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Electrodeposition of Ni-Zn-Cu Alloys with Varying Cu Contents Enhances Mild Steel Properties

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Abstract
This work examined the mechanical characteristics, phase structure, and morphology of Ni-Zn-Cu alloy coatings as a function of copper concentration. A mild steel substrate was electrochemically plated using ternary Ni-Zn-Cu alloys that had been produced beforehand. The Cu content was varied to create four distinct baths. The coating was made smooth by deposition, which was carried out for 20 minutes with a constant current density of 20 mAcm-2, pH of 3, and a constant magnetic field of 4.5 mT. Investigational alloy coatings were studied for their mechanical characteristics, surface morphology, hardness, and crystal structure. The findings revealed that the crystal structure of every single alloy that was deposited is a face-centered cubic. As the concentration of Cu increases, the lattice parameter decreases and the shape of the alloys changes from big nodules to smaller ones. The application of Ni-Zn-Cu alloys to substrates improves their mechanical characteristics, leading to increased use of mild steel in tooling, building, and transportation.

Key Words: Ni-Zn-Cu alloys; Mild steel; Electrodeposition; Cu Concentration; Mechanical properties

Introduction

Electroplating is a well-known traditional method for depositing a range of alloy coatings on a number of surfaces. Non-ferrous materials, on the other hand, have a number of challenges, including poor substrate-coating adhesion, whereas ferrous substrates are very easy to electrodeposit [1]. For many years, low carbon steel with a carbon content of 0.13 percent has been the most prevalent steel used in vehicle body panels and structural components. Their extensive use is due to a combination of inexpensive cost, great formability, weld ability, and high quality look after painting. Low carbon steel comes in a variety of grades that are utilized in the automobile sector [2]. The Zn-Ni alloy provides corrosion resistance. In a salt spray test, Ni concentration in the range of 10-15% resulted in corrosion resistance. In the automobile business, Zn-Ni is a suitable choice. The hardness of the Zn-Ni surface is much higher than that of uncoated steel. Zn-Ni coated steel has an excellent weld ability. It has a greater toughness and a lighter covering [3]. Dealloying a Zn-rich Zn-Cu alloy lowers the Zn concentration and produces open-framework Nano-porous structures, which are useful for energy storage, biosensors, and catalysis [4]. Because of their remarkable corrosion resistance in both acidic and alkaline environments, Ni-Cu alloys are particularly common [5, 6]. The micro hardness of pulse plated nickel coatings rose, and the grain size of deposits shrank when the duty cycle was reduced [7]. The electrodeposition of a Zn-Ni coating with a high nickel concentration inhibits Ni reduction significantly. The addition of Zn to the Ni lattice also resulted in a significant reduction in grain size [8].

The aim of this work is to study the electrodeposition process of ternary Ni-Zn-Cu alloy deposited on a mild steel substrate by the method of electrodeposition. This alloy was deposited to obtain a decorative surface on mild steel, to protect the surface from corrosion and to make it long lasting. The main focus of this research is to understand the effect of Cu concentration on mechanical properties, composition, morphology and phase structure of the Ni-Zn-Cu alloy coating.

Materials and Method

The electrodeposition was carried out using sulphate bath consisted of $NiSO_4.7H_2O$, $CuSO_4.7H_2O$, $ZnSO_4.7H_2O$, H_3BO_3 (as buffering agent) and saccharin (as additive), prepared by using AnalaR grade reagents and distilled water. The optimal bath conditions and operating parameters of the ternary Ni-Zn-Cu alloy bath with the variation of copper concentration is shown in Table 1. The electroplating process was carried out in a stirred solution on a pre-cleaned mild steel substrate with 1 cm2 exposed surface area. The solution was stirred at 600 rpm and 45°C for 5 min. Saccharin was used in the bath for obtaining uniformity in coating. Graphite was used as anode with exposed surface area of 2 cm^2 which is greater than cathode. The electrodeposition was accomplished for 20 min under magnetic field which was applied with the help of electromagnet. The applied magnetic field, current density, pH was kept constant at 4.5 mT, 20 $mAcm^{-2}$ and 3 respectively. The beaker was kept inside the electromagnet. The anode was kept 2 cm away from cathode. The whole electrodeposition process was carried out at room temperature. The detail of composition used during electrodeposition is given in Table 1.

Table 1: Composition of baths prepared at different concentrations of Cu

Sample no.	$NiSO_4.7H_2O$ (g/l)	$ZnSO_4.7H_2O$ (g/l)	$CuSO_4.7H_2O$ (g/l)	H_3BO_3 (g/l)	Saccharin (g/l)
01	40	35	0	30	1
02	40	35	10	30	1
03	40	35	20	30	1
04	40	35	30	30	1

The structure formation of Ni-Zn-Cu alloy coating was studied by using X-ray diffraction. A Cu objective was used to quantify the samples at a scan rate of 0.01°/sec with the step size of 0.05°; the scan area was ranged from 5° to 80°. The XRD patterns were obtained using an X-ray source with a 45 kV accelerating voltage and 40 mA current. To determine the morphology of the surface, scanning electron microscopy was used to examine the samples. The mechanical properties were measured using Shimadzu AGX-057B machine and Vickers hardness tester with AKASHI (HM-102) was used. Hardness measurements were taken with a 200 gf applied load for 10 seconds. The diamond indenter of pyramid shape was used for microhardness measurement.

Result and Discussions

The structure of deposited Ni-Zn-Cu alloy on mild steel substrate with the Cu concentration of 0, 2.2, 4.4 and 6.6 g were characterized by x-ray diffraction analysis and the data is represented in Fig 1. The crystal structure of all the samples is face centered cubic and lattice parameters were calculated from XRD data using procedure [9].

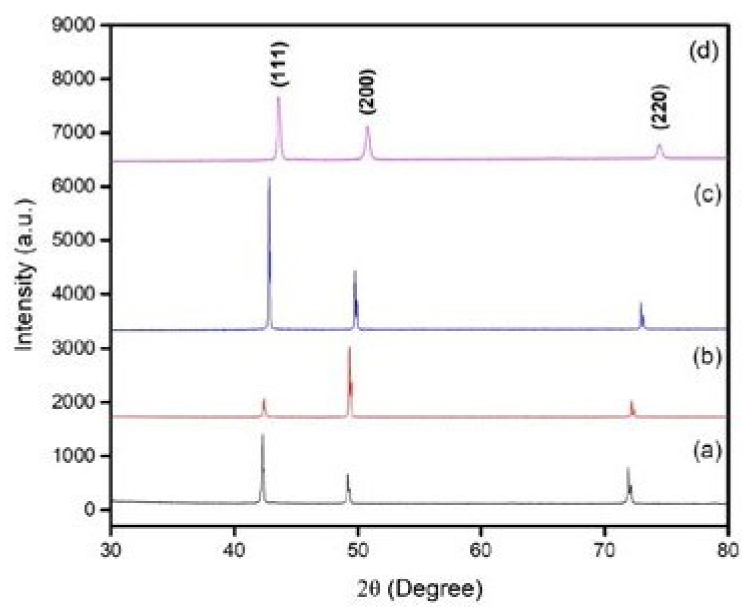

Figure 1: Stacking of X-ray diffraction patterns of Ni-Zn-Cu alloy coatings for all samples

Figure 1 shows the X-ray diffraction pattern of Ni-Zn-Cu alloy at different Cu concentrations with sharp peaks at 2θ=42.3°, 49.2° and 71.9° which represent the miller indices (111), (200) and (220) respectively. Peaks shifting from sample 1 to 4 towards the right, i.e. to higher 2θ values as Cu concentration is increases. This may be associated with a change in composition of the alloy [6].

The crystallites size of Ni-Zn-Cu alloy calculated by using Scherrer formula [10].

$$\text{Crystallites size(nm)} = \frac{0.9 \times \lambda}{\beta \times \text{Cos}\theta}$$

Where λ=1.54 nm is the wavelength, β is full width with half-maximum value (FWHM) and θ is the diffraction angle. The values of β and θ are calculated from X-ray diffraction pattern of the deposited alloy. the obtained data of lattice constant and crystallite size is given in the Table 2.

The graph between Cu concentration and Crystallite size is plotted and the effect of Cu concentration is observed on the Crystallites size of the deposited Ni-Zn-Cu alloy. Fig. 2 shows that the crystallites size is decreased by increasing Cu concentration in the deposits, which can be attributed to the increasing of the numbers of Cu atoms within the fcc Ni-Zn lattice it causes the increase of lattice strain which will further reduce the growth rate of crystallite. Consequently, it leads to a smaller crystallites size [11]. The lattice parameter "a" is decreased by increasing Cu concentration in the deposits. This can be attributed to the small atom radius of Cu (0.128 nm) [12]. The incorporation of small atoms into the lattice of the film would shrink the lattice and decrease the lattice parameters as shown in Fig.3.

Table 2: Effect of Cu concentration on Crystallite size and lattice parameter of Ni-Zn-Cu alloy

Sample no.	Cu concentration (g)	Crystallite size (nm)	Lattice parameter (Å)
01	0	42.2	3.7085
02	2.2	64.1	3.6985
03	4.4	50.2	3.6655
04	6.6	23.0	3.6007

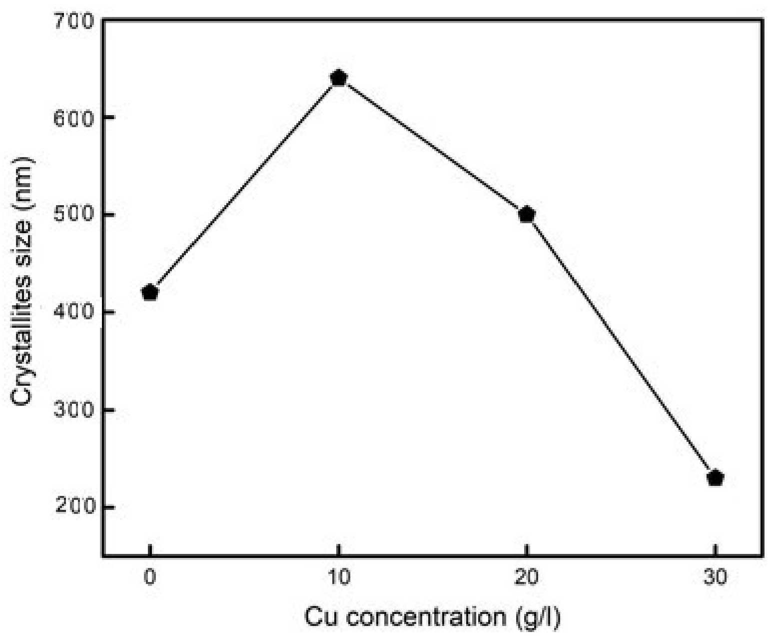

Figure 2: Effect on Crystallites size of Ni-Zn-Cu alloy coatings at various Cu contents

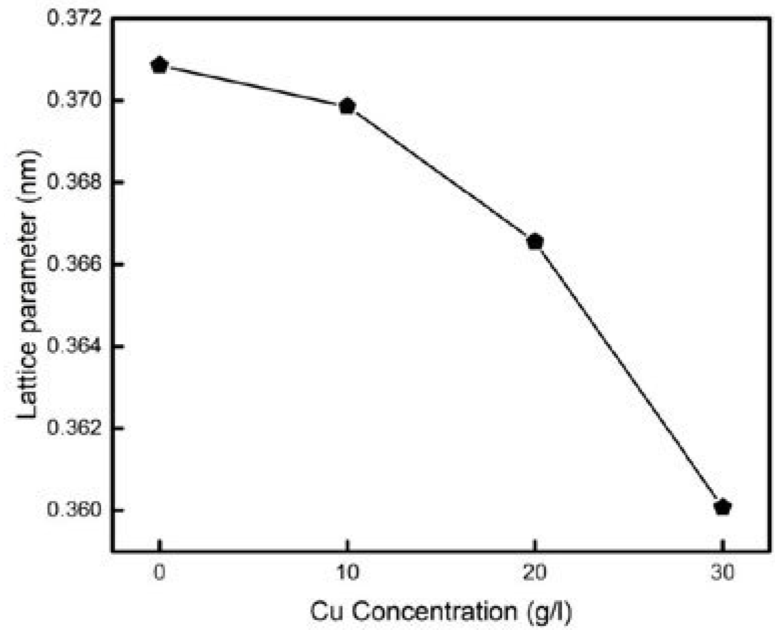

Figure 3: Effect on lattice parameter of Ni-Zn-Cu alloy coatings at various Cu contents

The morphology of the deposited alloy was tested by scanning electron microscope. The morphology of the sample with and without Cu addition was tested and the clear difference was observed in the SEM images. The SEM was performed at the magnification of x40 and x100 at the resolution of 1mm, 500μm and 100μm respectively with applied voltage of 5kV.

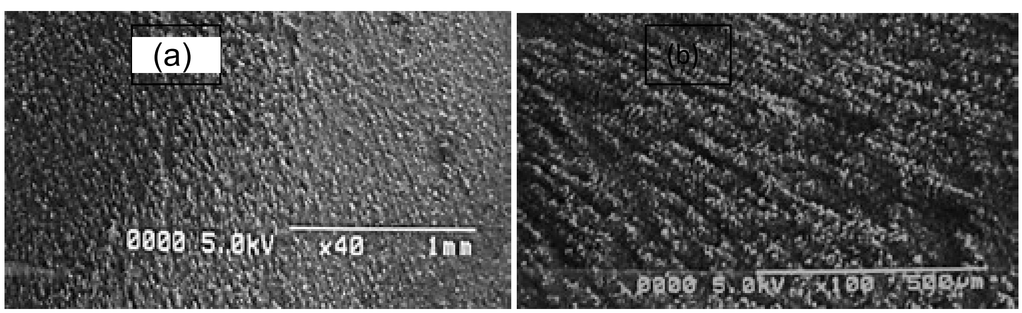

Figure 4: SEM images of Ni-Zn alloy without Cu concentration

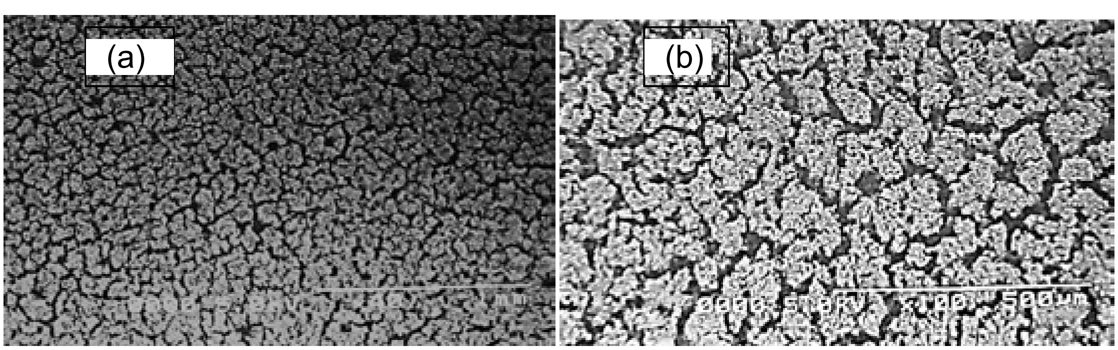

Figure 5: SEM images of Ni-Zn-Cu alloy with Cu concentration

Fig. 4(a) shows that the morphology of the Zn-Ni coating is based on rough large nodules. The surface of the coating does not look smooth. In Fig. 4(b) it can be seen that the structure of the nodules is blurry and not clearly visible and the voids on the surface of coating can be seen. Fig. 5(a) shows that the morphology of the Ni-Zn-Cu alloy has small nodules that are homogenously distributed. The structure of the deposited alloy is clearly visible. The coating surface has voids and major cracks can be seen on the surface of coating this could be due to the fact that stress on the surface increases with the addition of Cu concentration. The thickness of the coating can also be related to the formation of voids as more mass is being deposited due to which the stress is increasing on the surface. As the grain size is decreasing, it can be related to micro hardness of coating which shows that the micro hardness is decreasing with decrease in Crystallite size and increase in Cu concentration. In Fig. 5(b) it could also be seen that only one patch of the coating where cracks and voids are not present looks smooth and has refined grain size that cannot be distinguish by naked eye.

The mechanical properties including yield stress, ultimate tensile strength, Microhardness and elongation of the deposits are discussed below along with thickness of the Ni-Zn-Cu alloy coatings.

Thickness is referred as the amount of alloy deposited on material. The data obtained for calculations of thickness is given in Table 3.

Table 3: Thickness of Ni-Zn-Cu alloy coatings at various Cu concentrations

Sample no.	Concentration of Cu (g)	Thickness (µm)
01	0	12.49
02	2.2	12.36
03	4.4	24.51
04	6.6	36.48

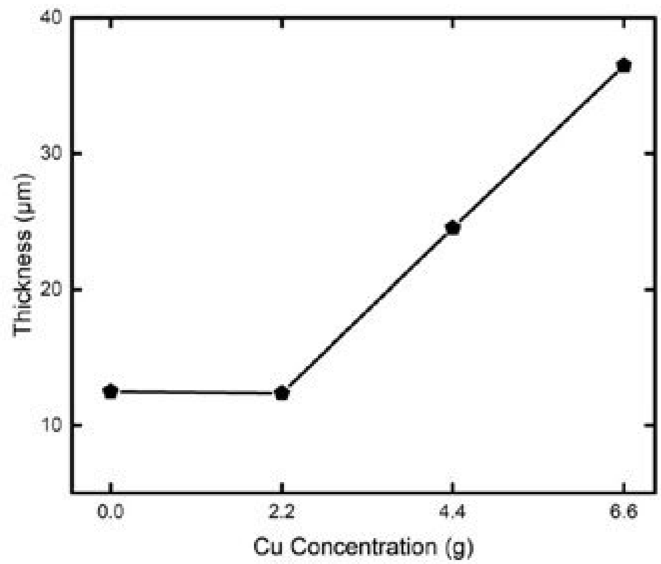

Figure 6: Effect of Cu concentration on Thickness of Ni-Zn-Cu alloy coatings at various Cu contents

The graph was plotted between thickness and variation of Cu concentration in which variation of Cu concentration is on x-axis and thickness is on y-axis. The thickness of the coating is increasing as the Cu concentration is increasing. There is a strange 1% decrease in the thickness of the coating at 2.2 g Cu concentration after which the thickness of the deposit increases with increase in concentration of Cu. This could be due to the change in microstructure of the coating with the addition of Cu [13].

Ultimate tensile strength is the ability of material's resistance to deformation under the action of applied tensile load. Micro hardness is the test of hardness by applying small amount of load on material. The ultimate tensile strength (UTS) and micro hardness of mild steel is 336.444 MPa and 255.002 HVN respectively.

Table 4: Micro hardness and UTS of Ni-Zn-Cu alloy coatings at various Cu concentrations

Sample no.	Concentration of Cu (g)	Ultimate Tensile Strength (MPa)	Microhardness (HVN)
01	0	348.954	518.138
02	2.2	367.099	473.779
03	4.4	379.787	454.789
04	6.6	393.349	424.356

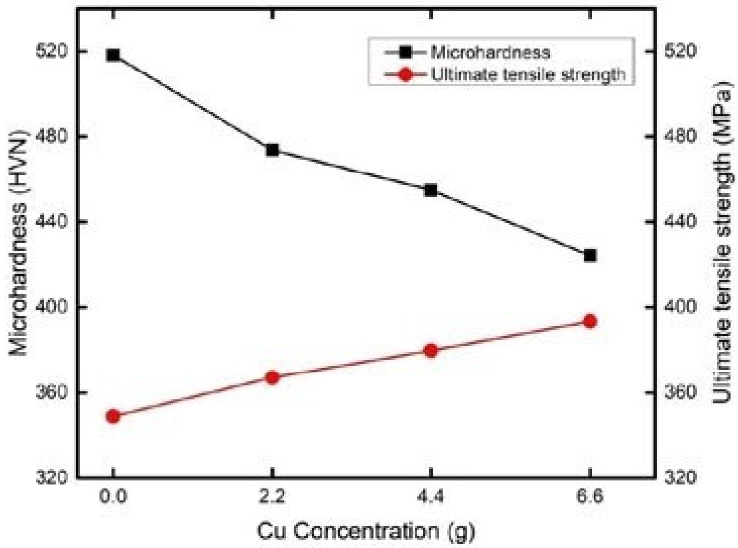

Figure 7: Effect of Cu Concentration on Micro hardness and UTS at various Cu contents

In Fig. 7 variation in ultimate tensile strength and micro hardness at different Cu concentration is shown, in which variation of Cu concentration is on x-axis, ultimate tensile strength and micro hardness are on y-axis. The ultimate tensile strength and micro hardness of bare mild steel was lower than that of Ni-Zn alloy coated mild steel. With the increase in Cu, content the ultimate tensile strength is increasing and micro hardness is decreasing. It is reasonable to attribute the higher tensile strength to higher ductility due to less saccharin addition in the electrolyte solution [14]. The decrease in micro hardness can be attributed to the fact that grain size and the micro hardness are almost the same, and the surface micro hardness increases with the increment of the grain size, the decrease in the hardness could be due to the grain refinement effect [15].

Elastic modulus is the ability of a substance to resist the deformation when stress is applied on it. Yield stress is the force needed to be applied on an object for changing it from elastic deformation to plastic deformation. The elastic modulus and yield stress of mild steel substrate is 200.955 GPa and 240.766 MPa respectively.

Table 5: Elastic Modulus and Yield Stress of Ni-Zn-Cu alloy coatings at various Cu contents

Sample no.	Concentration of Cu (g)	Yield stress after deposition (MPa)	Elastic Modulus after deposition (GPa)
01	0	295.367	231.370
02	2.2	263.186	230.129
03	4.4	258.092	229.990
04	6.6	246.744	225.208

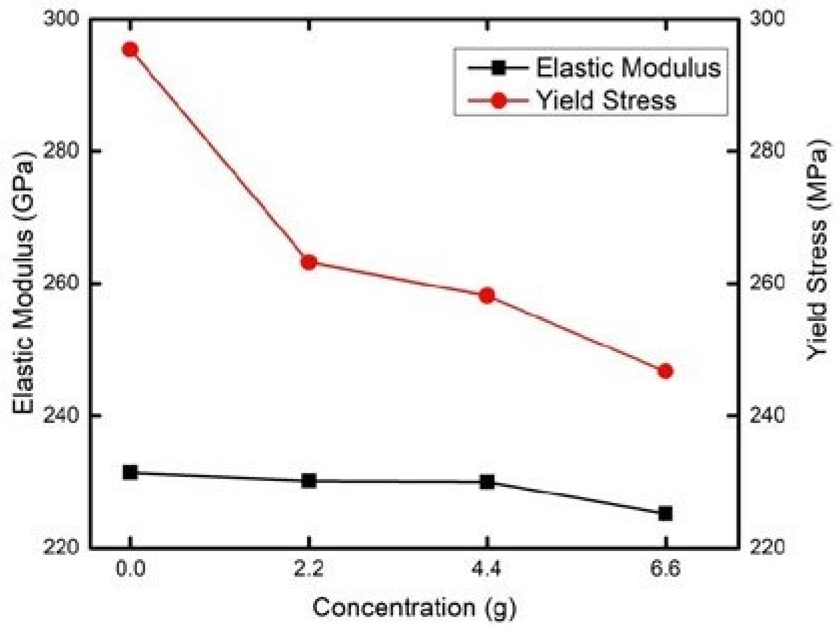

Figure 8: Variation in Elastic modulus with Cu concentration of Ni-Zn-Cu alloy coatings

In Fig. 8 variation in elastic modulus and yield stress at different Cu concentration is shown, in which Cu concentration is on x-axis, yield stress and elastic modulus are on y-axis. It could be seen that both elastic modulus and yield stress are decreasing. By increasing Cu concentration in the deposit, the yield stress tends to decreases. For 2.2, 4.4, 6.6 g of Cu concentration the yield stress decreases about 11%, 13% and 16.4% respectively. This could be due to the effect of strain rate on the deposits. The elastic modulus of Ni-Zn alloy deposits increases by 15.14%. Whereas: the elastic modulus decreases by 0.54%, 0.60% and 2.66% for 2.2, 4.4 and 6.6 g of Cu concentration respectively.

Elongation is the measure of deformation that occurs eventually before the material breaks when subjected to tensile load.

The data for elongation of mild steel with and without deposition is given in table below:

Table 6: Elongation of Ni-Zn-Cu alloy coatings at various Cu concentrations

Sample no.	Concentration of Cu (g)	Elongation before deposition (%)	Elongation after deposition (%)
01	0	18.784	36.634
02	2.2	18.784	39.503
03	4.4	18.784	39.911
04	6.6	18.784	40.224

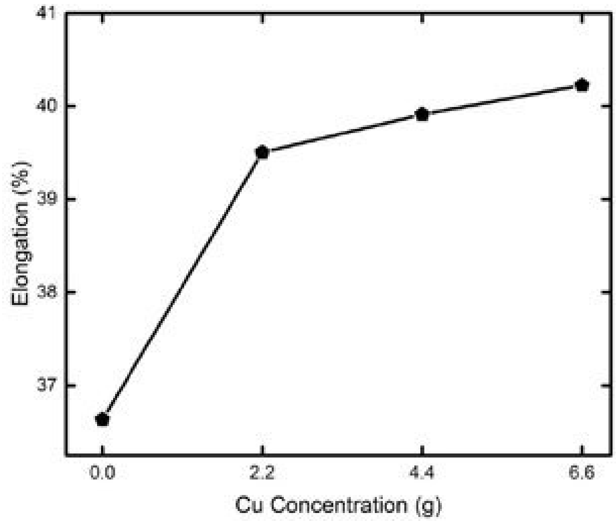

Figure 9: Variation in Elongation with Cu concentration of Ni-Zn-Cu alloy coatings

The graph was plotted between elongation and variation of Cu concentration in which variation of Cu concentration is on x-axis and elongation is on y-axis. The trend in Fig. 9 shows that the elongation is continuously increasing by increasing Cu concentration in the alloy. At 0 g the elongation is 36.634; 95.03% more than bare mild steel. As compare to 0 g, the Cu with 2.2, 4.4 and 6.6 g has percentage increase of about 8, 9 and 10% in elongation respectively.

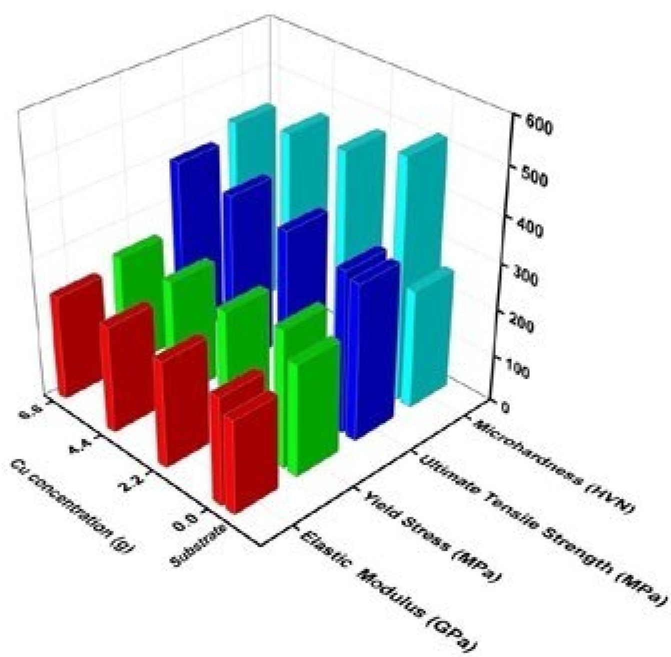

Figure 10: Effect on mechanical properties by Varying Cu concentration

This 3D bar graph is plotted in between variation of Cu concentration and the mechanical properties of substrate and the alloy deposited. This graph represents that Ultimate tensile strength and Elastic modulus are increasing with increase in Cu concentration. Micro hardness and yield stress are decreasing by increasing Cu concentration.

The comparison between elongation and Micro hardness is made to understand the trend better. For this purpose, the graph is plotted between hardness and elongation at x-axis and y-axis respectively. The trend is shown in Fig 11.

Inverse relation can relate micro hardness with elongation. As the micro hardness is decreasing the elongation is increasing and vice versa. Which shows that less the material is hard the more it can be elongated.

Conclusion

Mild steel substrates were electrodeposited with Ni-Zn-Cu alloy coatings using a sulphate bath. We looked at how the surface shape, phase composition, and mechanical characteristics changed as a function of Cu concentration. The following are the results:

Copper reduces the deposited alloy's grain size, crystallite size, and lattice characteristics. Ni-Zn alloy coated mild steel has higher yield stress, elastic modulus, and micro hardness than bare mild steel, however these properties decrease as Cu content increases. Copper content has a positive effect on ultimate tensile strength and elongation. The examined samples exhibit fcc structure, according to the results. A shift from big nodules to smaller ones with surface fractures characterises the deposit's morphology as Cu content rises.

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