gas nitriding process were investigated. Samples were cleaned with different cleaning chemicals at same conditions (65°C, 10 minutes). After cleaning parts were nitriding in the same batch. With the help of light microscope compound layer diffusion layer thickness measurements were measured ,and also hardness measurements were done. According to the observations done after nitriding, no significant differences were seen on the compound layer thickness and hardness values of the samples which were cleaned with different cleaning chemicals. Only Surtec 042 has higher compound (white) layer thickness than the other cleaning chemicals as defined active surfaces in literature and Surtec 101 had lower compound layer as defined passive [18].

On the other hand four different methods were investigated to create passive layers on surfaces for preventing gas nitriding. One of them was stop off masks, which is currently used in the industry and generally based on the mixture of refractory oxides and binder chemicals. Two different types of stop off masks were applied at the same thickness on 50CrMo4 sheets in order to compared which one is more effective. According to the results, no diffusion and compound layer formation were seen on samples and additionally hardness values were comparable with core hardness. Although, stop off maskings exhibited excellent performance to prevent gas nitriding, their application on small areas is difficult and they leave residual particles even after nitriding, which can cause problems on injector performance during assembly and can cause problems on motor performance.

Nickel and copper electroplatings are effective methods to create a homogenous passive layer to prevent gas nitriding. There are some special applications such as brush plating for small and selective areas. Samples were coated with nickel by electroplating in Watts type bath and copper coated in acidic copper sulfate type bath for different durations, and coating thicknesses to investigate its effectiveness. According to the observation performed after nitriding, nickel electoplating with thickness above 3.5 µm provided a good performance for preventing gas nitriding. In copper electroplating, adhesion problems due to unsufficient surface have been encountered. On areas without adhesion problems exist efficient screening is provided for gas nitriding. The minimum thickness required for stopping nitriding was not efficiently analysed for copper electrodeposited parts because of adhesion problem.

The potential of Sol-Gel coatings for preventing gas nitriding has also been tested within the scope of the work. For this purpose titania base Sol-Gel coatings are applied on steel parts by dipping process. However, these coatings did not show any nitriding prevention effect highly probaely due to their high porosity and insufficient thickness. Micro Raman and XRD investigations of the surfaces revealed the presence of anatase and $Fe_4N$ or $Fe_3N$ phases after nitriding experiments.

The results of this study showed that the already applied industrial techniques namely, stop off masks and copper or nickel electroplating are still the most efficient techniques for prevention of nitriding. Cleaning chemicals using in RBTR are not effective on gas nitriding process. Further studies are required for selection of the appropriate process on real injector parts.

## GAZ NİTRÜRLEMEYİ ENGELLEYEN PASİF YÜZEYLER

## ÖZET

Dizel motorun mevcut özelliklerini geliştirmek, egzoz emisyonu, yanma gürültüsünü ve yakıt tasarrufunu sağlayabilmek için yakıt enjeksiyon teknolojisi yakıtın yanmasını ve buharlaşmasını geliştirmeli ve bu sistemler yüksek basınca dayanıklı olmalıdır. Daha verimli yanma için geliştirilmekte olan yeni nesil enjeksiyon sistemlerinin yüksek basıç dayanımına sahip olmaları gerekmektedir.

Gaz nitrürleme enjektörün yüksek basınca ve yorulmaya karşı dayanımı açısından performansını geliştirmede önemli bir yere sahiptir. Bunun yanında korozyon direncinin artmasını da sağlayabilmektedir. Diğer taraftan enjektör gövdelerinde gaz nitrasyonu bazı hassas bölgeler yaratmaktadır ve bu bölgelerin nitrürleme etkisinden korunması gerekmektedir.

Enjektör üretimde, vida dişleri veya sızdırmazlık bölgeleri gibi, nitrürlenmesi istenmeyen yüzey alanları mevcuttur. Bu bölgelerde nitrürleme sonucu görülen gerilmeyi azaltmak amacıyla, nitrürlenmeyi engelleyici, pasif yüzeylere ihtiyaç duyulmaktadır. Günümüzde stop off (durdurucu) pastaları olarak tanınan bir çok nitrürlemeyi engelleyici ürün bulunmaktadır. Fakat enjektör gövdesinin karmaşık yapıda olması durdurucu pastaların homojen uygulanmasında zorluklara neden olmaktadır. Ayrıca bu ürünlerin nitrürleme sonrası yapıdan uzaklaştırılmasının gerekmesi proses içerisinde özellikle montaj sırasında bir çok soruna yolaçmaktadır. Uzaklaştırma sırasında durdurucu pastaların parça yüzeyinde partikül bırakması ve homojen uygulanamaması bu yöntemin en büyük sorunlarıdır.

Gaz nitrasyonu öncesi yıkama prosesi de önemli bir yere sahiptir. Parça yüzeyinde kalan yağ ve kimyasal kalıntıları nitrürleme sonrası bölgesel nitrür almayan bölgeler yaratmaktadır. Literatürde yıkama kimyasallarının nitrürlemeye etkilerinin araştırıldığı çalışmalar mevcuttur. Surtec firmasının yaptığı çalışmalarda iki ticari yıkama kimyasalının etkisi araştırılmış ve gaz nitrasyonu üzerinde farklı etkiler yarattığı gözlemlenmiştir. Bu parçaların bileşik tabaka kalınlıkları, diffüzyon tabakası kalınlıkları ve sertlik değerleri ölçülmüştür Surtec 042 isimli yıkama kimyasalının bileşik tabaka kalınlığını arttırdığı, yüzeyi daha iyi temizlediği “aktive” ettiği, Surtec 101 kimyasalının ise bileşik tabaka kalınlığını azalttığı gözlemlenmiştir. Bu çalışma kapsamında ise söz konusu iki kimyasal yanında RBTR’de kullanılan diğer yüzey temizleme kimyasalları da kullanılmıştır ve gaz nitrasyonu öncesi kullanılan yıkama kimyasallarının nitrürlemeye olabilecek etkileri incelenmiştir. Alınan sonuçlar ile fabrika için bir veri tabanı oluşturulması amaçlanmıştır.

Çalışma kapsamında ayrıca nitrürlemeyi engelleyecek pasif yüzeylerin geliştirilmesi ve denenmesi amaçlanmaktadır. Endüstride de kullanılan nikel ve bakır elektrolitik

kaplamalar ve durdurucu pastalar olarak nitelendirilen ürünler denenmiştir. Bu yöntemlerin yanı sıra Titanyum bazlı Sol-jel kaplamalar da olası bir yöntem olarak incelenmiştir.

Uygulanacak yöntemin ekonomik, seri üretime uygun ve kolay adapte edilebilen bir yöntem olması gözönüne alınmıştır.

Çalışma kapsamında yeni nesil enjektörlerde kullanılmayı planlanan 50CrMo4 malzemesi seçilmiştir, ayrıca iki farklı geometriye sahip numunelerin kullanımı tercih edilmiştir. Gerçek enjektör gövdeleri hem ekonomik kazanç sağlamak hem de analiz zorluğu nedeniyle kullanılmamıştır.

Deneysel çalışma sonucunda seçilen yöntemin daha sonra gerçek ürün üzerinde denenmesi planlanmıştır.

Gaz nitrasyon işlemi tüm numunelerde 520°C 10 saat ve $K_N$ 2 nitrasyon potansiyelinde yapılmıştır. Nitrürleme sonrası tüm numunelerin sertlik, difüzyon ve bileşik tabaka kalınlık ölçümleri yapılmıştır. Böylelikle pasivasyon etkisinin gözlemlenmesi amaçlanmıştır.

Yıkama kimyasallarının nitrasyon işlemine bir etkisinin olup olmadığını incelemek amacı ile yapılan denemelerde yıkama parametreleri sabit tutulup (65°C, 10 dakika ) sadece farklı temizleme kimyasalları ile yıkamalar yapılmıştır. Nitrürleme sonrası parçaların mikro sertlik cihazı ile sertlik ölçümleri ve optik mikroskop ile difüzyon tabakası kalınlığı ve bileşik tabaka kalınlığı ölçümleri yapılmıştır. Yapılan çalışma sonucunda yıkama kimyasallarının difüzyon tabakası ve sertlik sonuçlarının birbirine yakın değelerde olduğu görülmüştür. Sadece Surtec 042 kimyasalının bileşik tabaka kalınlığı diğer temizleme kimyasallarına göre farklılık göstermektedir. Bu farklılık yüzeyin daha aktif temizlendiği olarak yorumlanmaktadır.

Nikel ve bakır elektrolitik kaplamalar, Watts nikel banyosu ve asidik bakır banyosu kullanılarak farklı kaplama sürelerinde kaplanmıştır. Kaplama kalınlığının bu süre ile değişimi incelenmiştir. Nitrürleme sonrası hangi kaplama kalınlığının daha etkili olduğu araştırılmıştır. Yapılan denemeler sonrası 3,5µm kalınlığının üzerinde nikel kaplamanın nitrürlemeyi engelleyici etki gösterdiği gözlemlenmiştir. Bakır kaplamada ise homojen bir kaplama elde edilememiştir. Altlık malzemesine bakırın yapışmamasından dolayı bazı bölgelerde nitrürleme sonrası bileşik ve difüzyon tabakaları görülmüştür, ayrıca homojen bir kaplama elde edilemediğinden etkin kaplama kalınlığı ölçülememiştir.

Farklı durdurucu pastalar 50CrMo4 plakalar üzerine eşit miktarda uygulanarak gaz nitrürlemeye olan etkileri incelenmiştir. Kullanılan iki tür durdurucu pasta da, nitrürlemeyi tamamen engellemiştir. Nitrürleme sonrası bileşik tabaka ve difüzyon tabakası gözlemlenmemiş ayrıca sertlik değerlerinin düşük olduğu görülmüştür. Fakat uygulanan pastalar nitrürleme sonrası parça yüzeyinde partikül bırakmıştır. Bu da durdurucu pastaların en büyük problemidir.

Titana bazlı Sol-jel kaplamalar genellikle korozyonu engellemek amaçlı kullanılmaktadır. Titanyum oksit tabanlı Sol-jel kaplama bu çalışmada daldırma yöntemi ile 50CrMo4 plakalar üzerine uygulanmıştır. Daldırma işlemi iki farklı hızda

yapılmıştır. Gaz nitrasyonu sonrası yapılan XRD ve mikro Raman sonuçlarında yapıda anataz ve $Fe_4N$, $Fe_3N$ fazları gözlemlenmiştir. Anataz fazı amonyak ile bir faz oluşturmamasına rağmen Sol-jel kaplamaların gözenekli ve ince yapısı yüzünden azotun çelik içerisine yayındığı gözlemlenmiştir. Yapıda bileşik ve difüzyon tabakası da ışık mikroskobu ile bakıldığında gözlemlenmiştir. Parçaların sertliğinin yüksek olduğu da görülmüştür.

Yapılan denemeler sonucunda endüstride de kullanımı bulunan elektrolitik nikel ve bakır kaplamaların gaz nitrürlemeyi engelleyici en etkili yollar olduğu görülmüştür.

Ayrıca RBTR içerisinde kullanılan yıkama kimyasallarınınyapılan deneysel çalışma içerisinde gaz nitrürleme prosesine büyük bir etkisi olmadığı gözlemlenmiştir

# 1. INTRODUCTION

$CO_2$ emision reduction and energy efficiency is an important issue in automative industry. New components of injectors should be resistant to corrosion, fatigue and high pressure and also have complex geometry to enable effective combustion and vaporization of the fuel. Heat treatment methods such as carburizing and bainitization can not provide the required mechanical properties at high working pressures. Gas Nitriding is a promising method when compaired to other hardening methods. Gas Nitriding is a thermochemical treatment widely used to form nitrides on the surface. This technique is of great interest in industry as it forms a unique composite structure with a hard surface and a tough interior, so that the overall mechanical performance, wear and corrosion resistance of iron based alloys are greatly improved. However after nitriding, the complex geometry of the injector creates mean stress sensitive locations. There is a definite need for totally/partially passive surfaces to prevent formation of nitrided layers on these stress sensitive locations of the parts such as threads and sealing surfaces. Passive surface layers can be used to avoid the formation of nitrided layers on these areas.

Cleaning is a very important process before heat treatment processes, since residual films from cleaning chemicals affect gas nitriding process and also ineffective cleaning create local passivation and cloudy surfaces after gas nitriding. In the light of the results of previous experiments in RBTR, show that some of the cleaning chemicals create undesired inhomogeneous passivation on the surfaces [15, 16].
The aim of this study is:

1) To investigate effect of different surface cleaning chemical used in RBTR for overcoming erratic nitriding behavior due to inefficient cleaning.
2) To investigate the potential and applicability of different techniques for partial prevention of nitriding on samples. Three of these techniques namely stop off masks, nickel and copper electroplating are already used in the industry for prevention of nitriding. A further process, Sol-Gel coating is also investigated in this study. Up to now, this process is not used for prevention

of nitriding. However, due to it is easy of applicability, the potential of this method for prevention of nitriding is also analysed.

## 2. GAS NITRIDING

Nitriding is a thermochemical heat treatment process consisting of heating steels in a nitrogenous environment usually at a temperature between 400-590°C for a specifical period of time. Gas nitriding process is related to nitriding potential, time and temperature.Nitriding process develops a hard, fatigue, wear and corrosion resistant surface [3,4].

### 2.1 Mechanism of Nitriding

Nitriding is a thermochemical diffusion treatment in which the steel surface is enriched by nitrogen in a temperature range of 490- 580 ºC. Dry ammonia is used as a nitrogen supplying gas [5].

Active nitrogen atoms are released from the dissociation of ammonia molecules on the steel surface (Figure 2.1, and Figure 2.2).

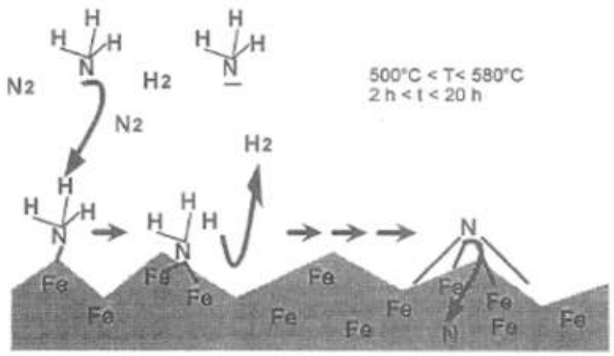



**Figure 2.1:** Nitriding mechanism [6].

During nitriding process ammonia is dissociated by selectively catalytic reactions at steel surface as described Figure 2.2.

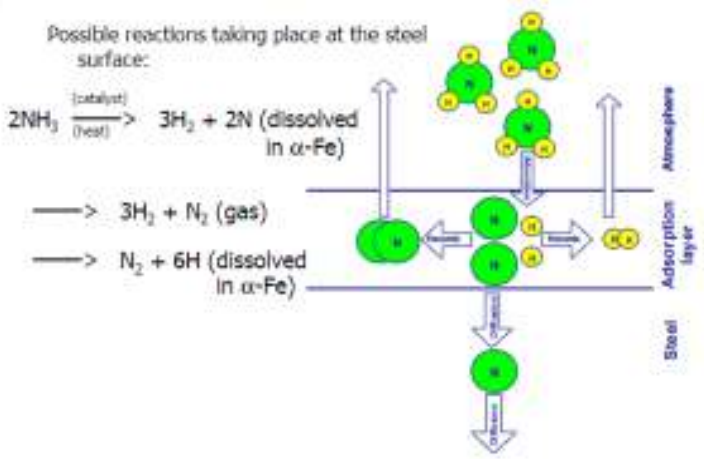



**Figure 1.1 :**

**Figure 1.2 : Figure 2.2:** Gas nitriding reactions [6]

The sequential reactions that occur during gas nitriding are given below equ. (2.1-2.6):

$$NH_3\,(g) \Leftrightarrow NH_3\,(ad) \quad \textbf{(2.1)}$$

$$NH_3\,(ad) \Leftrightarrow NH_2\,(ad) + H\,(ad) \quad \textbf{(2.2)}$$

$$NH_2\,(ad) \Leftrightarrow NH\,(ad) + H\,(ad) \quad \textbf{(2.3)}$$

$$NH\,(ad) \Leftrightarrow N\,(ad) + H\,(ad) \quad \textbf{(2.4)}$$

$$2H\,(ad) \Leftrightarrow H_2\,(g) \quad \textbf{(2.5)}$$

$$2N(Hx)(ad) \Leftrightarrow N_2\,(g) + (x\,H_2)(x=0,1,2,3) \quad \textbf{(2.6)}$$

Gas Nitriding process proceeds according to the binary Fe - N phase diagram. First nitrogen forms a solid solution with Fe when the solubility limit is excetled $Fe_xN$ phases starts to form (Figure 2.3) [9].

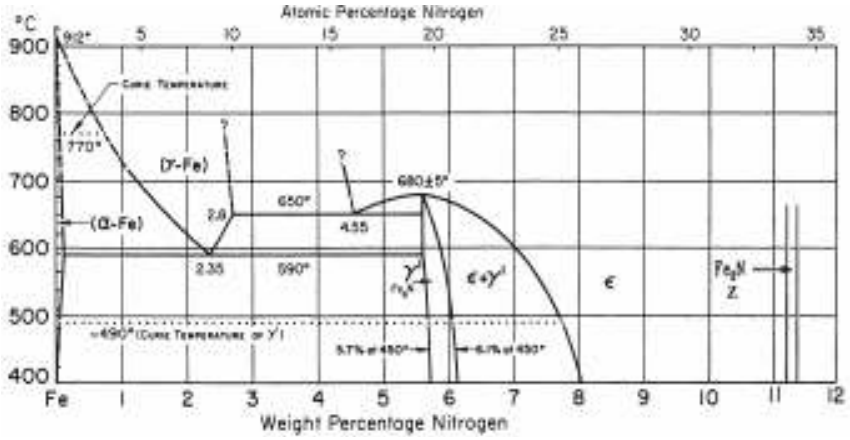



**Figure 2.3:** Iron – Nitrogen equilibrium phase diagram [9]

After the formation of this layer (compound) diffusion is controlled by diffusion of N through this layer.

Gas Nitriding involves a metal gas reaction between solid ferrite and an ammonia/hydrogen gas mixture. If local equilibrium between the gas phase and the surface of the metal prevails, the chemical potentials of nitrogen in the gas mixture and at the metal surface must be the same. Correspondingly, compositional changes and phase transformations may occur in the metal.

Nitrogen solubility at the surface of the iron is determined by equilibrium given in equ. 2.9.

$$NH_3 \Leftrightarrow H_2 + [N] \text{ (active nitrogen)} \quad \textbf{(2.9)}$$

hence (for dilute solution of N in Fe, Henry's law)

$$[a_N] \Leftrightarrow [\%N] = k.\ P_{NH_3} / P_{H_2}^{3/2} \quad \textbf{(3.0)}$$

where k is an equilibrium constant at a given temperature and $pNH_3$ and $pH_2$ are the partial pressure of $NH_3$ and $H_2$ in the gas mixture [10, 11].

Thus the nitriding rate dependence on partia pressure of ammonia and hydrogen is defined as nitriding potential ($K_N$) equ. 3.1.

$$K_N = P_{NH3} / P_{H2}^{3/2} \quad \textbf{(3.1)}$$

## 2.2 Structure of Nitride

The surface of the nitriding steel consists of two distinct layers. Outer part is called the compound layer (white layer) which is very hard, brittle and does not diffuse into the steel and remains on the immediate surface. Process variables that such as gas composition, duration and process temperature are the main parameters to control the depth (and structure) of the compound layer. Compound layer typically comprises two intermixed phases, gamma prime (γ') and epsilon (ε) ( $\gamma'$ $Fe_4N$ and/or ε $Fe_3N$). These two phases can be conceived as typical interstitial compounds with the Fe atoms arranged in a cubic close packed fashion (Figure 2.4 ). In both phases the octohedral interstitial sites are occupied with a nitrogen with long range.

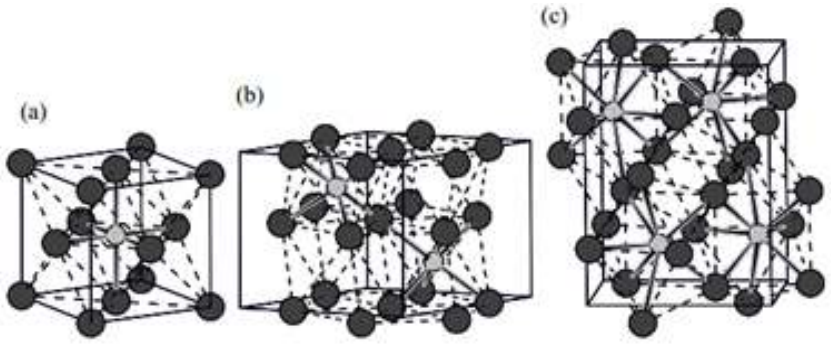



**Figure 2.4:** Crystal structure of (a)$Fe_4N_{3-y}$ ,(b)$Fe_3N_{1+x}$ γ', (c) $Fe_3C$ The darker spheres represent the iron atoms and the lighter spheres the nitrogen and carbon atoms.Fe-Fe bonds are indicated by dashed lines and.Fe-N, Fe C bond indicated by solid bold lines [12].

The inner section is called the diffusion layer. The diffusion layer enables a strong increase to the fatigue resistance and also increases the wear resistance.

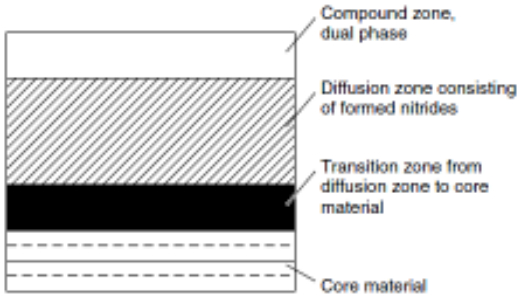



**Figure 2.5:**Schematics of nitriding case structure [10]

A typical nitrided structure formed on 42CrMo4 steel is given in Figure 2.6.

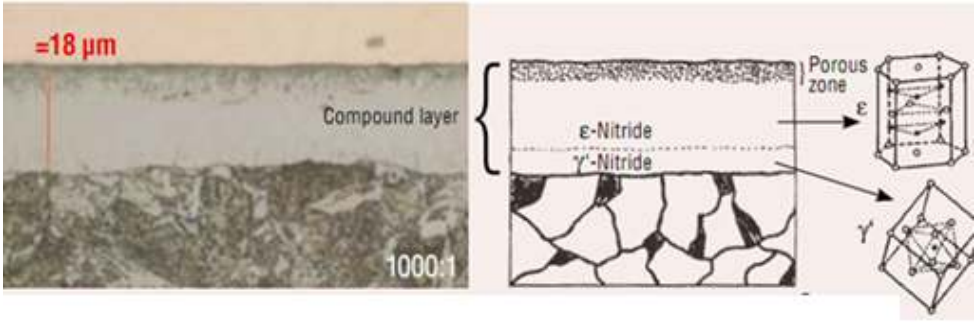



**Figure 2.6:** Compound layer structure of 42 CrMo4 after nitriding [13]

## 3. SURFACE CLEANING PROCESS BEFORE APPLICATION OF GAS NITRIDING

The cleaning is the process of removing undesired contaminations from a working piece. Cleaning technology is very important for nitriding. Residues such as oils, sulphur, silicon etc create unwanted surfaces for nitriding that create locally inhomogenous passivation on the sample surfaces [18]. According to the researches of Prof. Haase for Surtec Company, Surtec 042 and Surtec 101 cleaning chemicals were used to activate or passivate surfaces. 42CrMo4 and 34CrAlMo5 were used respectively as a test materials and samples were nitrided at 520 C at $K_N$ 10 nitriding potential. The hardness tests, diffusion layer and white(compound) layer thickness measurements were applied after nitriding. Reaction film between substrate surface and cleaning chemicals can affect the compound layer formation and surface hardness, which make the compound layer too thin and non-uniform. Thus the compound layer thickness will a parameter for determination of cleaning efficient (If the nitriding process does not lead to satisfactory results in terms of surface hardness, nitrogen depth profile, diffusion or compound layer thickness, etc., it means the overall reaction rate was too slow or the reactivity of the surface was low. This surface condition is termed as "passive" [22]. Result of trials claimed that Surtec 042 has activating effect on nitriding and on the contrary Surtec 101 has passivating effect. The passivation or activation were defined in this research as a 50-100 Hv differences on hardness or to prevention of compound layer formation [18,19, 20].

In literature it has been shown that surfactant cleaners which consist of anionic or non-ionic surfactants tend to decrease the rate of nitrogen diffusion [21]. If the cleaning agent residues are not removed by diligent rinsing, they can lead to passive layers. They are adsorbed on the steel surface in contact with the cleaning solution. Their negative effect of surface hardness after nitriding depends on their volatility; inorganic salts like silicates and phosphates have high melting points and do not vaporize at nitriding temperature [22].

**Table 3.1:** Literature summary of the effects of different surface cleaning chemicals on gas nitriding [16,17,18]

| Detergents | Composition | Sample | Preparation of sample before Nitriding | Nıtriding Parameter | Effect |
|---|---|---|---|---|---|
| **Surtec 042** | %10 w | 42CrMo4<br>25mm diameter<br>5mm thickness | cleaned with trichlorethyle | 520 °C for 4 h Kn:10. | Higher compound layer and higher hardness(activating) |
| **Surtec101** | 3 Vol%<br>10Vol% | 34CrAlMo5<br>25mm diameter<br>5mm thickness | The drying<br>at 80 °C for 30 min | 520 °C for 4 h (KN=10). | Lower compound layer(passivating) |
| **cleaning agent** | Sodiummetasilicate<br>non ionic surfactance: etyoxiated,<br>fatty alcol, and anionic surfactance<br>dodeycl benzene sulfotane<br>tripolyphosphate. | C15, 42Cr Mo4, 34Cr MoAl4 | samples were covered with agent solution(high above surface evaporated 80° C<br>=2mm<br>have %1-10 w | Nitriding in different temperatures (520 and 580 °C) with different duration (4 h-20h)<br>Nitriding potential Kn=0,7 | passivating |

### 3.1 Components and Functions of Cleaning Chemicals

During the mechanical treatment of the part, the material is covered by a deformed boundary layer. Outer side of the boundary layer is the reaction layer which consists of metal oxides and can also contain reaction products such as metals, metal sulfides or phosphorous compounds. During coating, such reaction layers are also formed on the surfaces which are thin but have excellent adhesion. This layer is named as a sorption layer. Compounds of the grease are bound by chemisorption or physisorption. This layer is composed of residues of the previous working steps, e.g. oil, grease, splinters, cleaner residues or water ingredients and have a thickness above 1µm (Figure 3.1).

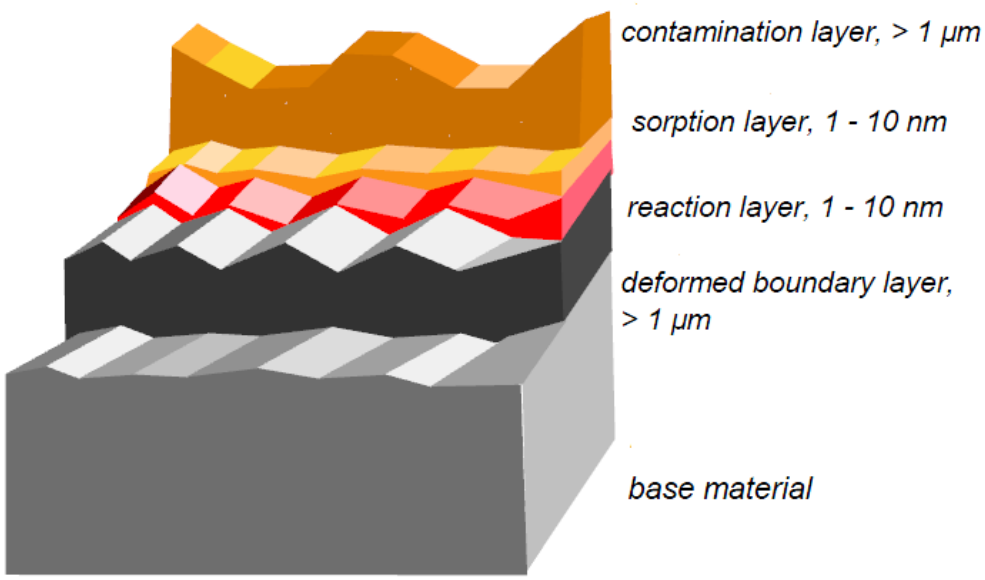



**Figure 3.1:** Surface layers on a working piece [7]

Surfactants reduce the surface tension between oil and water. The oil contracts and forms drops, which separate from the surface, are known as the roll-up effect. Impurities being trapped in the oil are removed together with the oil. Depending on the type of surfactant and on the type of impurity, the process can result in a complete emulsion or in a later demulsifying process [18].

### 3.2 Surfactants

Surfactants (a contraction of the term surface-active agent) are organic molecules with water – hating /oil loving end (hydrophobic) and water loving (hydrophilic) end [19].

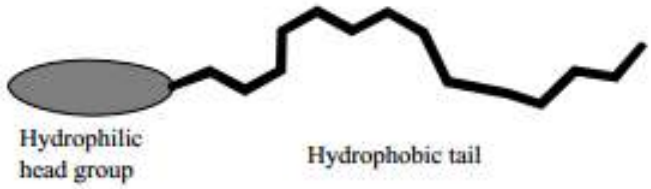



**Figure 3.2:**Schmatic illustration of a surfactance [19]

In a micelle, the surfactant hydrophobic group is directed towards the interior of the cluster and the polar head group is directed towards the solvent. The micelle, therefore, is a polar aggregate of high water solubility and without surface activity. When a surfactant adsorbs from aqueous solution at a hydrophobic surface, it normally orients its hydrophobic group towards the surface and exposes its polar group to the water. The surface has become hydrophilic and as a result, the interfacial tension between the surface and water has been reduced [20].
Surfactants are typically classified as anionic, nonionic, and cationic. The class of surfactant determines the class of the cleaner.

#### 3.2.1.1 Anionic surfactants

Anionic surfactants that has a negatively charged end of the molecule that gives it the hydrophilic part for the molecule. Sulfonates, sulfates, or carboxylates are negatively charged parts of the molecules that are usually neutralized by positively charged metal cat ions such as sodium or potassium. Examples include sodium alkyl benzene sulfonates, sodium stearate (a soap), and potassium alcohol sulfates. Anionic surfactants are ionic and they are made up of two ions—a positively charged, usually metal, ion and a negatively charged organic ion [22].

#### 3.2.1.2 Non ionic surfactant

The Non-ionic surfactants have no ions; their polarity comes from having an oxygen-rich portion of the molecule at one end and a large organic molecule at the other. The oxygen sources are usually derived from short polymers of ethylene oxide or propylene oxide. Just as in water chemistry, the oxygen is a dense electron-rich atom that gives the entire molecule a partial net-negative charge, which makes the whole molecule polar and able to participate in hydrogen bonding with water. Examples of nonionic surfactants are alcohol ethoxylates, nonylphenoxy polyethylenoxy alcohols, and ethylene oxide/propylene oxide block copolymers [21, 22].

#### 3.2.1.3 Cationic surfactants

Cationic surfactants have positively charged molecules usually derived from nitrogen compounds. They are not commonly used as cleaning agents in hard-surface cleaners because of the tendency of the cationic positively charged molecule to be attracted to hard surfaces. Many cationic surfactants have bacteriacidal or other sanitizing properties that are useful in creating disinfectants leaving a cationic disinfectant film on the surface [21, 22].

Classification of cleaning chemicals in RBTR as given in Table 3.2.

**Table 3.2:** Classification of cleaning chemicals in RBTR

| Cleaning Chemistry | Type of Surfactants | Based | Application Area | Purpose of Cleaning |
|---|---|---|---|---|
| A | Non-ionic | Amines , Carboxylic acid | Organic Corrosion Protection | Particle and oil removal |
| B | Cationic | Amines, Carboxylic acid, 2 amino ethanol, Citrate-(MEA)3 | Organic Corrosion Inhibitor | Oil removal after grinding, Cleaning before phosphate |
| C | Non-ionic | Aminoethanol, Etanolamin, Gluconic Acid, Neutrolize amine | protection | Oil and burr removal before phosphate |
| D | Non-ionic + Cationic | Ethoxylate BU ether, Coco amine ethoxylate, Nitrilotriethanol | Corrosion protection | Cleaning |
| SURTEC 101 | Cationic + Non-ionic | Amines | Corrosion protection | Cleaning |
| SURTEC 042 | Anionic + Non-ionic | Amines Neutralized organic acids | Corrosion protection | Cleaning |

## 4. METHODS OF PREVENTING GAS NITRIDING

There are several industrial techniques for preventing gas nitriding:

- Stop off Mask
- Electroplating
    - Nickel electroplating
    - Copper electroplating

### 4.1 Stop off Masks

Stop off mask is the most prefered method to prevent nitriding. This type of coating can be applied by dipping, spraying, brushing, silk screening, roll coating or extrusion. Stop off masks are generally based on a mixture of refractory materials or low thermal expantion oxide such as zirconium and aluminosilicate, sodium silicofluoride and sodium silicate,titanium oxide mixed with a binding chemical in different compositions (Table 4.1) [15, 16, 17].
Particles which occur during removal of the stop off coatings and non homogenous application are the disadvantages of this method.

**Table 4.1:** Properties and application methods of different Stop Off masks

| Composition | Ratio | Temperature | Time (min.) | Application | To remove |
|---|---|---|---|---|---|
| $ZrSiO_4$, $Al_2O_3$:$SiO_2$<br>Modifier i.e. sodium silicofluoride or ($Na_2SiF_6$)+ sodium silicate binder<br>Refractory oxide | $SiO_2$: $NaO_2$ <=2:1 | 25°C. | 30-60 | Brushing<br>Dipping | Quenched water and salth bath |
| Kaolin, alumina, silica sand, olivine, magnesite<br>clay materials of the aluminium or magnesium silicate type | 59,3 %W kaolinite 2,3 % w sodium silicate %38,4 by weight of water | 25°C. | | Brushing | |
| Alumina, Titania, and magnesia | solid material: fugitive carrier = 15: 85 | 25°C. | | Brushing | |

### 4.2 Electroplating Processes Used for Prevention of Gas Nitriding

Electroplating is a coating process through which metal ions in a solution are moved by an electric field to coat an electrode. The process uses electrical current to reduce cations of a desired material from a solution and coat a conductive object with a thin layer of the material, such as a metal. Electroplating is primarily used for depositing a layer of material to obtain a desired property [23].

Electroplating is one of the methods for preventing gas nitriding, deposits of bronze or copper and nickel are the most common stop off coatings. Thickness and density of plated coating are important in determining their effectiveness as passive layer. Minimum thickness of bronze or copper and nickel plate should be more than 1μm [24].

#### 4.2.1 Nickel electroplating

Nickel plating is similar to other electroplating processes uses soluble metal anodes. It requires a passage of direct current between two electrodes that are immersed in a conductive, aqueous solution of nickel salts. The flow of direct current causes one of the electrodes (the anode) to dissolve and the other electrode (the cathode) to become covered with nickel. The nickel in solution is present in the form of divalent positively charged ions ($Ni^{+}$). When current flows, the positive ions react with two electrons ($2e^{-}$) and are converted to metallic nickel ($Ni^{0}$) at the cathode surface

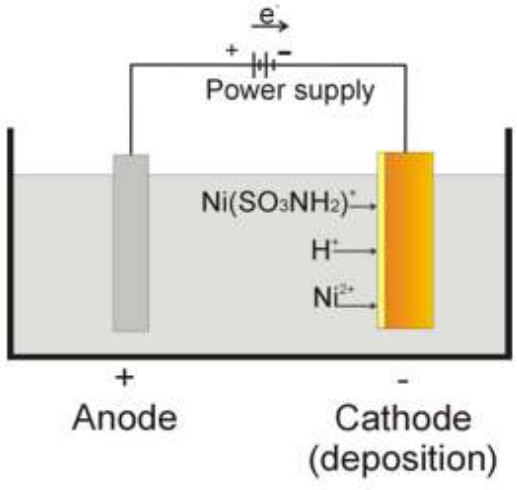



**Figure 4.1:** Schematic of the electrochemical plating of Ni [26]

The reverse occurs at the anode where metallic nickel is dissolved to form divalent positively charged ions which enter the solution. The nickel ions discharged at the cathode are replenished by those formed at the anode (Figure 4.1.) [23, 25].

#### 4.2.1.1 Types of nickel electroplating baths

**Watts type nickel electroplating bath**

Nickel Watts Bath uses most nickel plating processes such as engineering applications and electroforming. It is operated at elevated temperatures and is capable of being used with high current densities. The main components of this baths are:

- **Nickel sulfate**: The major source of the nickel ions in solution
- **Nickel chloride**: serves primarily to improve anode corrosion. Excessive amounts of chloride increase the corrosivity of the solution and the internal stress of the deposits
- **Boric acid:** Buffering agent
- **Wetting agents or surfactants**: control pitting; their function is to lower the surface tension of the plating solution so that air and hydrogen bubbles do not cling to the parts being plated [25, 27, 28].

**Bright type nickel electroplating baths**

Bright nickel plating solutions have nearly same formulation of the Watts formulation, but contain organic and other additives that act to produce a fully bright finish. Portions of the addition agent molecules may be incorporated into the deposit, resulting in a hard, fine-grained coating that contains incorporated sulfur. The sulfur causes the deposit to be electrochemically more reactive than sulfur-free matte, polished or semi-bright nickel deposits. Decomposition products of the additives accumulate in solution with time and are removed by purification with activated carbon [25, 27]

**Fluoborate type nickel ectroplating bath**

The fluoborate solution can be operated over a wide range of nickel concentrations, temperature, and current density. The fluoborate anion is aggressive and some materials that contact the solution are chemically attacked. The mechanical and

physical properties of deposits produced by the fluoborate bath are similar to those from Watts solutions. The nickel fluoborate solution has been used primarily for high-speed deposition of thick nickel [25, 27].

**Sulfamate type nickel electroplating bath**

Nickel sulfamate solutions are generally used for electroforming because of the low internal stress of the deposits, high rates of deposition, and superior throwing power. Throwing power is the relationship between current distribution and uniformity of coating thickness as influenced by geometric factors, and by the electrochemical characteristics of the solution (conductivity, cathode polarization and cathode efficiency). Throwing power is a measure of the extent to which a solution will produce deposits that are more uniform than those that would be produced in the absence of cathode polarization and cathode efficiency effects. Because of the very high solubility of nickel sulfamate, a higher nickel metal concentration is possible than in other nickel electrolytes, permitting to use lower operating temperatures and higher plating rates [23, 24].

High quality nickel deposits can be produced within the ranges of solution pH, temperature and current density given in Table 4.2.

**Table 4.2 :** Chemical composition and operating conditions of nickel electroplating solution

| **Baths Type/ Electrolyte Composition (g/L)** | **Watts Nickel** | **Nickel Sulfamate** | **Bright Nickel** | **Fluoborate Nickel** |
|---|---|---|---|---|
| **Nickel Sulfate ($NiSO_4.6H_2O$)** | 225-400 | | | |
| **Nickel Sulfamate $(NiSO_3NH_2)_2$** | | 300-450 | | |
| **Nickel Chloride ($NiCl_26H_2O$)** | 30-60 | 0-30 | 35 | 0-15 |
| **Nickel Fluoborate** | | | | 225-300 |
| **Boric Acid ($H_3BO_3$)** | 30-45 | 30-45 | 45 | 15-30 |

| Baths Type/ OperatingCondition | Watts Nickel | Nickel Sulfamate | Bright Nickel | Fluoborate Nickel |
|---|---|---|---|---|
| **Temperature ( °C )** | 44-66 | 32-60 | 54 | 38-70 |
| **Cathode current Density ( A/dm$^2$ )** | 3-11 | 0,5-30 | 3-10 | |
| **pH** | 2-4.5 | 3,5-5,0 | 3,5-4,5 | 2,5-4 |

Comparison of Nickel electroplating baths is given in Table 4.3.

**Table 4.3:** Comparison of different nickel electroplating process

| Baths Type | Easy-basic Application | Cheap | Good mechanic properties | Good mechanic properties | Demage Substrate |
|---|---|---|---|---|---|
| WATTS | OK | OK | OK | OK | NO |
| SULFAMATE | OK | NO | OK | OK | NO |
| FLOUBORATE | NO | NO | | | |

According to Table 4.3. Watts and sulfamate nickel baths will be effective because of easy and basic application. This baths are also have cost effective and good mechanical properties and do not damage the substrate.

#### 4.2.1.2 Interaction between nickel and ammonia

It is well known that nickel is a good for ammonia dissociation [29]. During termochemical surface treatments such as nitriding, steel is exposed to carbon and nitrogen carrying gas at an elevated temperature for a period of time, where by the gas decomposes and carbon or nitrogen diffuse through the steel surface [30]. The coating of nickel below 200 nm shows catalytic effect and nitrogen atoms diffuse through the steel surface at as faster rate [31].

Coating thickness is a very important parameter for nickel coatings, below µm ranges Ni coating shows good catalytic properties. Because of these properties nitrogen can diffuse through the metal surface and causes case hardening, but above µm ranges coating create good barrier for nitriding mechanism.

### 4.2.2 Copper electroplating

Copper electroplating is most prefered method of coating copper on metal substrate. Positively charged copper ion moves towards the negative cathode and when it reaches the cathode surface, it accepts two electrons,converts to the copper atom and deposits on the cathodes surface as represented at Figure 4.2.

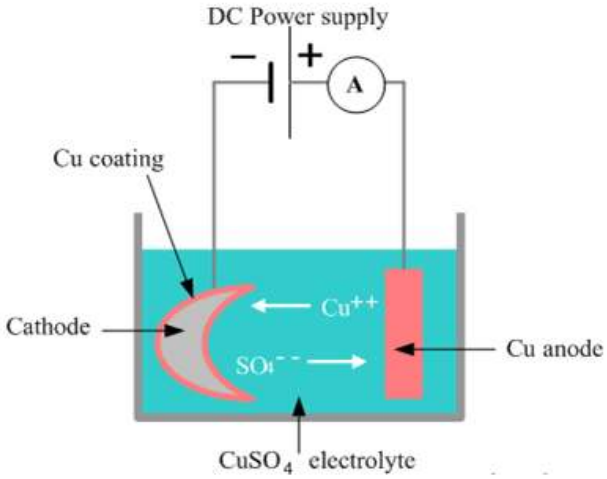



**Figure 4.2:** Schematic illustration of copper electroplating process [39]

#### 4.2.2.1 Types of copper electroplating baths

Three basic types of copper electroplating processes are commercially available. They are alkaline (several modifications of cyanide and non-cyanide); acid (sulfate and fluoborate); and mildly alkaline (pyro phosphate) complexed baths [39].

**Simple cyanide copper bath**

Cyanide solutions provide a medium for direct deposition of copper on base metals, particularly steel and zinc. Simple Cyanide copper bath electroplating is applied to steel as a "passive" coating in case of hardening process such as carburising and nitriding.

Cyanide copper platings which have low initial cost and operational economy are suitable for batch and barrel coating. This bath is restricted to strike and thin

deposits. Usually 1 to 3 microns are deposited. The bath composition is little difficult to control at room temperature due to its low cathode efficiency [40].

**Acidic copper bath**

Electrodeposition of copper from acidic solution is extensively used for electroforming, electrorefining, and electroplating.

The copper (II) ($Cu2^{+}$) salts in either the sulfate on the flouborate bath are highly ionized except for small amounts of less ionized complex salts formed with certain addition agents. The chemical cost of acid copper baths is low and they can have a wide range in composition. [39, 40].

**Copper pyrosphate bath**

Copper Pyroposphate is used for plating on plastics and printed circuits, requires more control. However, copper pyrophosphate solutions are relatively nontoxic when compones to cyanides [40]. Table 4.4 given the comparison of mechanical properties of different copper coating baths

**Table 4.4:** Comparison of copper electroplating properties

| Type of Copper Coating | Finish Appearance | Ductility |
|---|---|---|
| Copper Alkaline | Good | Good |
| Copper<br>Acid Sulfate or Fluoborate | Good appearance<br>Excellent leveling | Good to excellent |
| Copper<br>Pyrophosphate | Good Fine grained and<br>semi- bright | good |

**4.2.2.2 Interaction between ammonia and copper**

The soft annealing of copper can easily be carried out by using nitrogen when a small amount of hydrogen added. Usually 2 to 4 percent by volume of $H_2$ is sufficient to convert the atmospheric oxygen which enters the furnace into water, i.e. before copper oxide forms. It is important to ensure that when cooling the charge to below

350 °C, the metal is not oxidised by atmospheric oxygen [43]. Copper does not have a effect on catalytic decomposition of ammonia

## 5. POSSIBLE METHOD TO PREVENT GAS NITRIDING (SOL-GEL)

Sol-Gel techniques are currently used in corossion protection and glass, ceramic industry [32].

Sol-Gel is described as the formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid.

Sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. A gel consists of a three dimensional continuous network, which encloses a liquid phase. In a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel the particles have a polymeric sub-structure made by aggregates of sub-colloidal particles. Generally, the sol particles may interact by Van der Waals forces or hydrogen bonds. A gel may also be formed from linking polymer chains. In most gel systems used for materials synthesis, the interactions are of a covalent nature and the gel process is irreversible.

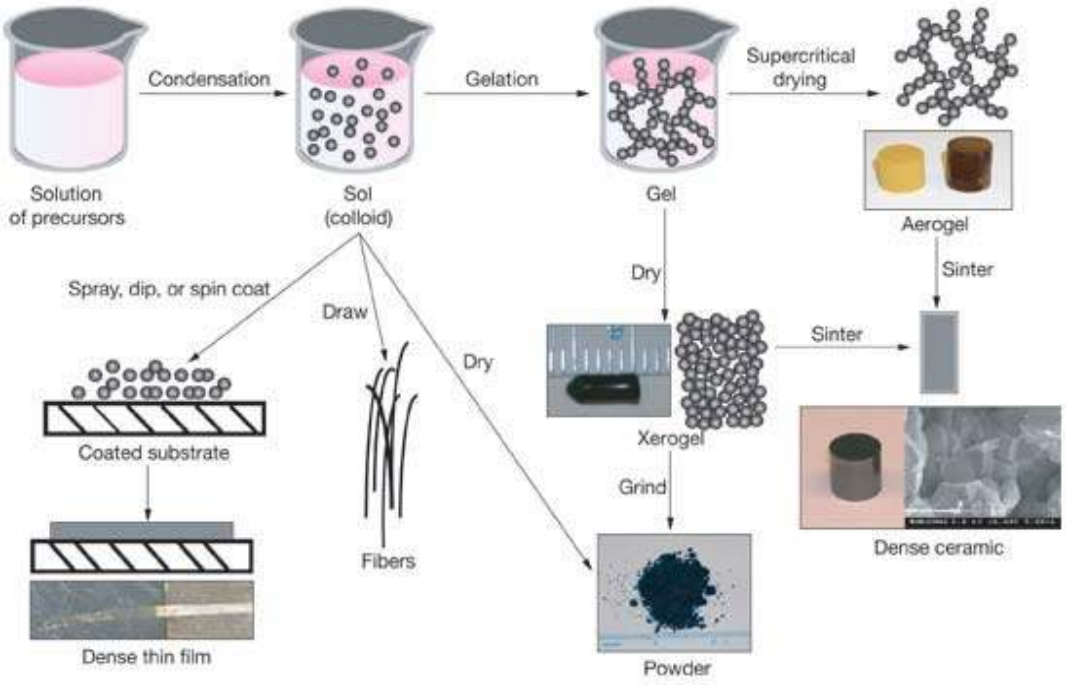



**Figure 5.1:** Steps of Sol-Gel proces [34]

The gelation process may be reversible if other interactions are involved. Sol-Gel synthesis may be used to prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films (Figure 5.1) [33, 34].

Sol-Gel involves the formation of metal oxo polymer network from moleculer precusors such as metal alkoxides or metalsalts. For example, the metal alkoxides may behydrolyzed to form a metal alkoxide gel as follows equation 3.1:

$$M\text{-}OR + H_2O \rightarrow M\text{-}OH + ROH \quad \textbf{(3.1)}$$

$$M\text{-}OR + M\text{-}OR \rightarrow M\text{-}O\text{-}M + ROH \quad \textbf{(3.2)}$$

$$M\text{-}OH + M\text{-}OH \rightarrow M\text{-}O\text{-}M + H_2O \quad \textbf{(3.3)}$$

**M** = Metal and **R** = Alykyl group.

Metal oxide formations strongly affect on the relative rates of hydrolysis and polycondensation. In addition to relative rates, the Sol-Gel process is affected by the reactivity of metal alkoxides, pH of medium, water: alkoxide ratio, reaction temperature, and nature of solvent and additive. By varying these processing parameters, materials with different microstructure and surface chemistry can be obtained.

Typically, Sol-Gel derived precipitates are amorphous in nature, requiring further heat treatment to induce crystallization. The calcination process frequently gives agglomeration and grain growth and may induce phase transformation [34].

Sol-Gel method can be a possible method for preventing gas nitriding, there are a few application of $Zr0_2$ based Sol-Gel coating as catalyzer on gas nitriding [35]. In spite of no research about Sol-Gel for preventing nitriding, Sol-Gel will possess good potential for prevent nitriding, because of easy application, low temperature requirement and possibility to mix a lot of elements such as $TiO_2$ which are also used in stop off masking.

### 5.1 General Applications of Sol-Gel Coatings

Dip coating and spin coating are two methods generally used for Sol-Gel application [36]. In dip coating method, the substrate is normally withdrawn as a vertical speed of $U_0$ from the liquid bath which is represented Figure 5.2. The moving substrate

entertails the liquid mechanically and splits the boundary layer in two parts, above the liquid bath surface, the outer layer returning to the bath, since the solvent is evaporating and draining the fluid film that terminates at a well defined drying line (x=0). At the receding drying line velocity ($U_{0)}$, the process is steady state with the liquid bath surface. The geometry and evaporation rate affect the thickness profile of coating [37].

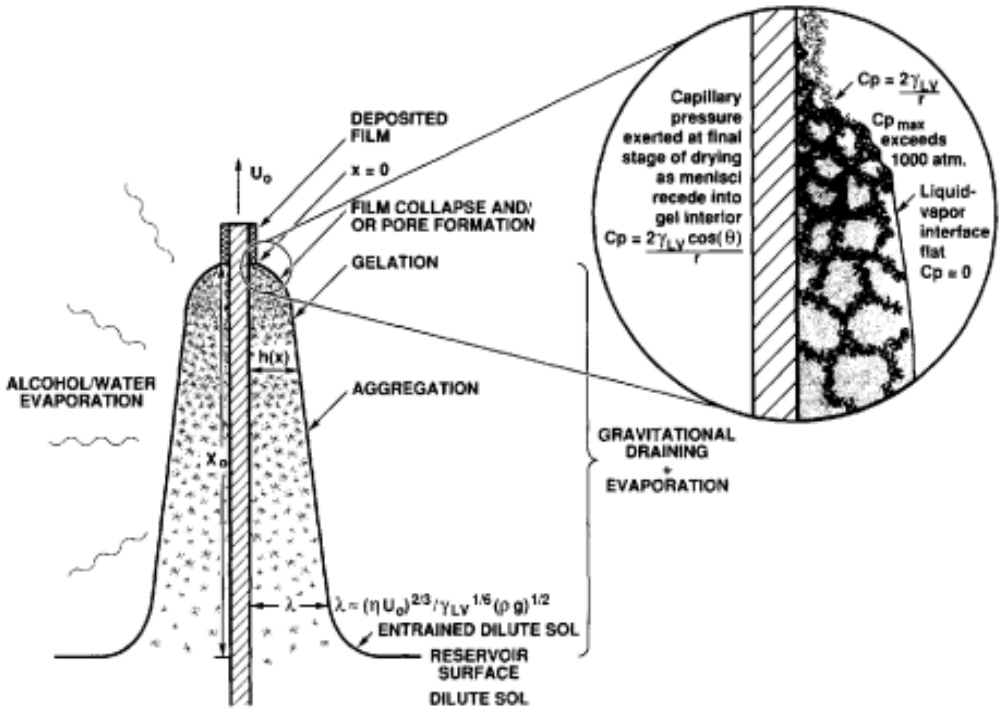



**Figure 5.2:** Sol-Gel dip coating process [37]

## 5.2 Sol-Gel $TiO_2$ Coating

$TiO_2$ and $SiO_2$ Sol-Gel coatings are generally utilized on glass substrate for photocataliytic effect and for corrosion protection. However $TiO_2$ Sol-Gel coatings are widespread use for corrosion protection [37].

# 6. EXPERIMENTAL STUDIES

## 6.1 Nitriding Atmosphere

In all of the experiments, for the ease of evaluation gas nitriding conditions in which a thick layer of compound layer are expected to occur are selected. In order to obtain high compound layer thickness, $K_N$ (nitriding potential) value must be higher. To ensure a thick compound layer in all experimental trials, all samples were nitrided at $K_N$ 2 nitriding potential at 520 ºC for 10 hours. The nitriding experiments were conducted in an industrial gas nitriding furnace (IPSEN,VDR-Type).
Gas nitriding process has three main steps: 1.Heating, 2.Gas Nitriding and 3.Cooling. An example of the process flow is given in Figure 6.1.

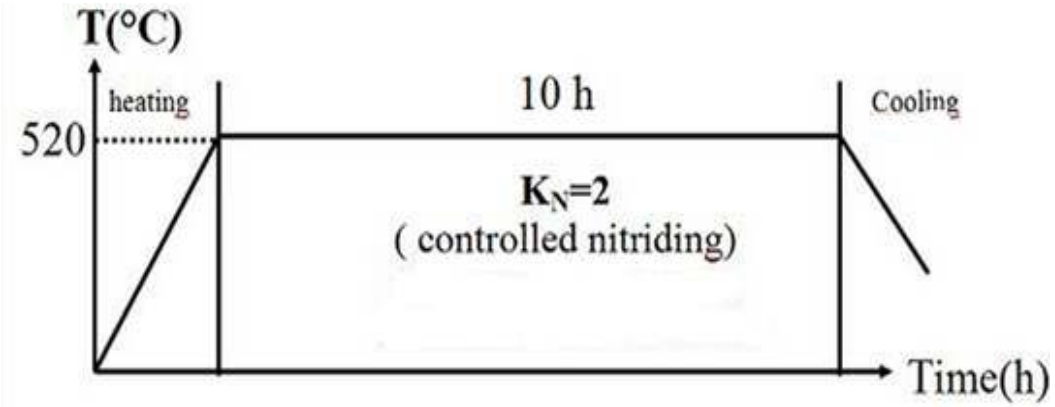



**Figure 6.1:** Description of the gas nitriding parameters used in the study

To keep the process under control, the partial pressure of hydrogen was measured by the sensors located in the furnace

## 6.2 Experiments on Surface Cleaning Process Before Application of Nitriding

Cleaning is a very important process before heat treatment processes, since residual films from cleaning chemicals and also ineffective cleaning create local passivation.
The aim of these group of trials were to observe effect of detergents on nitriding processes.

**Experimental flow of Cleaning Chemicals Trial**

The test material was $50CrMo_4$ and all tested samples were round shaped with a diameter of 30 mm and highest of 10 mm. Samples were cleaned ultrasonically for 10 minute at 65ºC with different cleaning chemicals and then dried at 150 ºC in a drying oven for 10 minutes and finally nitrided. 9 samples were used for each type of cleaning chemicals to have enough sttastical data. The cleaning chemicals used in these study are given in Table 6.1. After nitriding, samples were cut and embedded into bakalite (Struers Cito Press). Samples in the bakalite were polished with 1µm diamond paste. Hardness were measured by Struers Duramin 3300 microhardness machine with a 500 g load at 50µm distance of surface. For investigation of diffusion and compound layer, samples were etched Nital (%3) solution to see compound layer formation and (1/3) Adler (60 g Ferric chloride hexahydrate, 12 g Copper ammonia chloride, 100ml water, 200ml HCl) to see diffusion layer formation. Diffusion layer and compound layer thickness measurements were also investigated via light microscopy (Leica DM4000M) to analyse passivation effect.

A, B, C, D represented some special cleaning chemicals used in RBTR, because of secrecy of RBTR the name of the chemicals are not given.

**Table 6.1:** Cleaning chemicals and consentration used in study.

| Cleaning Chemicals | Concentration (%) |
|---|---|
| A | 5 |
| B | 5 |
| C | 3 |
| D | 5 |
| Surtec 101 | 2-10 |
| Surtec 042 | 3-10 |

## 6.3 Experiments on Methods to Prevent Gas Nitriding

### 6.3.1 Experiments on stop off masks

Stop off masks, currently used in the industry, are generally based on the mixture of

refractory oxides and binder chemicals. Two different stop offs were applied with the same thickness on 50CrMo4 sheets in order to compre which one is more effective on gas nitriding process.

**Experimental flow of stop off masks**

Samples were cleaned with alcohol before application of stop off on the surface. Two different stop off chemicals Luiso W 21 and 25 (DAM, Hartetechnic) diluted with water in different concentration were applied to the samples by dipping machine (speed 2 mm/sec), then samples were dried 30 min in room temperature and after drying, nitriding was performed at $K_N$ 2 nitriding potential 520 ºC, 10 hours.

Hardness measurements of stop off masks applied samples were measured from their cross section taking the hardness value at 50 µm depth as reference. Presence of the compound and diffusion layers were also investigated with light (optical) microscope.

### 6.3.2 Experiments of electroplating

Prior to electroplating the steel substrats was mechanically polished with different grades of magnetic papers (Allegro- 9µm, Doc-3µm,chem- 0,04 µm). After that it was ultrasonically cleaned in acetone for 10 min, cleaning in 10 vol% $H_2SO_4$ and 5 vol% $H_2SO_4$ for 30 seconds, then treated cathodically in a solution consisting of NaOH, $Na_2SO_4$ and $Na_2CO_3$ for 20 min at 10 mA/cm$^2$ current density and between all these steps sample was rinsed by immersion in distilled water.

Electroplated samples were then nitrided at $K_N$ 2 nitriding potential at 520 ºC for 10 hours. Nickel and copper coatings were not removed from the steel surface after nitriding.

#### 6.3.2.1 Experimental flow of nickel electroplating

$50CrMo_4$ sample with size of 10x5x60 mm were electroplated in a Watts type nickel electroplating bath (Table 6.2) and for a period of 60-30-20-10-5-2-1 and 0.5 minute. To analyse the passivation effect of sample, compound layer, diffusion layer thickness measurements and hardness measurements at 50 µm were realised. XRD analysis of coated samples was also conducted after gas nitriding .

**Table 6.2**:Watts bath composition

| Chemical | Const.(g/lt) |
|---|---|
| $NiSO_4.6H_2O$ | 400 |
| $NiCl_2.6H_2O$ | 55 |
| $H_3BO_3$ | 30 |

### 6.3.2.2 Experimental flow of copper electroplating

$50CrMo_4$ sample with size of 10x5x60 mm were electroplated in a acidic sulphate type copper electroplating bath (Table 6.3)and for a period of 60-30-20-10-5-3-1 and 0.5 minute. To analyse the passivation effect of sample,similar analysis were done

**Table 6.3:** Coating bath formulation of copper coating

| Chemical | Const.(g/lt) |
|---|---|
| Copper sulfate | 60-90 |
| Sulfuric acid | 150-225 |
| Chloride ion (ppm) | 30-80 |

## 6.4 Experiments on Sol-Gel $TiO_2$ coating

In this project Sol-Gel dip coating method was used. Using EAcAc as a chelating agent, the $TiO_2$ Sol was prepared from tetra-n-butyl titanate ($Ti(O\text{-}n\text{-}Bu)_4$) in the following process:

1) 20 ml ethanol and 1 ml EAcAc without further dehidration were mixed.
2) 2 ml ($Ti(O\text{-}n\text{-}Bu)_4$) were added to the solution and continuously stirred for 1h.
3) 0,2 ml distilled water added to the solution and stirred for 10 hours.
4) The solution was aged for 24 hours.

**Experimental flow of Sol-Gel coating**

The steel substrate was mechanically polished with different grades of magnetic papers (Allegro-9µm, Dac-3µm, chem-0,04µm). Then ultrasonically cleaned in acetone for 10 min and after that for 10 minute in alcohol. Metal substrate were subjected to coating by using parameters given in Table 6.4. All samples were immersed in the sol solution for 5 minutes and withdrawn with a speed of 0,5-1 mm/s. After drying naturally, the samples were heated in oven at 150 ºC for 30 min. Coating operation was repeated five or six times to increase the coating thickness. Then the samples were heat treated at 450 ºC for 30 min to enable oxide conservation.

**Table 6.4:** Parameters of Sol-Gel coating used in the study

| Sample | pH | Coating speed (mm/s) | Drying Temp.(ºC) | Coating Step | Phase transformation Temperature (ºC) |
|---|---|---|---|---|---|
| Sol_1 | 8 | 0.8 | 150 | 5 | 450 |
| Sol_2 | 8 | 0.5 | 150 | 6 | 450 |
| Sol_3 | 8 | 0.8 | 150 | 5 | 450 |
| Sol_4 | 8 | 0.5 | 150 | 6 | 450 |

The $TiO_2$ coated surfaces was analysed by XRD and micro Raman analysis to determine the phases on the coating after the heat treatment. Then hardness measurements and diffusion layer thickness measurement were conducted the passivation effect of Sol-Gel coatings.

# 7. RESULTS

## 7.1 Effects of Cleaning Process on Nitriding

The hardness, compound layer thickness of the samples subjected to gas nitriding under identical nitriding conditions was measured. For the evaluation, the compound and diffusion layer microstructure analysis the cross sections of the samples are given in Figure7.1.

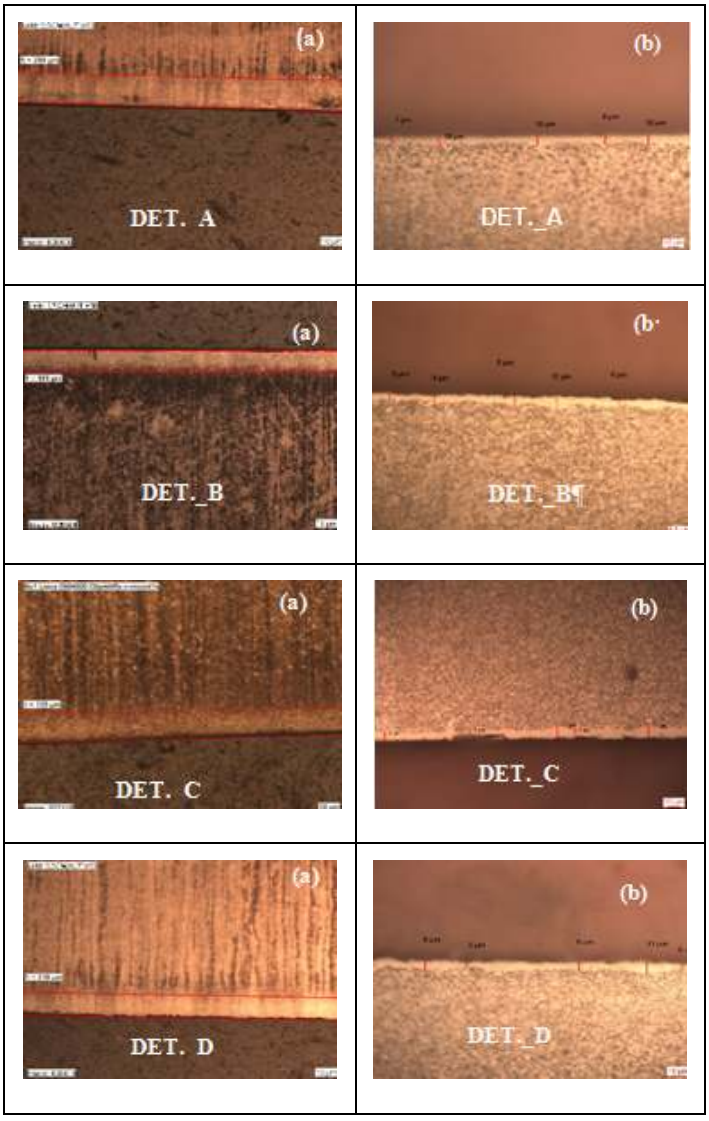



**Figure.7.1: a)** Diffusion layer (etched with Adler) (X50) **b)** Thickness of the compound layer (etched with Nital) (X500)

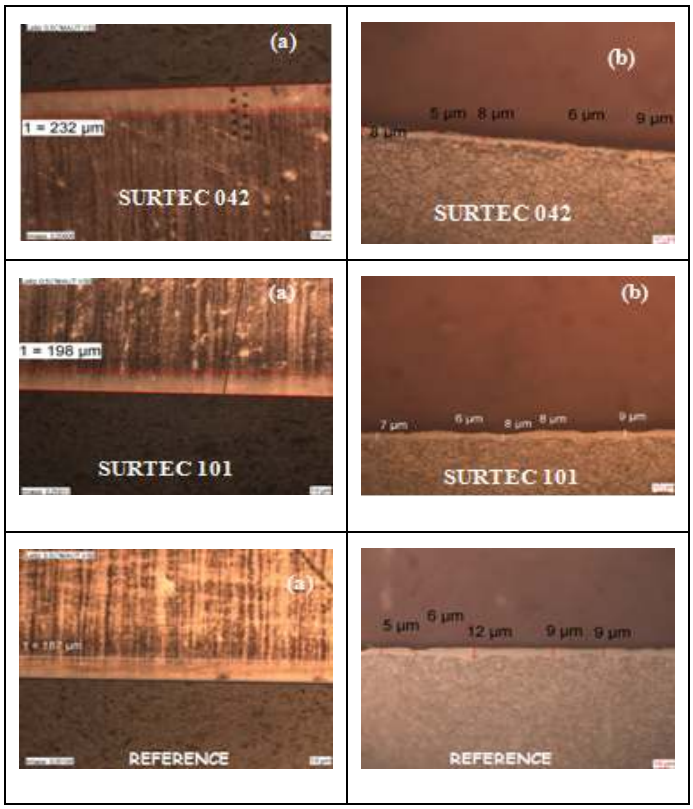



**Figure.7.1.(Continued):** a) Diffusion layer (etched with Adler) (X50) b)Thickness of the compound layer (etched with Nital) (X500)

According to micrographs in Figure 7.1 no appreciable differences on average compound layer thickness, except for Surtec 042 chemicals were observed. Moreover, the most homogenous compound layer thickness distribution was also present on samples treated with Surtec 042.

Result of analysis of hardness and compound- diffusion layer thickness summarized Table A.1.

Result of the analysis evaluated that hardness at 50 µm did not show significant differences for samples cleaned with different cleaning chemicals.

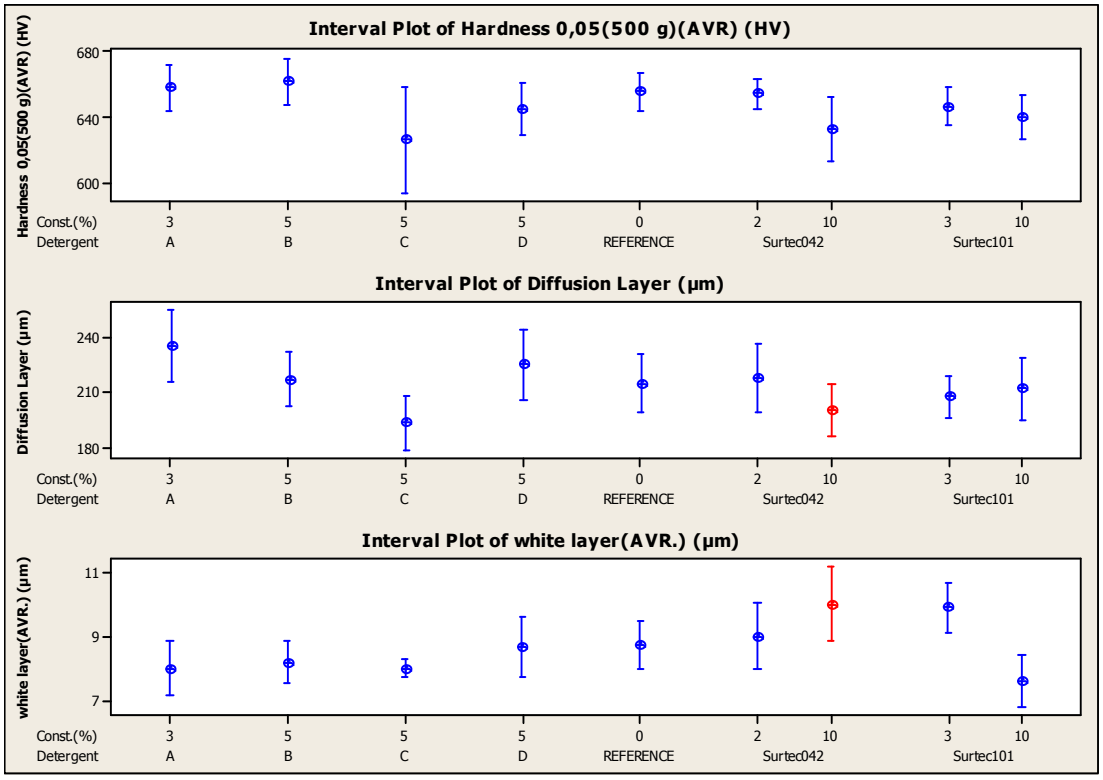



**Figure 7.2:** Result of hardness–diffusion and compound layer measurements of cleaning chemicals in RBTR.

Among all cleaning agents because of high compound layer thickness, Surtec 042 is a better cleaning chemical to clean surfaces, Surtec 042 is more effective for cleaning as referred in the literature [18].

## 7.2 Methods of Passive Layers to Prevent Gas Nitriding

### 7.2.1 Result of stop off masks experiments

Both stop off maskings used in the study were very effective in prevention nitriding. Analysis given in Figure 7.5 and Table 7.2 shows that no compound layer and diffusion layer formation occured after nitriding.

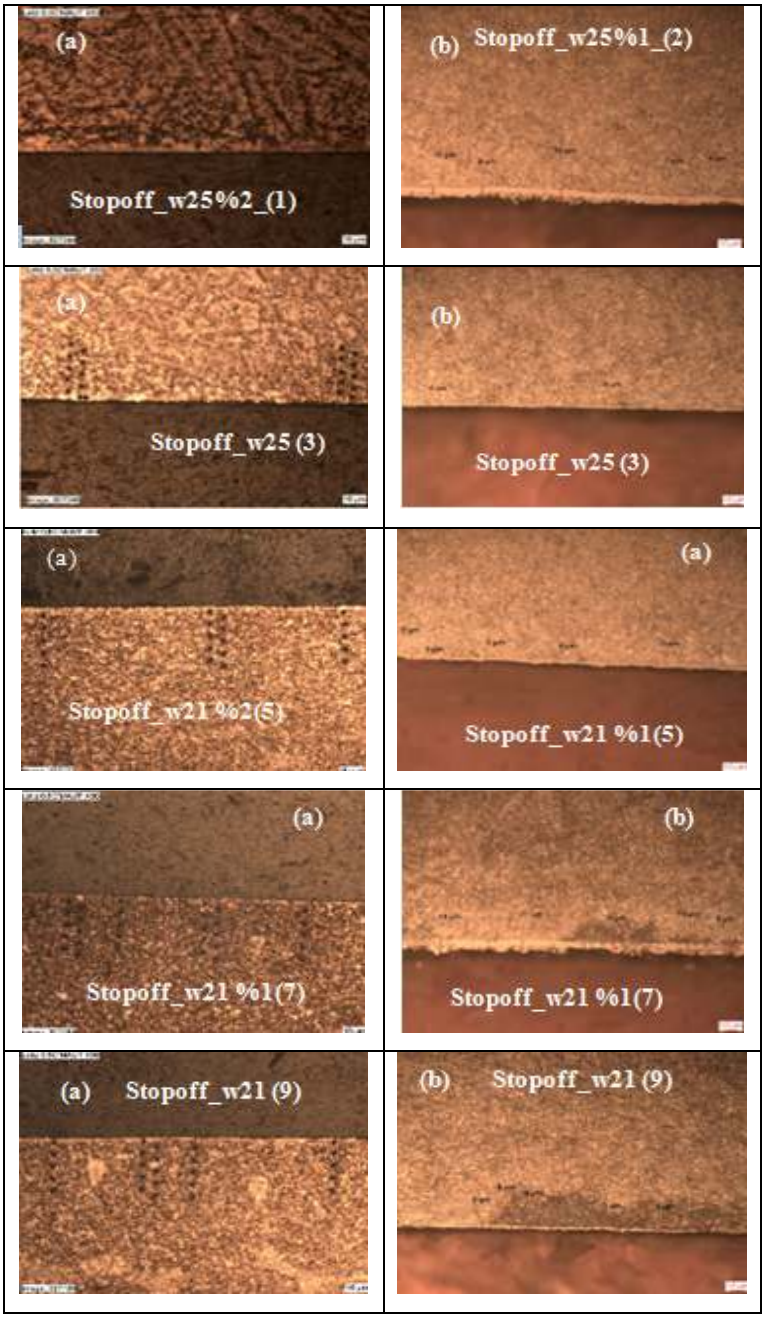



**Figure.7.3:a)** Diffusion layer (etched with Adler) (X50) **b)** Thickness of the compound layer(etched with Nital) (X500)

Nitriding Hardness at 50 µm distance on the cross section surface compound , and diffusion layer thickness were measured as shown in Table 7.2.

**Table 7.2:** Results of hardness, diffusion and compound layer measurements of Stop off masking:

| Sample Number | Chemical | Const (%water) | Hardness After Nitriding(avr.) (0,05µM-500g) | Diffusion layer thickness(µm) |
|---|---|---|---|---|
| ST_1 | w25 | 2% | 347 | 0 |
| ST_2 | w25 | 2% | 356 | 0 |
| ST_3 | w25 | 2% | 364 | 0 |
| ST_4 | w25 | 1% | 364 | 0 |
| ST_5 | w25 | 1% | 356 | 0 |
| ST_6 | w25 | 1% | 370 | 0 |
| ST_7 | w21 | 2% | 356 | 0 |
| ST_8 | w21 | 2% | 344 | 0 |
| ST_9 | w21 | 2% | 361 | 0 |
| ST_10 | w21 | 1% | 357 | 0 |
| ST_11 | w21 | 1% | 362 | 0 |
| ST_12 | w21 | 1% | 381 | 0 |
| ST_13 | w25 | 0% | 355 | 0 |
| ST_14 | w25 | 0% | 360 | 0 |
| ST_15 | w25 | 0% | 355 | 0 |
| ST_16 | w21 | 0% | 352 | 0 |
| ST_17 | w21 | 0% | 345 | 0 |
| ST_18 | w21 | 0% | 345 | 0 |
| R_1 | Reference | | 630 | 230 |
| R_2 | Reference | | 655 | 242 |
| R_3 | Reference | | 639 | 193 |

According to the Table 7.2, there was a passive stop off mask layer which prevents nitriding. Hardness of the sample was approximately the same of core hardness of 50CrMo4 (370 Vickers). And there are no significant differences on samples applied two different stop offs. Analysis were interpreted statistically which presented in Figure 7.4.

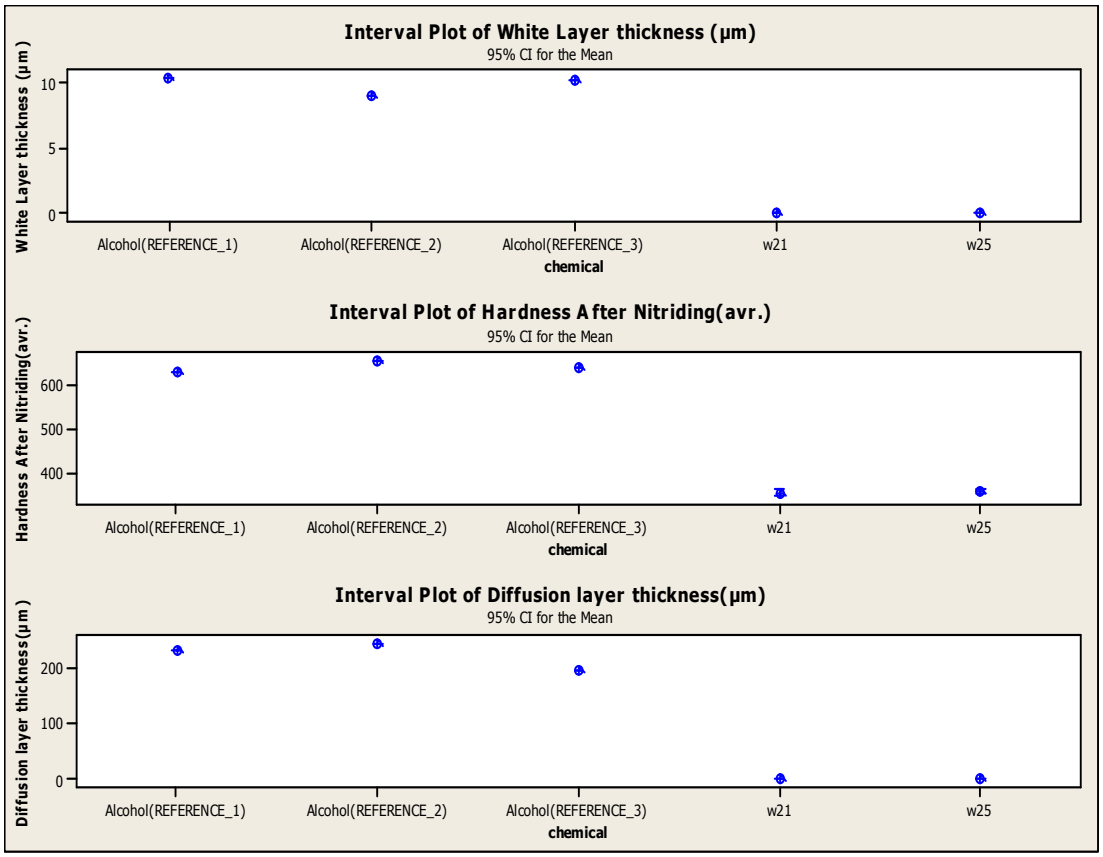



**Figure 7.4:** Result of compound, diffusion layer and hardness measurements of stop off masks trials

### 7.2.2 Result of electroplating experiments

#### 7.2.2.1 Nickel electroplating

Time dependent nickel electrodeposition experiments were conducted for obtaining nickel coatings with varying thickness. Coating thickness showed a linear dependence with deposition time Table A.3.Samples with different nickel coating thickness were subjected to nitriding in the same batch using 2.0 $K_N$ parameters. Optical investigations of the cross sections (Figure7.5.) and hardness measurements revealed that coating thickness is an important parameter for presentation of nitriding. The minimum nickel coating thickness required is 3µm.

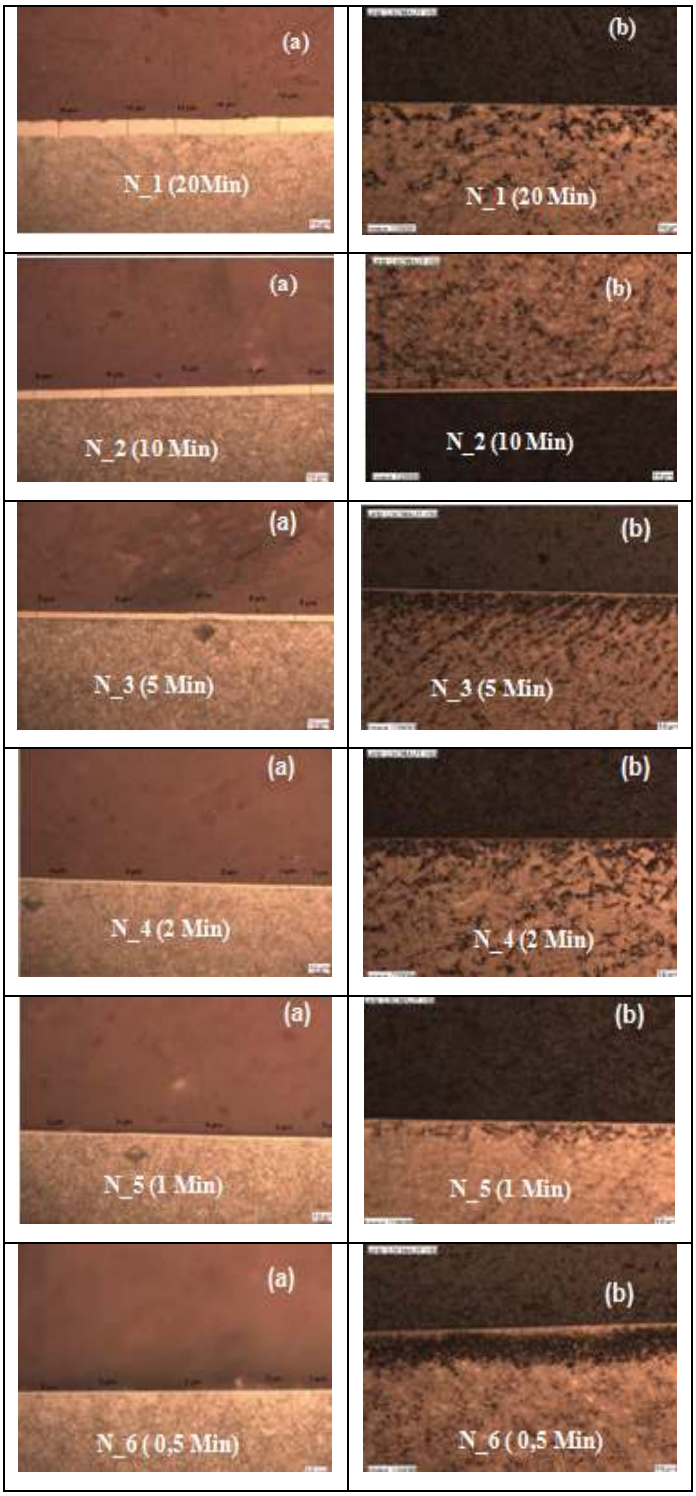



**Figure.7.5: a)** Thickness of the compound layer of the Nickel electroplated sample (20-0,5) (etched with Nital) (X500) **b)** Thickness of the Diffusion layer of the Nickel electroplated sample (20-0,5) (etched with Adler) (X50)

Details of the result of the measurement can be seen in Figure 7.6. There is a positive correlation between time and coating thickness. Nickel coating thickness increases with time.

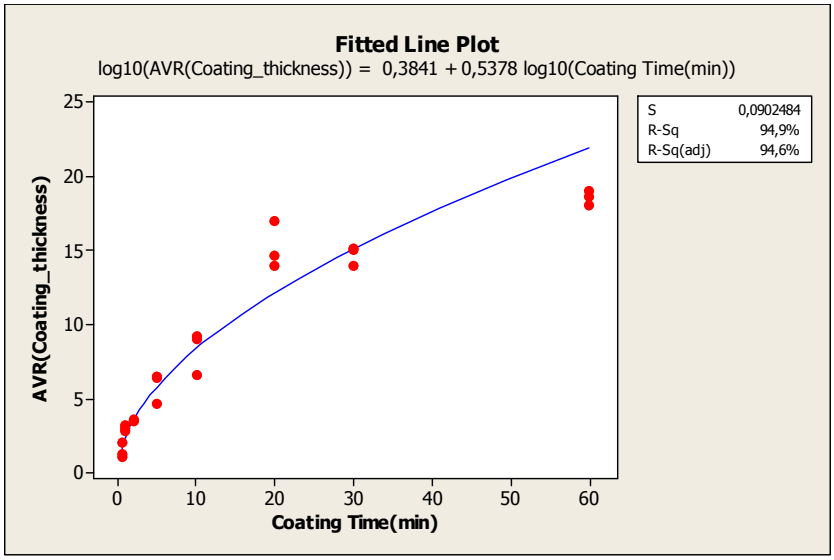



**Figure 7.6 :** Correlation of coating thickness and time of .nickel electroplating at 60-0.5 min

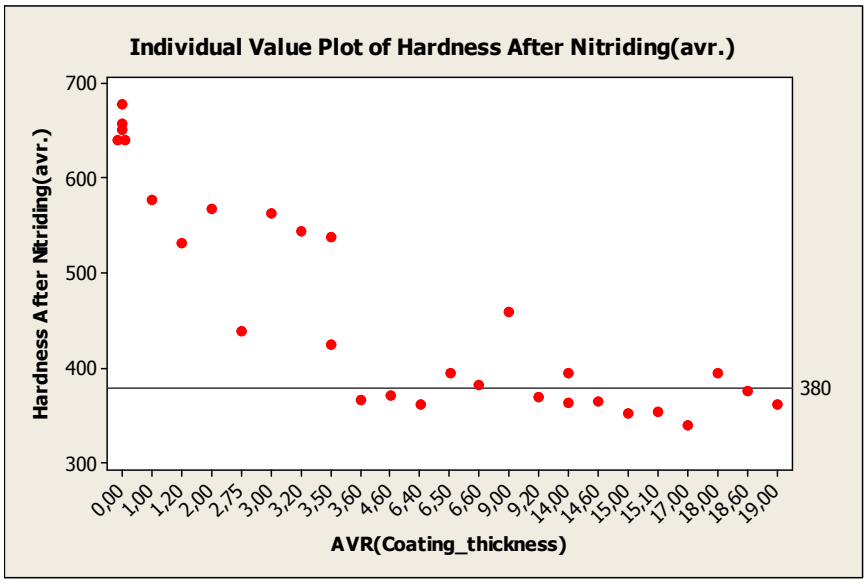
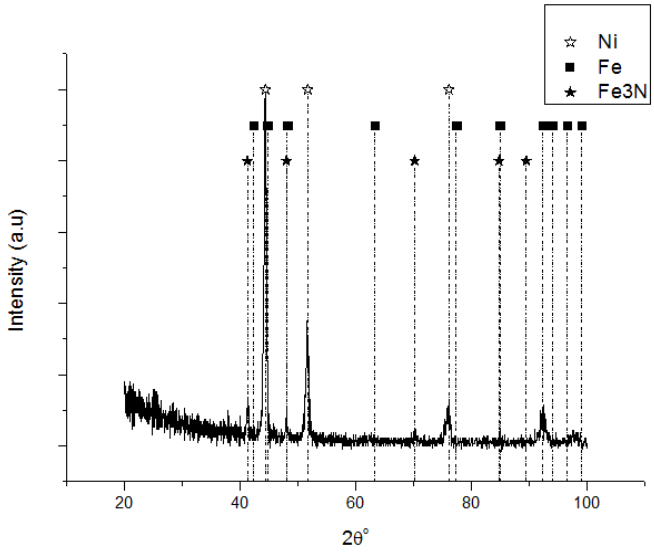



**Figure 7.7:** Nickel electroplating coating thickness- hardness comparision at 60-0,5min coating time

For the evaluation of structural changes in nickel coating and the presence of nitride layer XRD measurements were conducted after nitriding. For 2µm nickel coated

samples presence of iron nitride phases are clearly revealed.However when the coating thickness was 7 µm no $Fe_XN$ peaks were observed(Figure 7.8).

**(a)**




**(b)**

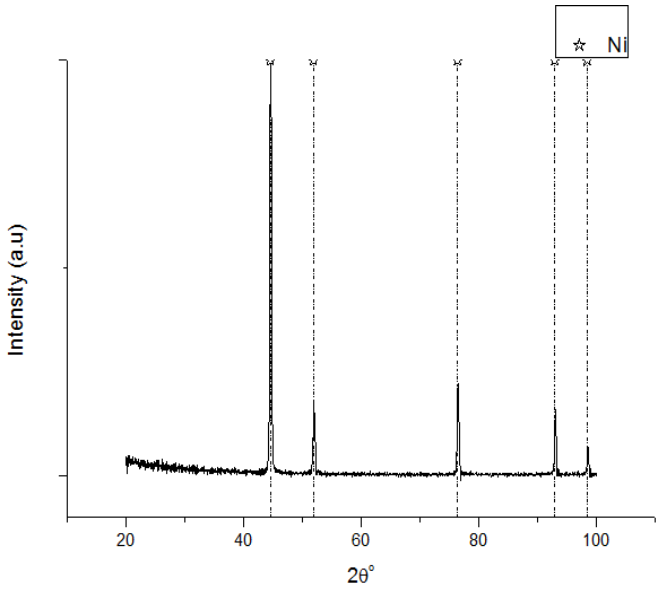



**Figure 7.8 : (a)** XRD measurements of Nickel electroplating sample at 2 min (2µm thickness) **(b)** XRD measurements of Nickel electroplating sample at 5 min (7µm thickness)

All experimental results are given in Figure 7.9.

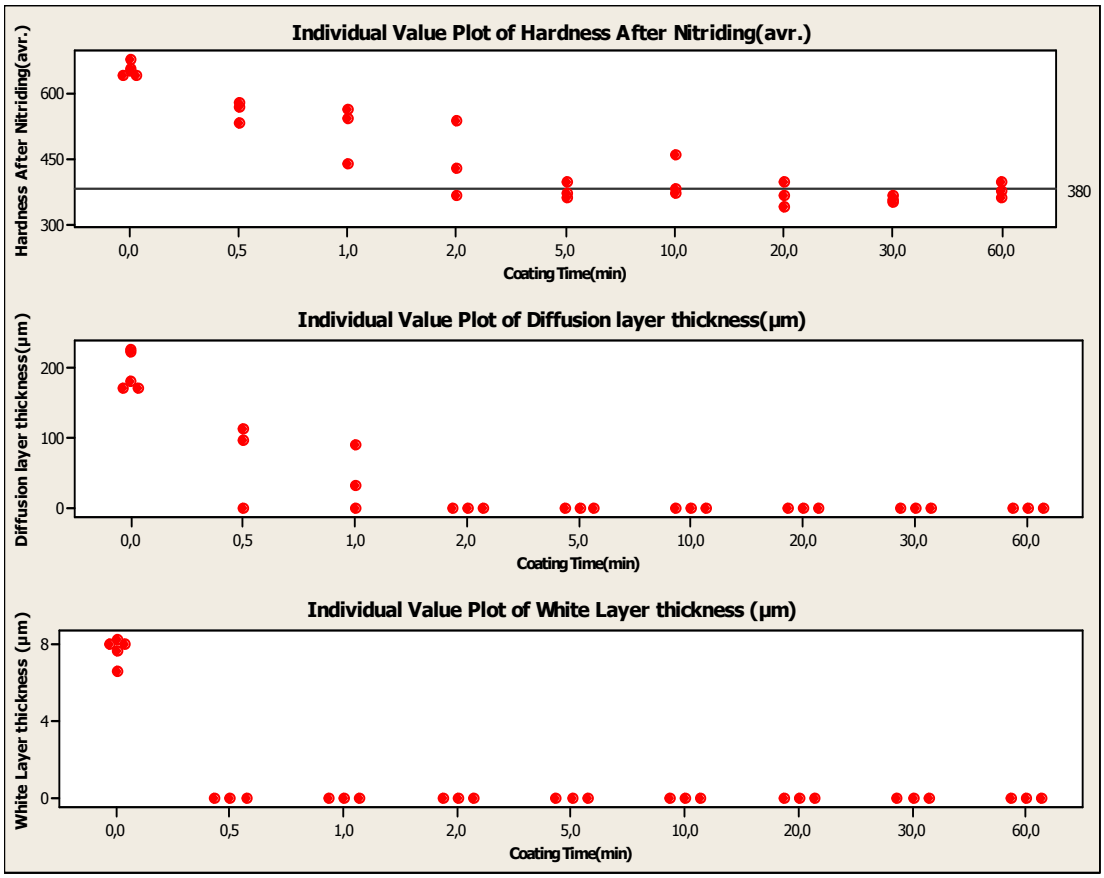



**Figure 7.9 :** Compound layer-diffusion layer thickness and hardness measurements results of Nickel electroplated samples

### 7.2.2.2 Copper electroplating

For deposition of copper on steel parts acidic solution are used due to the toxic effects on cyanide base coating solution that are generally used for deposition of copper on steel parts.

Utilization of acidic copper baths for electrodeposition created adhesion problems of copper to steel parts. Thus it was not possible to produce continuous copper layer on the substrates.The nitriding experiments on copper electrodeposited parts gave erractic results. In same veprans where copper layer is continuous efficient prevention of nitriding is achieved (Figure 7.10 and Table 7.4)

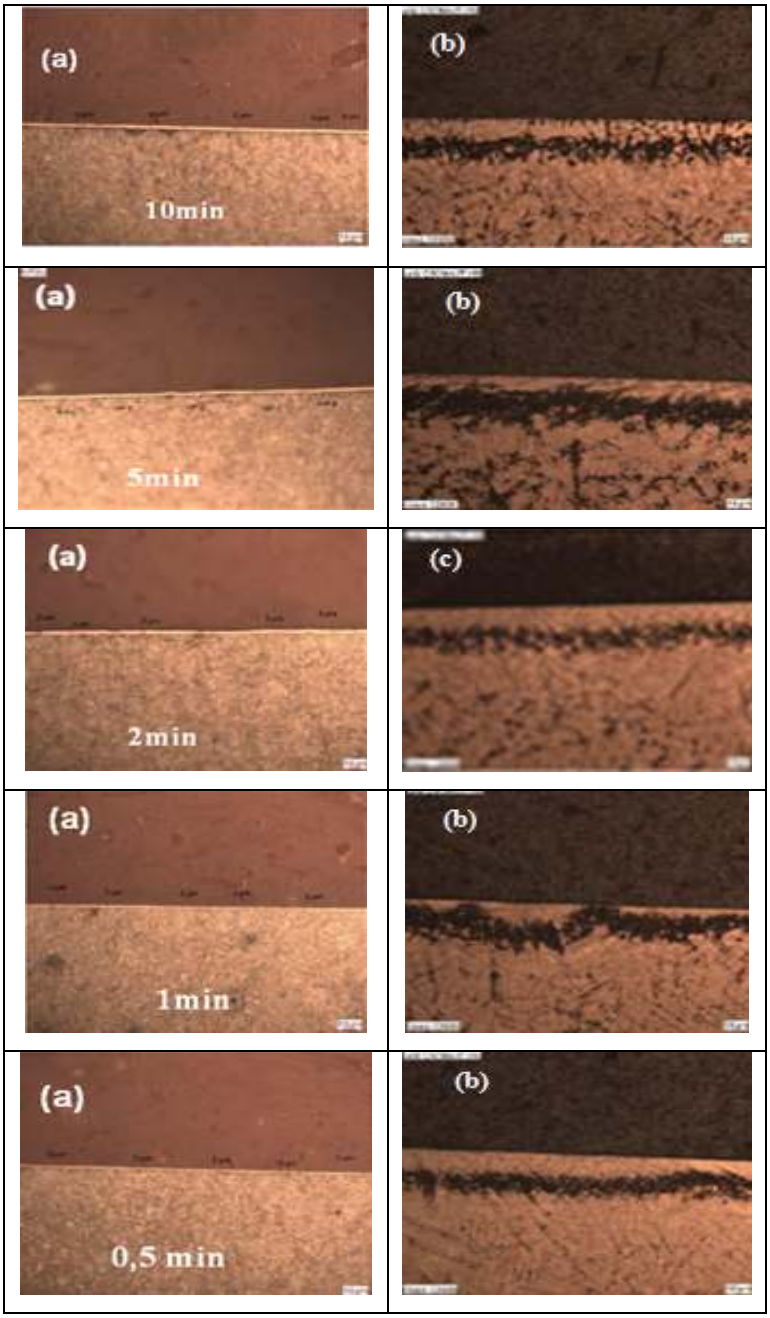
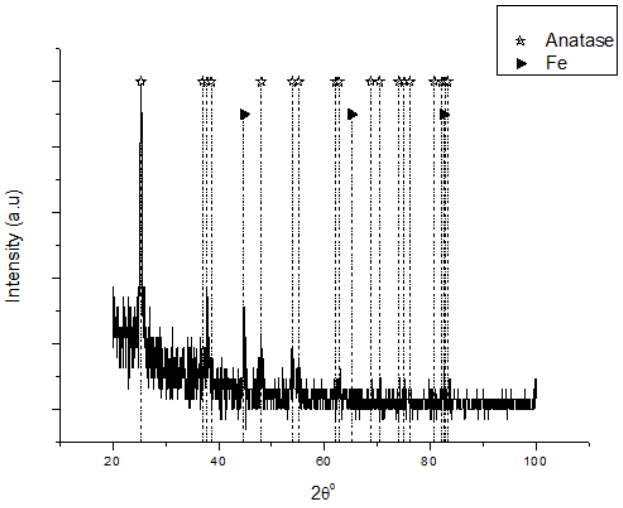



**Figure.7.10 : a)** Thickness of the compound layer of the Copper electroplated Sample (etched with Nital) (X500) **b)** Thickness of the Diffusion layer of the copper electroplated sample (etched with Adler) (X50)

## 7.3 Experiments of Titania Sol-Gel coating

Sol-Gel Titania coatings with different coatings are produced by dipping of surface cleaned steel samples into the Titania sol. After the deposition process, coated surface are subjected to heat treatment at 450 ºC to convert amorphouse titania into anatase form. The XRD patterns of heat traeted samples revealed theprecence of anatase on the surface (Figure 7.11). After nitriding in the XRD spectrum of these samples precence of iron nitride peaks besides anatase became observable, revealing the inefficiency of this coating for prevention of nitriding (Figure7.12).

**(a)**




**(b)**

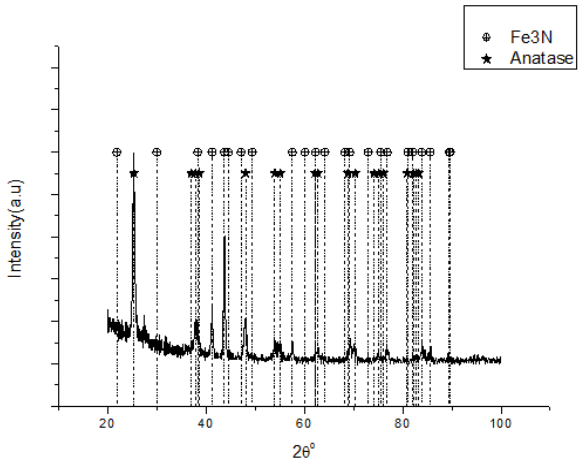



**Figure 7.11: a)**XRD analysis of Sol-Gel $TiO_2$ Coated Sample before gas nitriding,
**b)** XRD analysis of Sol-Gel $TiO_2$ Coated sample after nitriding

After Sol-Gel coating samples compound layer and diffusion layer thickness were measured via optical microscop. Samples coated in Sol-Gel method have nearly same compound layer thickness and diffusion layer thickness compared to reference sample (Figure 7.12 and Table 7.5)

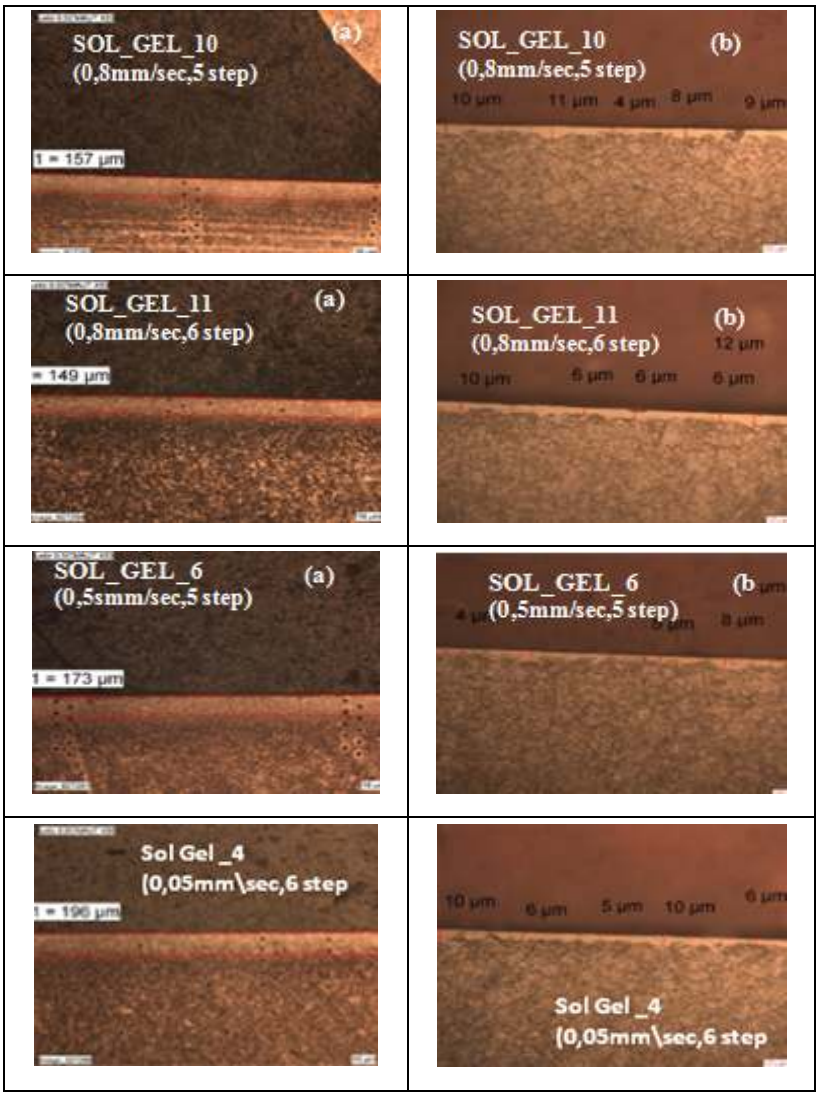



**Figure 7.12: a)** Thickness of the compound layer of Sol-Gel $TiO_2$ coated sampleswith different dipping speeds and coating steps (etched with Nital)(X500) **b)** Thickness of the diffusion layer of Sol-Gel $TiO_2$ coated samples(etched with Adler) (X50)

**Table 7.3:** Sol-Gel coating parameters and results of hardness ,diffusion and compound layer measurement

| Trial Number | Dipping Speed (mm/sec) | Coating Step (times) | Hardness After Nitriding(max.) (0,05µM- $Hv_{0,5}$) | Hardness After Nitriding(min.) (0,05µm- $Hv_{0,5}$) | Hardness After Nitriding(avr.) (0,05µm-$Hv_{0,5}$) | Diffusion layer thickness (µm) | Compound Layer thickness (µm) | XRD (Before Nitriding) | RAMAN | XRD (After Nitriding) |
|---|---|---|---|---|---|---|---|---|---|---|
| SG_1 | 0.8 | 5 | 688 | 625 | 663.3 | 236 | 9 | Anatase,Fe | Anatase | Anatase,$Fe_4N$ |
| SG_2 | 0.8 | 6 | 667 | 644 | 658.3 | 185 | 8 | Anatase,Fe | Anatase | Anatase,$Fe_4N$ |
| SG_3 | 0.5 | 5 | 685 | 626 | 646.7 | 216 | 9.1 | Anatase,Fe | Anatase | Anatase,$Fe_4N$ |
| SG_4 | 0.5 | 6 | 661 | 641 | 652 | 196 | 8.83 | Anatase,Fe | Anatase | Anatase,$Fe_4N$ |
| R_1 | | | 695 | 653 | 668.3 | 200 | 8.3 | | | |
| SG_5 | 0.5 | 5 | 650 | 620 | 634.3 | 196 | 8.9 | Anatase,Fe,$Ti0_3$ | | Anatase,$Fe_3N$ |
| SG_6 | 0.5 | 5 | 660 | 653 | 658 | 149 | 8.2 | Anatase,Fe,$Ti0_3$ | | Anatase,$Fe_3N$ |
| SG_7 | 0.5 | 6 | 674 | 625 | 646 | 177 | 6.6 | Anatase,Fe,$Ti0_3$ | | Anatase,$Fe_3N$ |
| SG_8 | 0.5 | 6 | 660 | 621 | 639 | 200 | 8.9 | Anatase,Fe,$Ti0_3$ | | Anatse,$Fe_3N$ |
| SG_9 | 0.8 | 5 | 657 | 634 | 643 | 196 | 8.1 | Anatase,Fe | | Anatse,$Fe_3N$,$Fe_4N$ |
| SG_10 | 0.8 | 5 | 670 | 637 | 657 | 157 | 6.6 | Anatase,Fe | | Anatse,$Fe_3N$,$Fe_4N$ |
| SG_11 | 0.8 | 6 | 657 | 634 | 647 | 173 | 7.8 | Anatase,Fe | | Anatse,$Fe_3N$,$Fe_4N$ |
| SG_12 | 0.8 | 6 | 654 | 624 | 639 | 177 | 7.6 | Anatase,Fe | | Anatse,$Fe_3N$,$Fe_4N$ |
| R_2 | | | 650 | 631 | 640.64 | 170 | 8 | | | |

## 8. CONCLUSIONS

- There were no significant differences in hardness and diffusion depths of nitrided samples that are treated with different cleaning chemicals. Nevertheless, only parts cleaned with Surtec 042 showed higher compound layer thickness as already given in literature. This result indicate indicated that Surtec 042 is a better cleaning chemical in terms of nitriding On the other hand Surtec 101 is the worst cleaning chemical for nitriding because of lower compound layer thickness.
- Nickel electroplating with a coating thickness of minimum 3.5µm is an efficient method for prevention of nitriding.
- In copper eelectroplating adhesion problems were encountered. On areas where no adhesion problems exist efficient screening is provided for gas nitriding. The minimum thickness required for stopping nitriding was not efficiently analysed for copper electrodeposited parts because of adhesion problem .
- No significant differences were seen on the surface of the samples which were exposed to both types of stop off masks used in the studies. No diffusion and compound layer formation were seen on samples' surfaces and after nitriding approximate hardness values were nearly obtained when compared to initial values before nitriding.
- The potential of titania base Sol-Gel coatings for prevention of nitriding of steel is investigate. However, these coatings did not show any nitriding prevention effect high probably due to their high porosity and insufficient thickness.
- The results of this study showed that the already applied industrial techniques namely, stop off masks and copper or nickel electroplating are still the most efficient techniques for prevention of nitriding.
- Further studies are required for selection of the appropriate process on real injector part

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## APPENDICES

**APPENDIX A:Tables:** Result of hardness measurements, diffusion and compound layer thickness

**Table A.1:** Results of hardness, diffusion and compound layer measurements of cleaning chemicals trials

| Sample Number | Detergent Type | Const. (%) | Hardness at 50 µm (Hv 0,5) | Compound layer Thickness (µm) (Avg) | Diffusion Layer Thickness (µm) (Avg) |
|---|---|---|---|---|---|
| D_1 | Surtec042 | 10 | 626 | 10 | 210 |
| D_2 | Surtec042 | 10 | 652 | 9.4 | 167 |
| D_3 | Surtec042 | 10 | 662 | 12.1 | 218 |
| D_4 | Surtec042 | 10 | 640 | 11.4 | 220 |
| D_5 | Surtec042 | 10 | 650 | 12 | 204 |
| D_6 | Surtec042 | 10 | 650 | 9.4 | 173 |
| D_7 | Surtec101 | 3 | 664 | 10.8 | 210 |
| D_7 | Surtec101 | 3 | 644 | 9.4 | 206 |
| D_8 | Surtec101 | 3 | 659 | 10 | 212 |
| D_9 | Surtec101 | 3 | 651 | 11 | 216 |
| D_10 | Surtec101 | 3 | 658 | 8.7 | 208 |
| D_11 | Surtec101 | 3 | 643 | 10.5 | 234 |
| D_12 | Surtec042 | 10 | 611 | 9.6 | 206 |
| D_13 | Surtec042 | 10 | 620 | 8.2 | 202 |
| D_14 | Surtec042 | 10 | 582 | 8 | 202 |
| D_15 | Surtec101 | 3 | 613 | 8.2 | 202 |
| D_16 | Surtec101 | 3 | 638 | 11 | 177 |
| D_17 | Surtec101 | 3 | 647 | 9.6 | 202 |
| D_18 | Surtec101 | 10 | 630 | 9.5 | 200 |
| D_19 | Surtec101 | 10 | 609 | 8.9 | 216 |

| | | | | | |
|---|---|---|---|---|---|
| D_20 | Surtec101 | 10 | 637 | 6.8 | 183 |
| D_21 | Surtec042 | 2 | 665 | 11 | 234 |
| D_22 | Surtec042 | 2 | 629 | 10.3 | 214 |
| D_23 | Surtec042 | 2 | 651 | 10 | 189 |
| R_1 | REFERENCE | alcohol | 630 | 10.4 | 230 |
| R_2 | REFERENCE | alcohol | 655 | 9 | 242 |
| R_3 | REFERENCE | alcohol | 639 | 10.2 | 193 |
| D_24 | D | 5 | 643 | 8.5 | 210 |
| D_25 | D | 5 | 670 | 8.6 | 240 |
| D_26 | D | 5 | 640 | 7.9 | 230 |
| D_27 | B | 5 | 682 | 8.4 | 188 |
| D_28 | B | 5 | 660 | 9.3 | 204 |
| D_29 | B | 5 | 628 | 9.4 | 230 |
| D_30 | A | 3 | 661 | 8.2 | 268 |
| D_31 | A | 3 | 637 | 8.1 | 220 |
| D_32 | A | 3 | 632 | 8 | 240 |
| D_33 | Surtec101 | 10 | 618 | 6.1 | 224 |
| D_34 | Surtec101 | 10 | 644 | 7.6 | 234 |
| D_35 | Surtec101 | 10 | 652 | 7.1 | 252 |
| D_36 | Surtec042 | 2 | 649 | 9.5 | 224 |
| D_37 | Surtec042 | 2 | 670 | 9.4 | 194 |
| D_38 | Surtec042 | 2 | 655 | 8.8 | 266 |
| R_4 | REFERENCE | alcohol | 679 | 6.6 | 220 |
| R_5 | REFERENCE | alcohol | 659 | 8.2 | 244 |
| R_6 | REFERENCE | alcohol | 668 | 8.3 | 200 |
| D_39 | B | 5 | 641 | 7.4 | 220 |
| D_40 | B | 5 | 660 | 8.4 | 220 |
| D_41 | B | 5 | 658 | 7.9 | 190 |
| D_42 | D | 5 | 632 | 6.5 | 276 |

| | | | | | |
|---|---|---|---|---|---|
| D_43 | D | 5 | 621 | 9.9 | 226 |
| D_44 | D | 5 | 660 | 7.9 | 192 |
| D_45 | A | 3 | 656 | 6.5 | 276 |
| D_46 | A | 3 | 682 | 9.9 | 226 |
| D_47 | A | 3 | 667 | 8.6 | 211 |
| D_48 | Surtec042 | 2 | 660 | 6.9 | 200 |
| D_49 | Surtec042 | 2 | 652 | 7.9 | 232 |
| D_50 | Surtec042 | 2 | 656 | 7.4 | 208 |
| D_51 | Surtec101 | 10 | 660 | 7.9 | 190 |
| D_52 | Surtec101 | 10 | 655 | 6.9 | 198 |
| D_53 | Surtec101 | 10 | 655 | 7.8 | 212 |
| D_54 | C | 5 | 685 | 8.2 | 201 |
| D_55 | C | 5 | 665 | 7.64 | 198 |
| D_56 | C | 5 | 667 | 8 | 208 |
| D_57 | B | 5 | 681 | 8.615 | 235 |
| D_58 | B | 5 | 669 | 6.9 | 228 |
| D_59 | B | 5 | 677 | 7.5 | 240 |
| D_60 | A | 3 | 674 | 7.6 | 216 |
| D_61 | A | 3 | 673 | 8.919 | 204 |
| D_62 | A | 3 | 639 | 6.3 | 254 |
| D_62 | D | 5 | 673 | 8.5 | 195 |
| D_63 | D | 5 | 613 | 10.69 | 230 |
| D_64 | D | 5 | 650 | 9.5 | 227 |
| R_7 | REFERENCE | alcohol | 682 | 8.3 | 187 |

**Table A.2:** Nickel electroplating parameter and results of hardness, diffusion and compound layer measurements

| Sample Number | Coating Time (min) | pH | Speed (rpm) | Current (mA) | Voltage (mV) | Coating thickness(µm) (Avg.) | Hardness After Nitriding (Avg.) (0,05µM-Hv 0,5) | Diffusion layer thickness (µm) | Compound Layer thickness (µm) |
|---|---|---|---|---|---|---|---|---|---|
| N_1 | 20 | 3.5 | 250 | 0,36 | 2,3 | 14 | 395 | 0 | 0 |
| N_2 | 10 | 3.5 | 250 | 0,36 | 2,3 | 9 | 460 | 0 | 0 |
| N_3 | 5 | 3.5 | 250 | 0,36 | 2,3 | 6.5 | 396 | 0 | 0 |
| N_4 | 2 | 3.5 | 250 | 0,36 | 2,3 | 3.5 | 538 | 0 | 0 |
| N_5 | 1 | 3.5 | 250 | 0,36 | 2,3 | 3 | 563 | 0 | 0 |
| N_6 | 0,5 | 3.5 | 250 | 0,36 | 2,3 | 2 | 568 | 0 | 0 |
| R_1 | REFERENCE | | | | | 0 | 679 | 220 | 6.6 |
| N_7 | 20 | 3.5 | 250 | 0,36 | 2,3 | 14.6 | 366 | 0 | 0 |
| N_8 | 10 | 3.5 | 250 | 0,36 | 2,3 | 6.6 | 383 | 0 | 0 |
| N_9 | 5 | 3.5 | 250 | 0,36 | 2,3 | 4.6 | 372 | 0 | 0 |
| N_10 | 2 | 3.5 | 250 | 0,36 | 2,3 | 3.6 | 367 | 0 | 0 |
| N_10 | 1 | 3.5 | 250 | 0,36 | 2,3 | 3.2 | 544 | 90 | 0 |
| N_11 | 0,5 | 3.5 | 250 | 0,36 | 2,3 | 1.2 | 532 | 113.6 | 0 |
| R_3 | REFERENCE | | | | | 0 | 640 | 170 | 8 |
| N_12 | 20 | 3.5 | 250 | 0,36 | 2,3 | 17 | 341 | 0 | 0 |
| N_13 | 10 | 3.5 | 250 | 0,36 | 2,3 | 9.2 | 370 | 0 | 0 |
| N_14 | 5 | 3.5 | 250 | 0,36 | 2,3 | 6.4 | 362 | 0 | 0 |
| N_15 | 2 | 3.5 | 250 | 0,36 | 2,3 | 3.5 | 426 | 0 | 0 |
| N_16 | 1 | 3.5 | 250 | 0,36 | 2,3 | 2.75 | 439 | 30 | 0 |
| N_17 | 0,5 | 3.5 | 250 | 0,36 | 2,3 | 1 | 578 | 97 | 0 |
| N_18 | 60 | 3.5 | 250 | 0,36 | 2,3 | 19 | 363 | 0 | 0 |
| N_19 | 60 | 3.5 | 250 | 0,36 | 2,3 | 18 | 396 | 0 | 0 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| N_20 | 60 | 3.5 | 250 | 0,36 | 2,3 | 18,6 | 377 | 0 | 0 |
| N_21 | 30 | 3.5 | 250 | 0,36 | 2,3 | 18 | 353 | 0 | 0 |
| N_22 | 30 | 3.5 | 250 | 0,36 | 2,3 | 15 | 364 | 0 | 0 |
| N_23 | 30 | 3.5 | 250 | 0,36 | 2,3 | 15,1 | 355 | 0 | 0 |
| R_5 | REFERENCE | | | | | 0 | 651 | 180 | 7,6 |

**Table A.3:** Copper electroplating parameter and results of hardness, diffusion and compound layer measurements

| Sample Number | Coating Time (min) | PH | Speed (rpm) | Amper (mA) | Coating thickness(µm) (Avg.) | Hardness After Nitriding(avg.) (0,05µm- $Hv_{0,5}$) | Diffusion layer thickness (µm) | White Layer thickness (µm) |
|---|---|---|---|---|---|---|---|---|
| C_1 | 20 | 5 | 100 | 0,15 | 3.8 | 427 | 0 | 0 |
| C_2 | 10 | 5 | 100 | 0,15 | 3 | 533.66 | 123.8 | 6.5 |
| C_3 | 5 | 5 | 100 | 0,15 | 3 | 539 | 107.4 | 5 |
| C_4 | 2 | 5 | 100 | 0,15 | 2.6 | 387 | 88 | 0 |
| C_5 | 1 | 5 | 100 | 0,15 | 2.2 | 567 | 163.2 | 0 |
| C_6 | 0,5 | 5 | 100 | 0,15 | 2 | 568.33 | 180.8 | 4.3 |
| R_1 | 0 | 0 | 0 | 0 | 0 | 679 | 220 | 6.6 |
| R_2 | 0 | 0 | 0 | 0 | 0 | 658.67 | 244 | 8.2 |
| C_7 | 10 | 5 | 100 | 0,15 | 3 | 611.33 | 0 | 10.4 |
| C_8 | 5 | 5 | 100 | 0,15 | 2.5 | 581 | 45.8 | 4 |
| C_9 | 2 | 5 | 100 | 0,15 | 0 | 528.33 | 128 | 5.4 |
| C_10 | 1 | 5 | 100 | 0,15 | 0 | 477.6 | 64.2 | 1.4 |
| C_11 | 0,5 | 5 | 100 | 0,15 | 1.5 | 547 | 115.6 | 3.7 |
| R_3 | 0 | 0 | 0 | 0 | 0 | 640.64 | 170 | 8 |
| C_12 | 10 | 5 | 100 | 0,15 | 0 | 618.3 | 153.33 | 6.3 |
| C_13 | 5 | 5 | 100 | 0,15 | 0 | 578 | 102.1 | 7.2 |
| C_14 | 2 | 5 | 100 | 0,15 | 1.8 | 630.33 | 173.7 | 4.81 |

**CURRICULUM VITAE**


| | |
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