SYNTHESIS AND CHARACTERIZATION OF NI – TIB$_2$ COMPOSITE COATINGS ON STEEL BY PULSE ELECTRO DEPOSITION

K.Boopathy[1],P.Dinesh[2],E.Manikandan[3],P.Dhanasekaran[4], R.Boopathi[5]

Final year, Department of Mechanical Engineering, Sri Shanmugha College Of Engineering and Technology, Pulipalayam, Salem
Assistant Professor, Department of Mechanical Engineering, Sri Shanmugha College Of Engineering and Technology, Pulipalayam, Salem

boopathy.boopathy769@gmail.com
mageshboopathykr@gmail.com

Abstract— **The project involves the coating of ultrafine titanium diboride (TiB_2) dispersed Nickel on mild steel substrate and characterizing the same. The mild steel substrate was coated with Ni by electro deposition and it was characterized by SEM, XRD. The Ni coated substrate was coated with TiB_2 by pulse electro deposition and it was characterized by SEM, XRD. This is to increase the properties like abrasion, wear resistance, corrosion protection, lubricity or aesthetics. Nickel is a chemical element with symbol Ni and atomic number 28. It is a silvery-white lustrous metal with a slight golden tinge. Nickel belongs to the transition metals and is hard and ductile. Titanium is a chemical element with symbol Ti and atomic number 22. It is a lustrous transition metal with a silver color, low density and high strength. It is highly resistant to corrosion in sea water, regain and chlorine. X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.SEM provides detailed high resolution images of the sample by rastering a focused electron beam across the surface and detecting secondary or backscattered electron signal. An Energy Dispersive X-Ray Analyser (EDX or EDA) is also used to provide elemental identification and quantitative compositional information**

I. INTRODUCTION

Electroplating is a process of deposition on a cathode part immersed into an electrolyte solution, by the material of anode which is dissolved into the solution in form of the metal ions. It is a process using electrical current to coat that anode material as a thin film onto a conductive substrate surface. An important feature is that a very large number of pure metals, ceramics, alloys, composites which can be electrodeposited with grain size less than 100 nm. Electroplating is widely used in various industries for coating metal objects with a thin layer of a different metal. The layer of metal deposited has some desired property, which the metal of the object lacks. Electroplating increases life of metal and prevents corrosion.

The application of electroplating deposits has a desired property like abrasion, wear resistance, corrosion protection, lubricity or aesthetics onto a substrate lacking the desired property. A modification in the electroplating process is the pulse electroplating. This process involves the swift alternating of the potential or current between two different values resulting in a series of pulses of equal amplitude, duration and polarity, separated by zero current. By changing

the pulse amplitude and width, it is possible to change the deposited film's composition and thickness. The improved properties can be obtain as it is possible to get non dendritic, coherent deposits at much higher current densities than with the straight direct currents. The additional higher over potentials results in higher nucleation rates which results in finer grain size. Pulse plating improves the deposit properties viz. Hardness porosity, ductility, electrical conductivity, finer grain size plating thickness distribution. Traditional applications of electro deposition will continue, while new ones will emerge rapidly, especially in the fields of nano electronics, biotechnology, and energy engineering.

1.1 COATINGS

Materials used in day to day applications are prone to wear, corrosion and several other surface phenomena. These are mainly caused due to the exposure to atmosphere which is prone to cause the surface defects. These results in the failure of the material thereby increasing the expenses incurred. The decreased service life can be prevented by these coating that enhance the desired properties. These include coating of secondary phase particles on to the substrate helping the material to withstand adverse conditions. These coatings can be electro coatings or electro less coatings. The electro coatings are widely used due to its success in extending the life of the component.

1.2 ELECTROPLATING

Electroplating is a process that uses electric current to reduce dissolved metal cations so that they form a coherent metal coating on an electrode. The term is also used for electrical oxidation of anions onto a solid substrate. Electroplating is primarily used to change the surface properties of an object .It is also used to build up thickness on undersized parts or to form objects by electroforming.

1.3 ELECTRO DEPOSITION

Electro deposition is a type of electroplating where in direct current is used for the deposition of the anode material. Electro deposition is the process of coating a thin layer of one metal on top of a different metal to modify its surface properties. It is done to achieve the desired electrical and corrosion resistance, reduce wear and friction, improve heat tolerance and for decoration. Electro deposition is a surface

coating method that forms an adherent layer of one metal on another. Composite electro deposition is a method of co-depositing fine particles of metallic, non-metallic compounds or polymers into a plated layer to improve material properties. Electrodeposition yields a porosity free finished product by adjusting electro deposition parameters e g, bath composition, pH value, temperature and overpotential, which affect the nucleation and the grain growth during electrocrystallization. Electrodeposition continues to be widely used for protective or decorative coatings, challenging new applications have been found in the electronics industry.

1.4 CONCEPTS OF PULSE AND PULSE REVERSE TECHNIQUES

In electroplating, a negatively charged layer is formed around the cathode as the process continues. When using DC, this layer charges to a defined thickness and obstructs the ions from reaching the part. In PED, the output is periodically turned off to cause this layer to ischarge somewhat. This allows easier passage of the ions through the layer and onto the part.
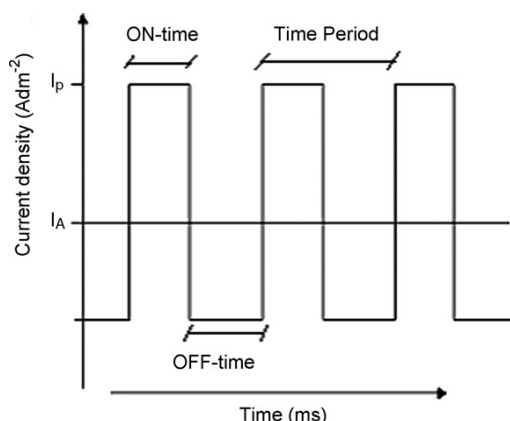

Fig 1.4.1 Pulse Waveform

1.5 PULSE ELECTRODEPOSITION—DECIDING FACTORS

1.5.1 CHARGING OF THE ELECTRICAL DOUBLE LAYER (EDL) AT THE METAL ELECTROLYTE INTERFACE

The charges are provided to EDL, to raise its potential to the value required for metal deposition at the rate corresponding to I_A. The I_P supplied consists of two parts, (1) a capacitive current, which charges the double layer and (2) a faradic current(I_F), which corresponds to the rate of metal deposition.

1.5.2 MASS TRANSPORT

The important factor for mass transport in PC plating is pulse limiting current density(I_L). The value of I_L depends on pulse parameters, particularly T_{ON}. Longer the T_{ON}, smaller would be the value of I_L. The pulse T_{ON} must be short to stay below the I_L, but sufficiently long to fully charge the double layer. The value of the pulse I_L might far exceed DC limiting current density.

1.6 PULSE ELECTRO DEPOSITION PARAMETERS

In the conventional DC plating there is only one parameter, namely current density (I), which can be varied. But in PED, we have three independent variables, viz, (i) ON-time (T_{ON}), (ii) OFF-time (T_{OFF}) and (iii) peak current density

(IP).In PC, the duty cycle corresponds to the percentage of total time of a cycle and is given by:

duty cycle = T_{ON}

$T_{ON} + T_{OFF} = T_{ONf}$

Where f is frequency, defined as the reciprocal of the cycle time(T).

Frequency = $1/T_{ON} + T_{OFF} = 1/T$

In practice, pulse plating usually involves a duty cycle of 5% or greater and T_{ON} . PC will deposit metal at the same rate as DC provided the average pulse current density equals the latter. The average current density (I_A), in pulse plating is defined:

I_A = peak current (I_P) × duty cycle (γ)

In case of PRC technique, the average current ($\bar{I}_A$) is as given below:

$$(\bar{I}_A) = I_C T_C - I_{AA} T_{AA}/T_{AA} + T_C.$$

1.7 PROCESS

In pulse plating, an interrupted current or potential is used. The current may or may not drop to zero between pulses. Three parameters are independently variable in practical pulse plating: pulse peak current, on time and off time, which determine the physical characteristics of the deposits obtained from the given electrolyte.

II.   EXPERIMENTAL WORK

2.1 PREPARATION OF MILD STEEL PLATE

Mild steel plate of dimension 3.5cm x 2 cm x 0.2cm has been prepared from cutting a large plate. The nominal composition of the base metal is C(0.21%), Si(0.12%), Mn(0.63%), S(0.16), P(0.4%). This steel is selected as the substrate of the coating for the present study as model plain carbon steel used for structural applications. The steel samples were metallographically polished and cleaned in dilute HCl(40% by volume) before electroplating without any activation pretreatment.

2.2 WATT'S BATH SOLUTION

Watt's bath solution is prepared with the distilled water and salts taken as per the standards given in the table below. Initially 80g of (Nickel sulphate) $NiSO_4.6H_2O$ is dissolved in 200ml of distilled water and 20g of Nickel chloride($NiCl_2.6H_2O$) and 10g of Boric acid (H_3BO_4)is added gradually while stirring using a magnetic stirrer. The solution is stirred continuously for 5 hours. Watt's bath solution is ready for the deposition.

TABLE 2.1 COMPOSITION FOR WATT'S BATH SOLUTION

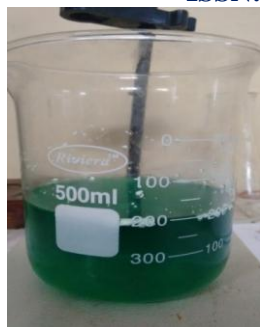|	
Nickel Sulphate ($NiSO_4.6H_2O$)	40%
Nickel Chloride ($NiCl_2.6H_2O$)	25%
Boric acid (H_3BO_4)	6%

Fig 2.1 Watt's Bath Solution

2.3 ELECTROLYTIC DEPOSITION DETAILS

This solution is taken as the electrolyte. A Ni plate of 99.99% purity was used as the anode, and a low carbon steel plate was used as the cathode. The plate is coated for about 30 minutes. Finally the Ni coated plate is taken for characterization techniques such as SEM, XRD analysis.

TABLE 2.2 PARAMETERS FOR ELECRODEPOSITION

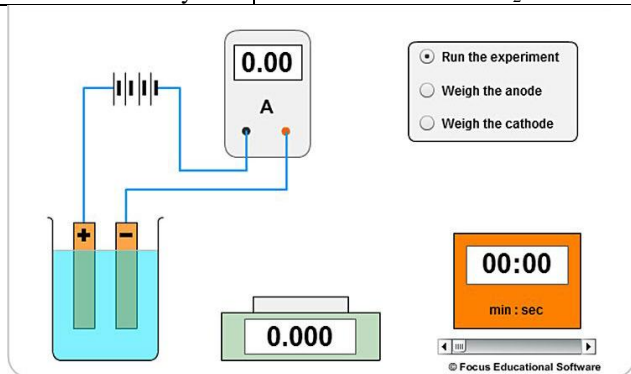| Ph	3.5-5
Temperature	55-65° C
Time	30 mins
Current density	2-5 A /dm$_2$

Fig 2.2 Electrolytic Deposition

Fig 2.3 Nickel Coated Sample

2.4 MATERIAL CHARACTERIZATION
2.4.1 HARDNESS TESTING

Table 2.3 Optical emission spectroscopy analysis

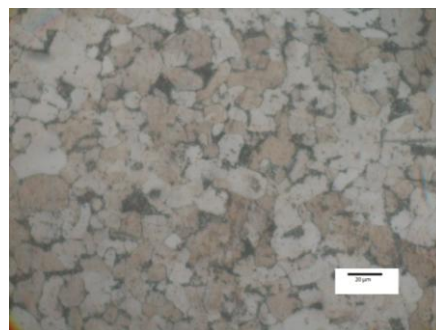| ELEMENTS	C	Si	Mn	P	S
% COMPOSITION	0.212	0.122	0.632	0.163	0.043

Fig 2.4 Optical microstructure of mild steel at 500x magnification

The low carbon steel steel sample is analyzed using an optical emission spectroscope to check the composition. It is revealed from the above table that the sample is low carbon steel with a carbon composition of 0.212. It is further confirmed from the obtained microscopic analysis using an optical microscope.

2.4.2 MICROHARDNESS RESULTS

The hardenss values are obtained using the vickers hardness tester. These values shows a marked increase in the hardness values of the nickel coated sample. It confirms that hardness has been increased on coating, thus improving the wear resisitance of the sample.

Table 2.4 Tabulation for vickers hardness values

TRIAL	Mild steel(HV)	Nickel coated on mild steel(HV)
1.	180	290
2.	175	284
3.	172	294
Average	176	290

Load: 100g

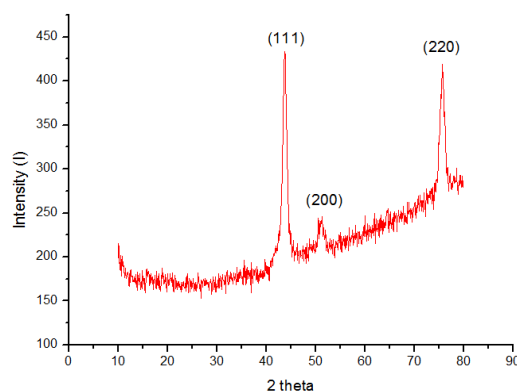### A. *XRD ANALYSIS OF NICKEL COATED STEEL PLATE*

Fig 2.5 XRD Graph for nickel coated on mild steel sample

The above image is the XRD analysis result. The peaks of confirms the presence of the nickel. Deposited on the

low carbon steel. Thus it is evident from these that the low carbon has been coated using Ni. The XRD result was taken on pure nickel (99.9%) coated on the low carbon steel sample.
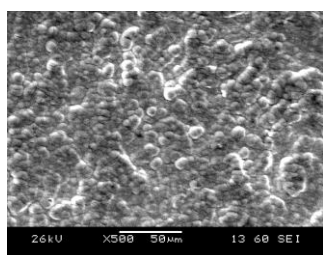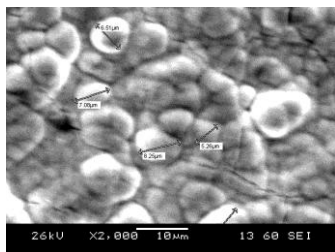
SEM ANALYSIS OF NICKEL COATED PLATE

Fig 2.6 SEM images of nickel coated on mild steel

The above given are the SEM images of the nickel coated plated that confirm that nickel is being coated on the low carbon steel for the given current density and coating time are 5A/dm^2 and 30 mins respectively. The SEM images clearly shows that the particle size varies from 5 to 8 μm with dendritic structure.

2.5 PREPARATION OF TITANIUM DIBORIDE POWDERS

The starting materials for preparation of TiB_2 were synthesized by hydrolyzing titanium tetra isopropoxide ($Ti[OCH(CH_3)_2]_4$, 97% purity,) with four molar equivalents of distilled water in IPA solvent (Isopropyl Alcohol, 99% purity) under vigorous stirring. Three different TTIP concentrations in IPA were prepared: 0·033, 0·050 and 0·1 M. The B_4C : Ti : H_2O molar ratio of the starting material was x : 1 : 4, where x varied from 1·3 to 2·5. The resulting dark suspension was stirred for 105 min at room temperature, the volatile components were removed under vacuum at 140°C. The powder then was heat treated at 900–1200°C in a graphite crucible in 1 atm argon. Then the characterization should be done on the powders.

Fig 2.7. Shows hydrolysis + stirring and addition of B_4C + stirring respectively

2.5.1 PULSE ELECTRODEPOSITION

In pulse electrodeposition (PED) the potential or current is alternated swiftly between two different values. This results in a series of pulses of equal amplitude, duration and polarity, separated by zero current. Each pulse consists of an ON-time (TON) during which potential and/current is applied, and an OFF-time (TOFF) during which zero current is applied. It is possible to control the deposited film composition and thickness in an atomic order by regulating the pulse amplitude and width. They favor the initiation of grain nuclei and greatly increase the number of grains per unit area resulting in finer grained deposit with better properties than conventionally plated coatings.

Table 2.5 Composition Pulse Electrodeposition For Solution

Nickel chloride($NiCl_2.6H_2O$)	26%
Nickel sulphate ($NiSO_4.6H_2O$)	24%
Boric acid(H_3BO_4)	6%
Titanium diboride	12gm
Sodium dodecyl sulfate	2gm

The beaker consist of Nickel chloride($NiCl_2.6H_2O$) 26%, Nickel sulphate ($NiSO_4.6H_2O$) 24%, Boric acid(H_3BO_4) 6%, Titanium diboride 12gm, Sodium dodecyl sulfate 2gm.

Fig 2.8 pulse electrodeposition unit

The sample material mild steel is taken to pulse electrodeposition the time taken to pulse electrodeposition is 40 minutes. The process is done by 55-65∘ C.

Fig 2.9 Nickel titanium diboride coated on mild steel sample

2.6 RESULTS AND DISCUSSIONS FOR NICKEL TITANIUM DIBORIDE
Table 2.6 Tabulation for Vickers hardness values

TRIAL	Mild steel(HV)	Nickel coated on mild steel(HV)	Titanium diboride coated on mild steel(HV)
1.	180	290	456
2.	175	284	468
3.	172	294	462
Average	176	290	462

Load : 100g

It is clear from the above values that there is an increase in the hardness value of the coated sample. This increase shows that the strength of the low carbon steel has been improved. It further denotes that these coatings are used to improve the wear resistance of the substrate which is evident from the increase in the hardness values.

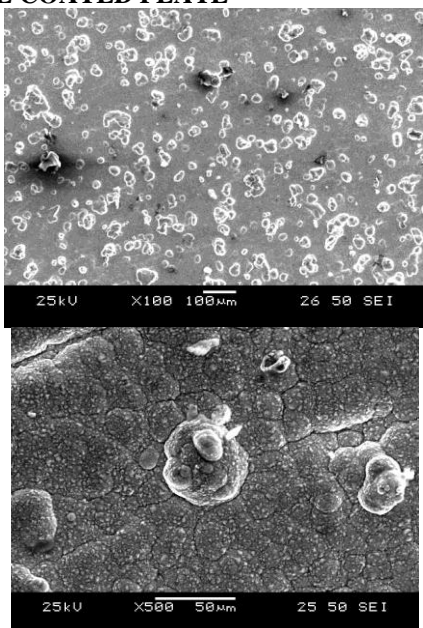### 2.6.1 SEM ANALYSIS OF NICKEL TITANIUM DIBORIDE COATED PLATE

Fig 7.2.2 SEM Image of nickel titanium diboride coated plate

The above given are the SEM images of the nickel titaniumdiboride coated plated that confirm that titanium is being coated on with low carbon steel for the given current density and coating time are 5A/dm^2 and 40 mins respectively.

The SEM images clearly shows that the particle size varies from 18 to 30 μm with dendritic structure.

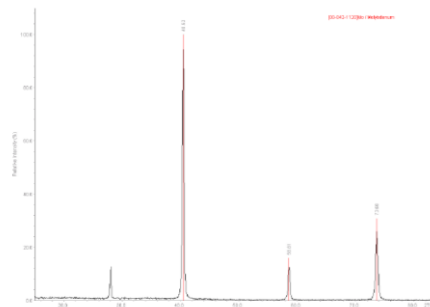### 2.6.2 XRD ANALYSIS OF NICKEL TITANIUMDIBORIDE COATED STEEL PLATE

Fig 2.10 XRD Image of nickel titaniumdiboride coated steel plate

The above image is the XRD analysis result. The peaks of confirms the presence of the nickel titaniumdiboride. Deposited on the low carbon steel. Thus it is evident from these that the low carbon has been coated using TiB$_2$. The XRD result was taken on nickel titaniumdiboride coated on the low carbon steel sample.

APPLICATION
It is used in ship body
It is used as chemical containers
It is used in missiles

III.   CONCLUSION

This review indicates the advantages and disadvantages of employing ED and PED technique in plating. Pulse current produces invariably fine-grained structures so that physical, chemical and mechanical properties are changed advantageously for many metals and alloys. Pulse and the related techniques enable the production of newer types of deposits, which were considered impossible so far. Pulse technique might become a commonly used tool for other electrochemical processes. By this mechanical properties of materials is increased.

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