# ELECTRODEPOSITION OF Ni-Mg-Zn COATING BY VARYING TEMPERATURE ON MILD STEEL CHAIN AND IT'S SURFACE CHARACTERIZATION, CORROSION AND WEAR PROPERTIES.

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**ABSTRACT**

Chrome plating is one of the conventional methods to prevent rust formation on mild steel but the problem with that it is a carcinogenic agent. Alternate materials for the chromium were Nickel, Magnesium, Zinc, Cobalt, and Tungsten. One of the main applications of mild steel was Chain and chain drives which are used in ship anchors, crane lifting, and heavy load lifting. To prevent the occurrence of corrosion on the chain the surface is coated with Ni-Mg-Zn alloy using electro-deposition. Suitable source materials for the alloy coating were identified and their electrolyte optimization parameters were found. Comparative studies of the coating were done at three different temperatures 30$^{o}$C, 50$^{o}$C, and 70$^{o}$C. Surface characterization of thin films was done with the help of SEM (Scanning Electron Microscopy), EDS (Energy dispersive spectroscopy), and XRD (X-Ray Diffraction), Hardness, Surface roughness, and Wear (Pin on Disc Method). The corrosion behavior of the coated chain is studied with the help of EIS (Electrochemical impedance spectroscopy).

**Key Words:** Chain rusting, Alloy coating, Electrodeposition, Corrosion prevention, Nanotechnology.

## 1. INTRODUCTION

Materials selected for the coating are Nickel, Zinc, and Magnesium. The properties of each of the materials were discussed below. Nickel has good ductile and malleable properties. The melting point of Nickel is 1453$^{o}$C and the boiling point is 2913$^{o}$C. Due to its high thermal stability and poor reaction to acids, it is widely used in the manufacturing of stainless steel and carbon steel. A study on Ni-Zn multilayered alloy coating from an aqueous bath at different current densities 2.0, 3.0, 4.0, 5.0 A/dm$^2$ reveals that the corrosion property of the material increases to the optimal layer of deposition and then decreases [1]. Zinc is mainly used as the galvanizing agent for mild steel to prevent its surface from corrosion and rust formation. It is a widely used element in the electro galvanizing process and dies casting process. Zinc along with oxide plays a key role in semiconductors and fluorescent lamps. The melting point of Zinc is 420$^{o}$C. Steel is used to build the majority of maritime and offshore constructions, which increases the risk of accidents. corrosion deterioration causes The main cause of corrosion is electrochemical processes that lead to the degradation of metals Making a protective barrier is one method of reducing the impact of corrosion application of a barrier creates a defense between the metal and corrosive surroundings metal finishes electroplated. Zinc-based metallic paints To safeguard steel components and structures, cadmium (Cd) and zinc (Zn) are used. via rusting. But any sort of Cd coating, including being a carcinogen and based on cyanide and Cd compounds the usage of Cd is an increasing problem for the environment and health. There are limits to coating. The key metal for galvanic conversion is zinc preventing rust in industrial steel building applications. There are numerous ways to get zinc. Chains have been used in shipping and offshore structures primarily for direct mooring of vessels, such as when they are attached to anchors, and also as dampers in cable mooring, where the chain is primarily at rest on the seabed but acts as a restraint through weight and inertia as the cable is loaded. Most of the time, chains were vulnerable to abrasion from bottom sediments, wear between links and adjacent restraints, and wear between links. They were also susceptible to corrosion, which was known to be particularly bad for chain link components that were subjected to abrasion and wear. Poorly documented data exists regarding chain wear under different conditions and in different climates.

## 2. PROJECT OVERVIEW

### 2.1 PROBLEM STATEMENT:

- The process of a substance deteriorating due to a chemical reaction with its surroundings is called corrosion
- Metal corrodes when an exposed surface makes contact with a gas or liquid; exposure to warm temperatures, acids, and salts speed up the process.
- For example: The steel used for Ship anchoring Corrodes faster due to the salt contents of ocean

### 2.2 SCOPE OF THE PROJECT:

The proposed sample is useful to increase the corrosion resistance behaviour of mild steel. This process is also useful to increase the lifespan of the mild steel material. They protect against corrosion, wear, thermal stress and it can withstand abrasive conditions, but are not always applicable. The truth is, Zn-Ni coatings offer manufacturers valuable options for meeting ever-increasing regulatory, warranty, and performance requirements that affect their products. In reality, Zn-Ni coatings give manufacturers useful choices for satisfying the ever-increasing performance, warranty, and regulatory criteria that are relevant to their goods.

### 2.3 OBJECTIVE :

- To make the mild steel corrosion resistant
- To increase the lifetime of the steel
- Good performance in wear

## 3. LITERATURE REVIEW

- Yuwan Tian , Chaofang Dong , Gui Wang , Xuequn Cheng , Xiaogang Li "The effect of nickel on corrosion behaviour of high-strength low alloy
- Steel rebar in a concrete-pore-simulating solution: Zinc is a key component in both the electro galvanising and die-casting processes.
  The melting point of Zinc is 420oC. To safeguard steel components and structures, cadmium (Cd) and zinc (Zn) are used. via rusting.
  But any sort of Cd coating, including being a carcinogen and based on cyanide and Cd compounds the usage of Cd is an increasing problem for the environment and health

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- R.S. Bhat and V.B. Shet, Development and Characterization of Zn-Ni, Zn-Co and Zn-Ni-Co Coatings, Surf. Eng., 2020-A study on Ni-Zn multi-layered alloy coating from an aqueous bath at different current densities 2.0, 3.0, 4.0, 5.0 A/dm2 reveals that the corrosion property of the material increases to the optimal layer of deposition and then decreases.
  Zinc along with oxide plays a key role in semiconductors and fluorescent lamps. Zinc is mainly used as the galvanizing agent for mild steel to prevent its surface from corrosion and rust formation

- A. Tozer and I.H. Karahan, Structural and Corrosion Protection
  Properties of Electrochemically Deposited Nano-sized Zn-Ni Alloy - Zinc is a widely used element in the electro galvanizing process and dies casting process. The melting point of Zinc is 420oC. To safeguard steel components and structures, cadmium (Cd) and zinc (Zn) are used. via rusting. But any sort of Cd coating, including being a carcinogen and based on cyanide and Cd compounds the usage of Cd is an increasing problem for the environment and health.

- R.S. Bhat and V.B. Shet, Development and Characterization of Zn-Ni, ZnCo and Zn-Ni-Co Coatings-layered alloy coating from an aqueous bath at different current densities 2.0, 3.0, 4.0, 5.0 A/dm2 reveals that the corrosion property of the material increases to the optimal layer of deposition and then decreases.
  Zinc along with oxide plays a key role in semiconductors and fluorescent lamps. Zinc is mainly used as the galvanizing agent for mild steel to prevent its surface from corrosion and rust formation

- C. Muller, M. Sarret and M. Benballa, Some Peculiarities in the Codeposition of Zinc–Nickel Alloys- The key metal for galvanic conversion is zinc preventing rust in industrial steel building applications. Zinc-based metallic paints is used to safeguard steel components and structures.

- Corrosion of working chains continuously immersed in seawater Robert E. Melchers · Torgeir Moan · Zhen Gao- The chain is primarily at rest on the seabed but acts as a restraint through weight and inertia as the cable is loaded. Most of the time, chains were vulnerable to abrasion from bottom sediments, wear between links and adjacent restraints, and wear between links. They were also susceptible to corrosion, which was known to be particularly bad for chain link components that were subjected to abrasion and wear.

- S. Rashmi, L. Elias, and A. Chitharanjan Hegde, "Multilayered Zn-Ni alloy coatings for better corrosion protection of mild steel,"- Nickel has good ductile and malleable properties. The melting point of Nickel is 1453oC and the boiling point is 2913oC.

  Due to its high thermal stability and poor reaction to acids, it is widely used in the manufacturing of stainless steel and carbon steel.

## 5. EXPERIMENTAL PART:

A mild steel chain of diameter 6mm and height of 2.5cm is used as the base substrate. A standard 200ml beaker is used for electrolyte preparation. Initially, the chain sample is well cleaned with the help of de-ionized water and then treated with an ultrasonic cleaner at different frequencies to remove rust and surface impurities. The samples are treated with acetone before and after exposure to ultrasonic cleaner. The sample is then dipped in 10% diluted HCl solution for 2 minutes to activate the surface for effective coating. The chain acts as the anode while the stainless steel acts as the anode. The standard current density of 1 $A/dm^2$ is maintained for coating. Table-1 gives the electrolytic composition of Ni-Mg-Zn thin film,

**Table-1:** Electrolytic Bath Composition of Ni-Mg-Zn.

| Source Material | Concentration (g/l) |
|---|---|
| Nickel Sulphate | 60 |
| Nickel Chloride | 30 |
| Magnesium Sulphate | 30 |
| Zinc Sulphate | 15 |
| Tri-sodium citrate | 25 |
| Ammonium citrate | 80 |
| Boric Acid | 10 |
| Citric Acid | 10 |

$P^H$ of the bath is initially found to be 7 with the help of $p^H$ paper. The coatings were done at three different temperatures 30$^oC$, 50$^oC$, and 70$^oC$ from the same bath. The $p^H$ of the bath fluctuates between the values 4 and 7 and a timing of 30 minutes is provided for coating all three temperature samples.


**Fig-1 :** Electrolytic Bath Composition of Ni-Mg-Zn

## 6. RESULTS AND DISCUSSION

### 6.1-EIS (Electron Impedance Spectroscopy)- Corrosion Behaviour

The corrosion behaviour of the thin films coated at different temperatures was studied with the help of the EIS technique. Sodium chloride solution is used as a corrosion medium. Equivalent circuit of resistance 106Ω, 11.7Ω, 17.3Ω, 2.34Ω and capacitance of 7.72μF, 57.9μF, 249μF, 65.4μF is maintained for sample 1,2,3,4 respectively.

**Table-2 :** Electron Impedance Spectroscopy Results

| Sample Number | Ecorrosion (Voltage) | Icorrosion (Ampere) | Corrosion rate (mm/year) | Polarization resistance (Ω) |
|---|---|---|---|---|
| 1 | -0.80791 | 0.00015312 | 1.7792 | 237.13 |
| 2 | -0.90319 | 0.0005941 | 6.9034 | 60.823 |
| 3 | -0.57368 | 0.00020945 | 2.4338 | 146.47 |
| 4 | -0.72271 | 0.00053883 | 6.2612 | 38.111 |

### 6.2-XRD INTERPRETATION

The X-Ray diffraction pattern is one of the popular techniques used to find the crystal size of the sample. XRD machine type of Goniometer is used for analysis. X-rays of wavelength 1.54060Å with continuous scanning mode are used to find the crystal parameters. Current and voltage of 30mA and 45kV are set for the anode material which is copper. A temperature of 25°C is maintained throughout the process of scanning. Ni-Mg-Zn coated at 30°C and 50°C is having a crystal structure of cubic while the sample coated at 70°C is having orthorhombic crystal. XRD peaks of Ni-Mg-Zn coated at 30°C and 50°C is having miller indices of (411), (712), (701) while the sample coated at 70°C is having miller indices of (1210) and (2108).

The size of the crystal is found using the following relation,

$$D = \frac{0.945 \times \lambda}{\beta \times \cos\theta}$$

Micro-strain (ε) of the crystal is found using the relation given below,

$$\varepsilon = \frac{\beta \times \cos\theta}{4}$$

Dislocation density (**δ**) is found by the following relation,

$$\boldsymbol{\delta} = \frac{\mathbf{1}}{\mathbf{D^2}}$$

**Table-3 :** XRD Results

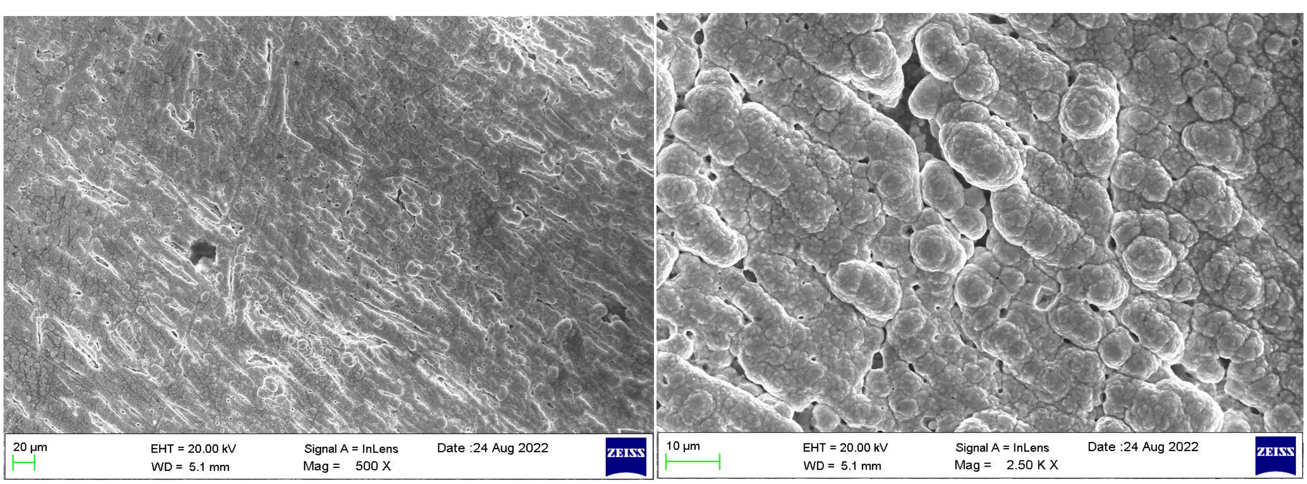
| **Particulars** | **Ni-Zn-Mg at 30°C** | **Ni-Zn-Mg at 50°C** | **Ni-Zn-Mg at 70°C** |
|---|---|---|---|
| β ($\times 10^{-3}$ radians) | 2.233 | 2.679 | 1.3395 |
| θ (°) | 21.478 | 21.492 | 22.319 |
| Particle Size-D (nm) | 7.002 | 5.84 | 0.0012 |
| Micro-Strain ($\times 10^{-4}$ ε) | 5.194 | 6.232 | 3.098 |
| Dislocation Density **(δ)** **(**×1011 m2) | 20399 | 29320 | 0.07243 |
| d-Spacing (Å ) | 2.105 | 2.104 | 2.030 |

**6.3-SEM STUDY**

A scanning electron microscope (SEM) projects and scans a focused stream of electrons over a surface to create an image. The electrons in the beam interact with the sample, thereby producing various signals that can be used to obtain information about the surface's topography and composition.

Figure 1 shows the SEM images of the Ni-Mg-Zn alloy coatings acquired at c.d. It should be observed that the micro-structure of the coatings closely correlates with the deposition c.d., and the surface appearance significantly changes with c.d., going from a flaky pyramidal structure at 1.0 A dm-2 to a smooth porous structure at high deposition c.d. The anti-corrosive properties and aesthetic appeal of the alloy coatings with c.d. were reflected in the variance in surface topography.

**Sample 1:**



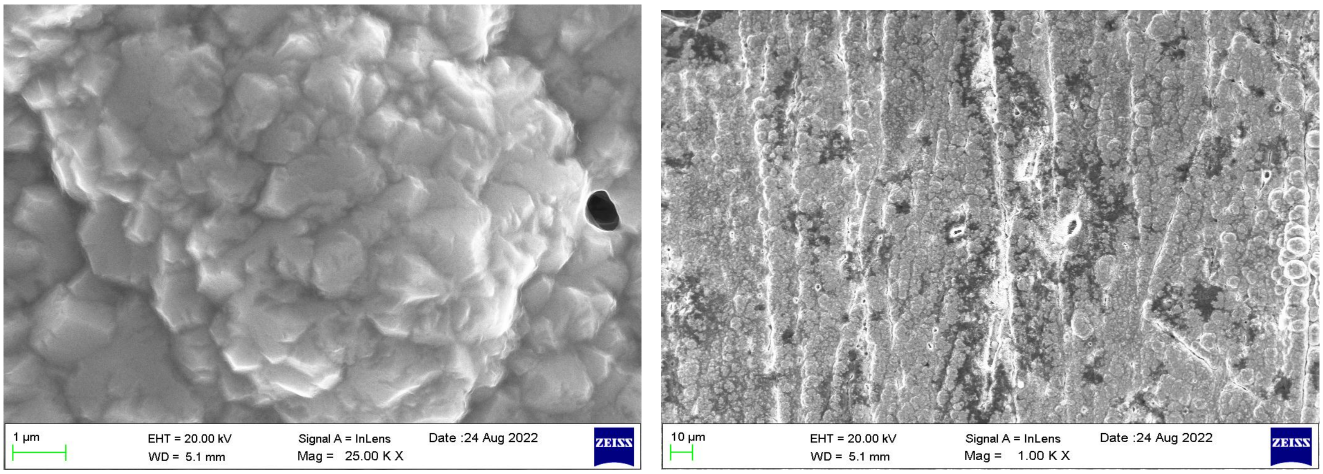



**Fig-2 :** SEM images of Ni-Mg-Zn coating of sample 1(30°C) deposited at c.d. 1.0 A $dm^{-2}$ from optimal bath.

**Sample 2:**

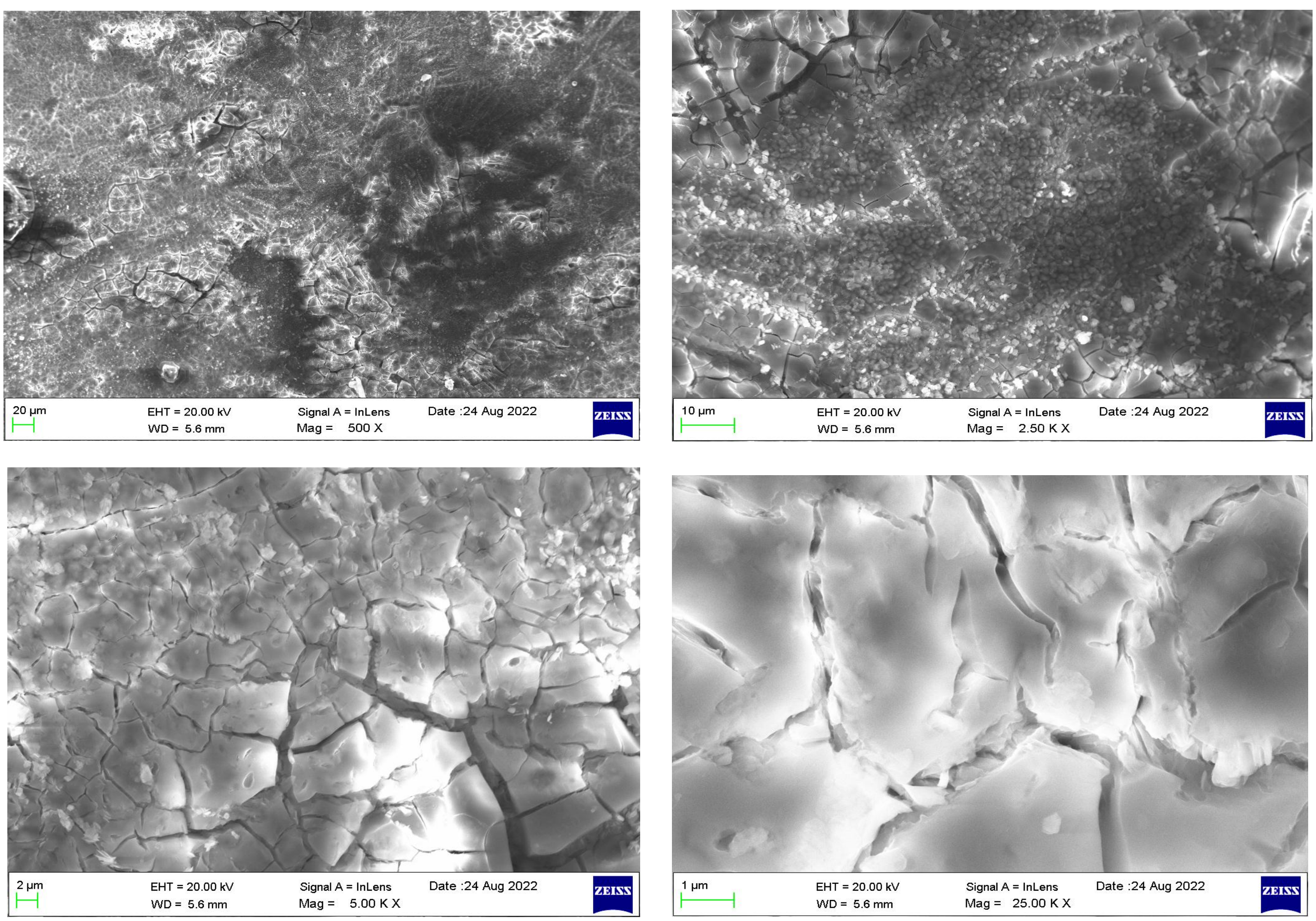



**Fig-3 :** SEM images of Ni-Mg-Zn coating of sample 2(50°C) deposited at c.d. 1.0 A $dm^{-2}$ from optimal bath.

**Sample 3:**

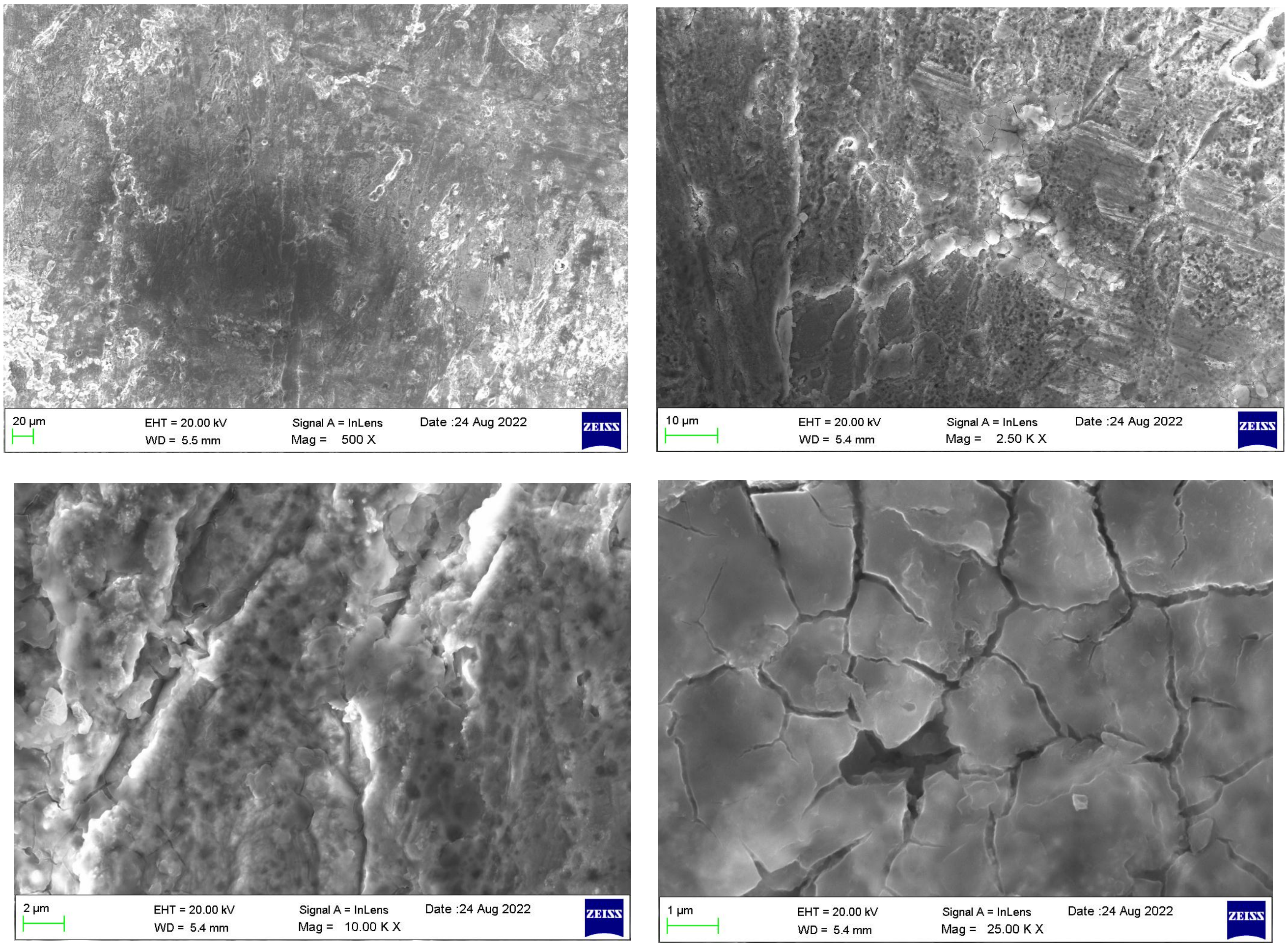



**Fig-4 :** SEM images of Ni-Mg-Zn coating of sample 3(70°C) deposited at c.d. 1.0 A $dm^{-2}$ from optimal bath.

### 6.4-EDS (Energy dispersive X-ray spectroscopy)

The qualitative and semi-quantitative X-ray micro-analytical technique known as Energy Dispersive X-ray Spectroscopy (EDXS), sometimes referred to as EDX Analysis and EDS Analysis, can reveal information on the elemental composition of a sample. Metals and specific kinds of polymeric materials with distinctive elemental fingerprints can be identified using it.

The information generated by Energy Dispersive X-ray Analysis can also help in identifying coatings present in the material.

**Sample 1:**

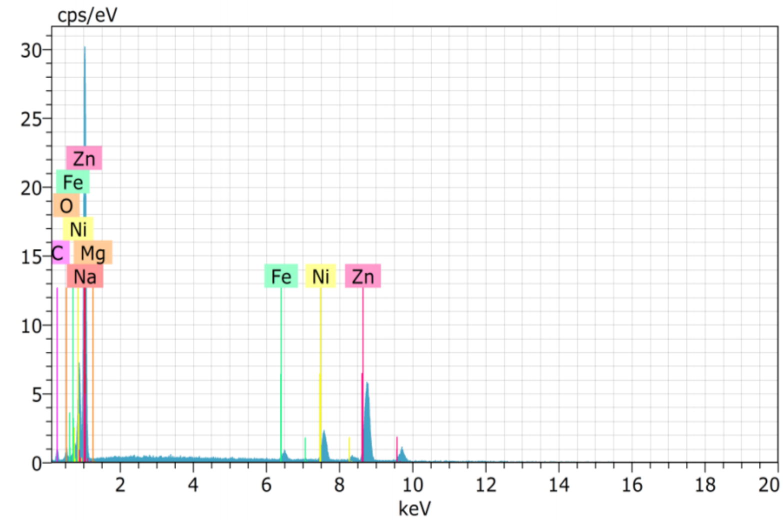



**Fig-5 :** EDS Result of Sample 1.

Spectrum: BM 1562

El AN Series unn. C norm. C Atom. C Error (1 Sigma)

[wt.%] [wt.%] [at.%] [wt.%]

-----------------------------------------------------

Na 11 K-series 29.94 42.77 52.21 2.00

Zn 30 K-series 24.64 35.20 15.11 0.82

C 6 K-series 7.28 10.40 24.31 2.11

Ni 28 K-series 5.43 7.75 3.71 0.23

O 8 K-series 1.52 2.17 3.80 0.52

Fe 26 K-series 1.19 1.71 0.86 0.09

Mg 12 K-series 0.00 0.00 0.00 0.00

-----------------------------------------------------

Total: 70.00 100.00 100.00

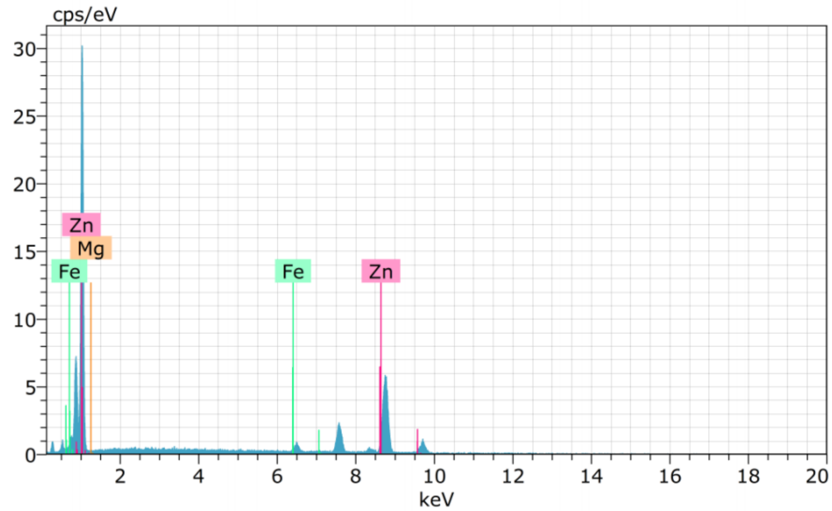



**Fig-6 :** EDS Result of Sample 1

Spectrum: BM 1562

El AN Series unn. C norm. C Atom. C Error (1 Sigma)

[wt.%] [wt.%] [at.%] [wt.%]

-----------------------------------------------------

Zn 30 K-series 29.24 95.34 93.89 0.97

Fe 26 K-series 1.28 4.17 4.81 0.10

Mg 12 K-series 0.15 0.49 1.30 0.06

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Total: 30.67 100.00 100.00

**Sample-2:**

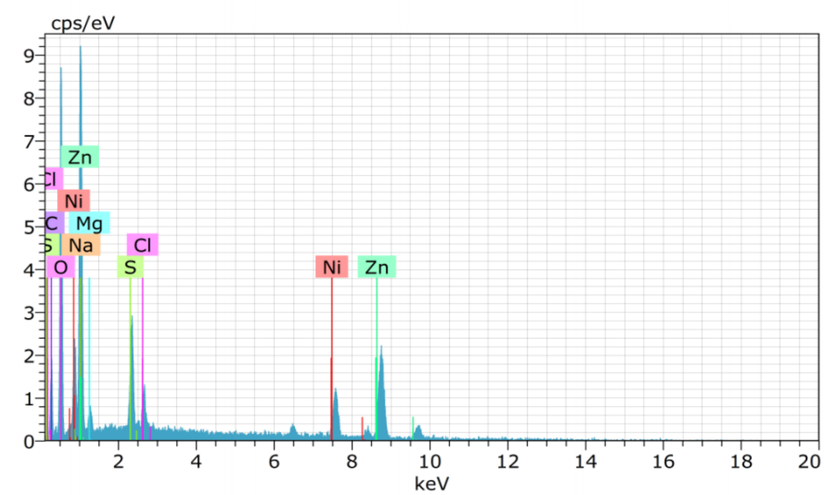


**Fig-7 :** EDS Result of Sample 2

Spectrum: BM 1563

El AN Series unn. C norm. C Atom. C Error (1 Sigma)

[wt.%] [wt.%] [at.%] [wt.%]

-----------------------------------------------------

O 8 K-series 28.25 38.78 45.70 4.41

Na 11 K-series 13.85 19.02 15.60 0.98

C 6 K-series 13.79 18.94 29.72 3.17

Zn 30 K-series 10.03 13.77 3.97 0.42

S 16 K-series 2.74 3.76 2.21 0.15

Ni 28 K-series 2.11 2.89 0.93 0.12

Mg 12 K-series 1.09 1.49 1.16 0.12

Cl 17 K-series 0.98 1.34 0.71 0.08

-----------------------------------------------------

Total: 72.83 100.00 100.00

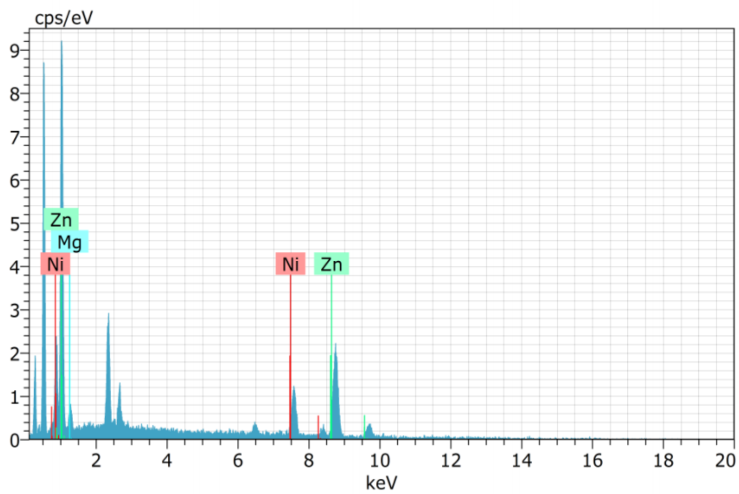


**Fig-8 :** EDS Result of Sample 2

Spectrum: BM 1563

El AN Series unn. C norm. C Atom. C Error (1 Sigma)

[wt.%] [wt.%] [at.%] [wt.%]

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Zn 30 K-series 16.67 67.36 54.51 0.68

Ni 28 K-series 4.96 20.04 18.07 0.25

Mg 12 K-series 3.12 12.60 27.43 0.29

-----------------------------------------------------

Total: 24.74 100.00 100.00

**Sample-3:**

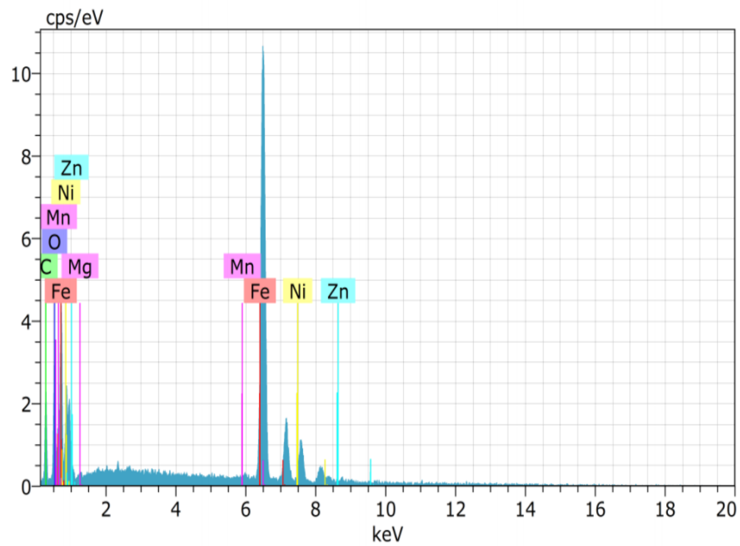


**Fig-9 :** EDS Result of Sample 3

Spectrum: BM 1564

El AN Series unn. C norm. C Atom. C Error (1 Sigma)

[wt.%] [wt.%] [at.%] [wt.%]

-----------------------------------------------------

Fe 26 K-series 29.22 45.67 20.69 0.86

C 6 K-series 13.90 21.72 45.75 2.85

O 8 K-series 10.67 16.68 26.37 1.99

Mn 25 K-series 5.24 8.19 3.77 0.21

Ni 28 K-series 4.22 6.60 2.84 0.20

Zn 30 K-series 0.60 0.93 0.36 0.09

Mg 12 K-series 0.13 0.20 0.21 0.05

-----------------------------------------------------

Total: 63.99 100.00 100.00

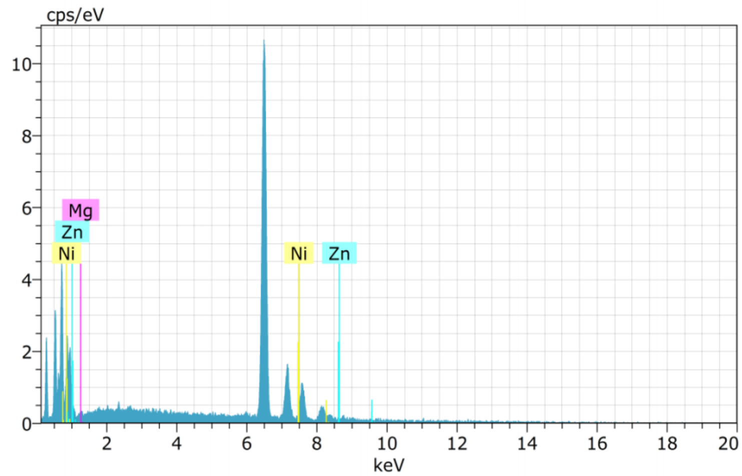


**Fig-10 :** EDS Result of Sample 3

Spectrum: BM 1564

El AN Series unn. C norm. C Atom. C Error (1 Sigma)

[wt.%] [wt.%] [at.%] [wt.%]

-----------------------------------------------------

Ni 28 K-series 4.06 85.27 77.79 0.20

Zn 30 K-series 0.35 7.40 6.06 0.08

Mg 12 K-series 0.35 7.33 16.15 0.07

-----------------------------------------------------

Total: 4.76 100.00 100.00

**6.5-Roughness Test:**

To quickly and precisely determine a material's surface texture or surface roughness, a roughness tester is utilized. A roughness tester displays the mean roughness value (Ra) and the measured roughness depth (Rz) in microns (m).

The greater the corrosion resistance, the lower the roughness values.

**Fig-11 :** Roughness test

**Table-4 :** Roughness Test Results

| | **Ra (Micrometer)** | **Rz (Micrometer)** | **Ry (Micrometer)** |
|---|---|---|---|
| **Sample 1 (30)** | 0.02 | 0.17 | 0.03 |
| **Sample 2 (50)** | 0.07 | 0.65 | 0.10 |
| **Sample 3 (70)** | 0.08 | 0.72 | 0.11 |

**6.6-Wear:**

Surface interactions, specifically the removal and distortion of material from a surface as a result of the mechanical action of the contacting item through motion, constitute the process of wear.

**Table-5 :** Wear Test Results

| MATERIAL (MILD STEEL) | WEAR (microns) | FRICTIONAL FORCE (N) | COEFFICIENT OF FRICTION | TEMPERATURE (°C) |
|---|---|---|---|---|
| **SAMPLE 1 30** | 17 | 6.7 | 0.66 | 29 |
| **SAMPLE 2 50** | 19 | 8.0 | 0.81 | 31 |
| **SAMPLE 3 70** | 5 | 6.4 | 0.63 | 32 |

**WEAR (microns) vs TIME (sec)**

**Sample-1:**

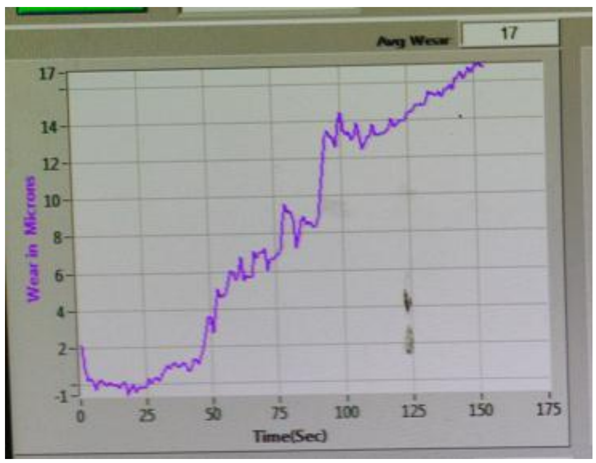


**Fig-12 :** WEAR (microns) vs TIME (sec) of Sample 1

**Sample-2:**

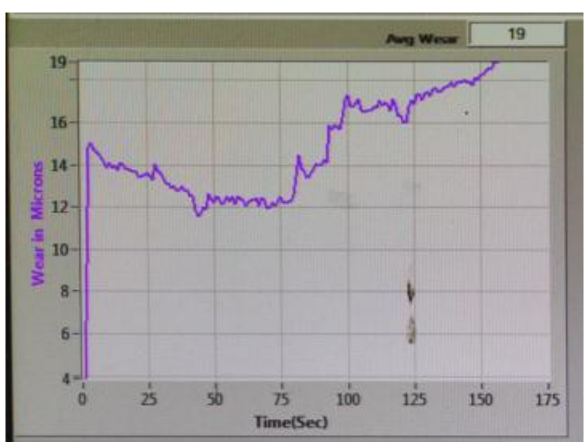


**Fig-13 :** WEAR (microns) vs TIME (sec) of Sample 2

**Sample-3:**

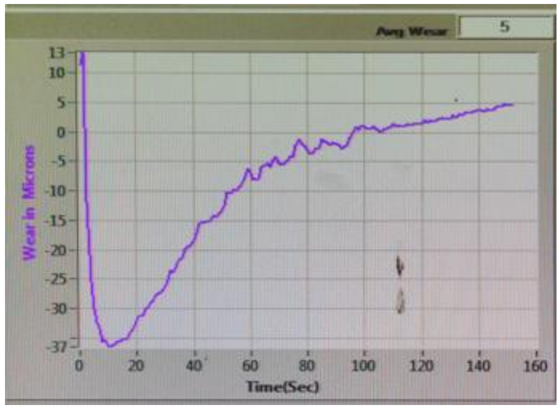


**Fig-14 :** WEAR (microns) vs TIME (sec) of Sample 3

**FRICTIONAL FORCE (N) vs TIME (sec)**

**Sample-1:**

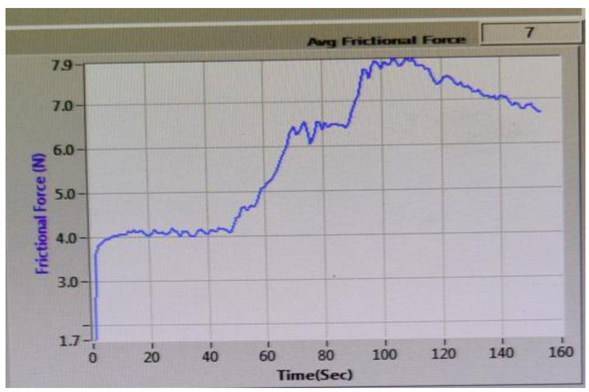


**Fig-15 :** FRICTIONAL FORCE (N) vs TIME (sec) of Sample 1

**Sample-2:**

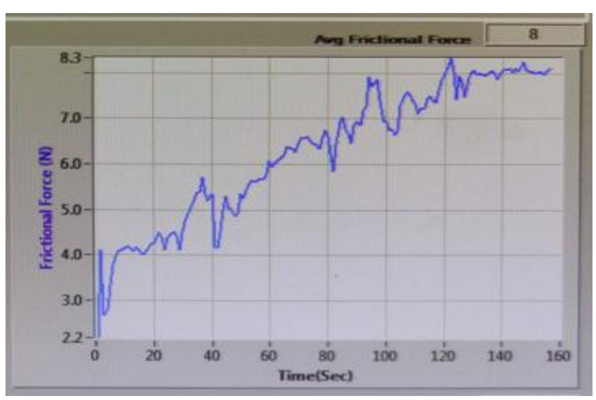


**Fig-16 :** FRICTIONAL FORCE (N) vs TIME (sec) of Sample 2

**Sample-3:**

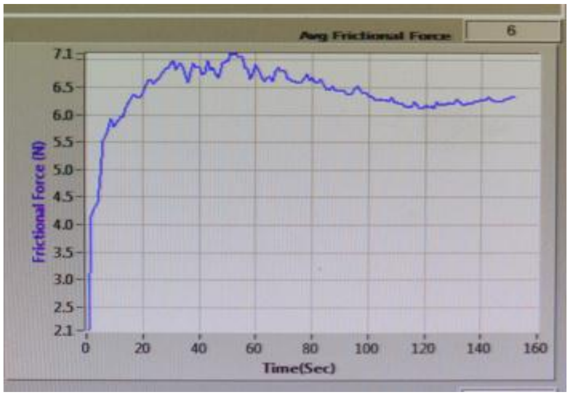


**Fig-17 :** FRICTIONAL FORCE (N) vs TIME (sec) of Sample 3

**COEFFICIENT OF FRICTION vs TIME (sec)**

**Sample-1:**


**Fig-18 :** COEFFICIENT OF FRICTION vs TIME (sec) of Sample 1

**Sample-2:**

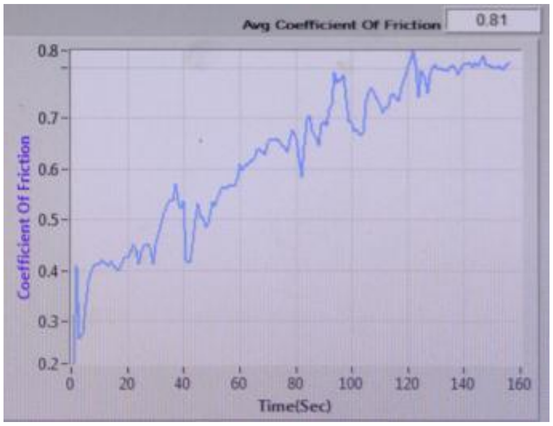


**Fig-19 :** COEFFICIENT OF FRICTION vs TIME (sec) of Sample 2

**Sample-3:**

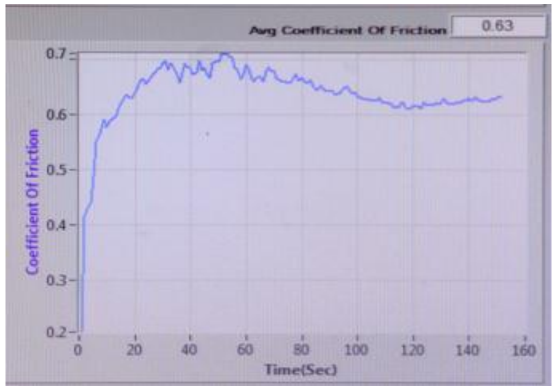


**Fig-20 :** COEFFICIENT OF FRICTION vs TIME (sec) of Sample 3

**TEMPERATURE(°C) vs TIME(sec)**

**Sample-1:**

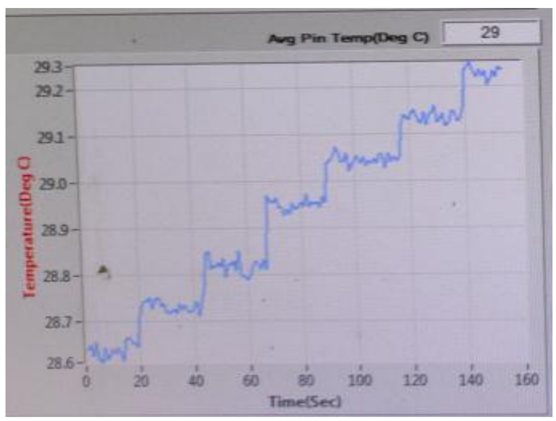


**Fig-21 :** TEMPERATURE(°C) vs TIME(sec) of Sample 1

**Sample-2:**

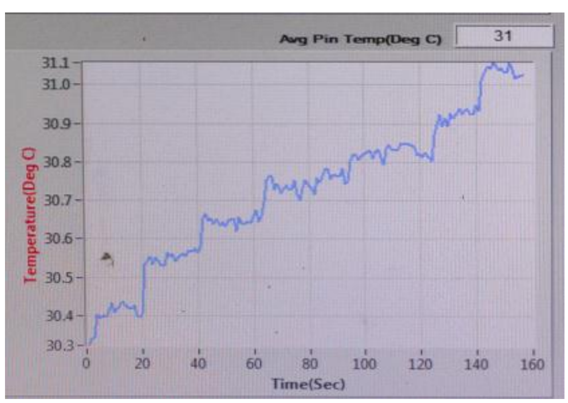


**Fig-22 :** TEMPERATURE(°C) vs TIME(sec) of Sample 2

**Sample-3:**

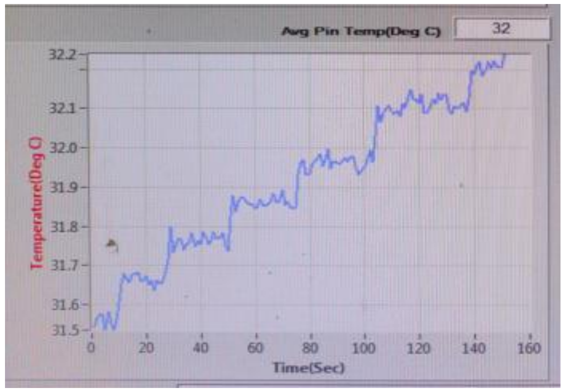


**Fig-23 :** TEMPERATURE(°C) vs TIME(sec) of Sample 3

## CONCLUSION:

A stable bath has been developed for electroplating of Zn-Ni-Mg alloy coatings on mild steel using the dip method. Experimental investigations were performed with the following results.

- The EIS (Electron Impedance Spectroscopy) results indicated that sample 1(at 30) and sample 2(at 70) give better corrosion resistance while compared with other samples.
- The XRD results indicated that the intensity of peak Zn was the prominent step responsible for improved corrosion resistance of Mild steel chain.
- The wear result indicates that sample-3 performs better wear resistance.

## 7. REFERENCES:

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