ISSN: 2641-1784

Research Article

Advance in Environmental Waste Management & Recycling

Improvement in Mechanical Properties of Mild Steel by Zn-Co-Ni Coating at Different Co Concentrations

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Submitted: 07 Sep 2022; **Accepted**: 22 Sep 2022: **Published**: 26 Sep 2022

Citation: *Ahmad N., Nasir N., Shifa, MS., Tahir, MB., Wattoo, AG., et all. (2022). Improvement in Mechanical Properties of Mild Steel by Zn-Co-Ni Coating at Different Co Concentrations. Adn Envi Was Mana Rec, 5(3), 295-303.*

Abstract
Zn-Co-Ni alloy was deposited on mild steel substrate prepared by electrochemical deposition method using sulfate bath. The effect of Co concentration on the surface morphology, microstructure, crystal structure, Vicker's hardness and mechanical properties were studies. Deposition was carried out at suitable working parameters such as temperature, current density, pH and deposition time. Magnetic field was used for coating smoothness and enhancing deposition rate. X-ray diffraction, scanning electron microscopy and mechanical properties were used to investigate the crystal structure, surface morphology and microhardness respectively. The result shows that, when increasing the Co concentration, the microhardness, ultimate tensile strength, yield stress and elastic modulus increased and elongation of Zn-Co-Ni alloy is decreased. Micrographs shows that, globular like morphology change into smooth morphology by increasing the Co concentration. The lattice parameter is decreased by increasing Co concentration. Result also shows that substrate become more applicable by deposition.

Keywords: Electrodeposition, Mild Steel, Microhardness, X-ray Diffraction, Lattice Parameter

Introduction

Mild steel is broadly used in building construction because of its low coast and better mechanical properties. Thus, the use of mild steel is limited due to damage of the metal surface by corrosion and wear intensity. Electrodeposition is a surface designing method utilized improve the properties of metals like mild steel because of their advance applications [1, 2].

An alloy is a metal combine with some alloying agents. Indeed, an alloy is regarded as a combination of metals or a combination of one or more metals with a non-metallic element. Electrochemical deposition of alloy is broadly used in specific applications like physics, mechanics or chemical, for example, Co alloy because of their magnetic properties or nickel alloy because of their reactant properties. The addition of third metal these alloy leads to a good soft magnetic coating with high corrosion resistance and high catalytic performance [3].

Electrochemical deposition zinc and toxic nature of cadmium has been widely used in various applications, including coatings for car, electronic parts and number of industries. The electrodeposit zinc is based on its appropriate cathodic and barrier defensive properties. By including the eighth group element, such as nickel, iron and cobalt, into the system, the zinc coatings made in this way can greatly enhance the anti-corrosion properties [4, 5].

Nickel-cobalt alloy exhibits many physical properties that make these materials widely used in many high-technology applications. Magnetic, mechanical properties of the Ni-Co deposits imposed the structures and alloy composition. These parameters are influenced by variables such as electronic bath, pH, temperature and working current density. Therefore, the deposition of the Ni-Co alloy with the predictable properties depends on the understanding of the effects of electrode polarity and electrode phenomena [6].

In this study, the Zn-Co-Ni alloy was deposited on mild steel substrate prepared by electrochemical deposition method under constant magnetic field. By varying cobalt content in the ternary Zn-Co-Ni alloy, the structure, surface morphology, composition, grain size and mechanical properties was examined. Mild steel is used in furniture, structural steel, wires, fencing, pipeline, gates, bridges, tunnels, machinery parts, transformer, generators, rail track, train station, airports and electric motor, etc. Mild steel has the problem of rusting, degradation and pure mild steel is not much decorative. By Zn-Co-Ni deposit on mild steel, magnetic properties, rusting, decorative and life span will be improved. The properties of mild steel will be improved by variation of cobalt under constant magnetic field.

Material and Method

In this study, the mild steel having deposition area (1×1) cm^2 was taken for sample preparation taken as working cathode. Graphite rod was used as an anode for electrochemical deposition. The 35 g/l zinc sulfate heptahydrate ($ZnSO_4.7H_2O$), 40 g/l nickel sulfate heptahydrate ($NiSO_4.7H_2O$) and cobalt sulfate heptahydrate ($CoSO_4.7H_2O$) with different concentration of 0, 10, 20 and 30 g/l salts were used. The boric acid was used as a buffering agent at a constant concentration of 30 g/l and 1 g/l saccharin was used as an additive for the smoothness of the coating. All the reagent used of laboratory grade i.e. product of SIGMA-ALRICH, chosen from the laboratory and utilized.

Constant magnetic field of 4.5 mT, for the smoothness of the film and enhancing the deposition rate was used. Before using, electrolytic bath cleaned with distilled water and then ethanol. Doubly distilled water was used for electrolytic solution. 50 ml electrolytic solution was used for each sample. Solution was stirred well used magnetic stirrer.

The pH was maintained at 3-4, whereas the temperature of the bath kept at 45 °C. For the electrochemical deposition process the current density was maintained at 20 mA/cm2. Electrochemical deposition was carried out for 20 minutes. The coated mild steel was rinsed with distilled water to remove excess electrolyte around the sample and then dried.

The crystal structure of coatings was determined using X-ray diffraction (XRD) with voltage of 45 kV and current 40 mA with the Cu Kα radiation (λ = 1.54 Å) and a step size of (0.05o). Diffraction patterns were recorded in the (2θ range) upto 80° at a scanning rate of (0.01° sec^{-1}).

The surface morphology and microstructure of electrodeposition of Zn-Co-Ni alloy coating was investigated by scanning electron microscopy. Mechanical properties of investigated alloy were measured using shimadzu A6X-057B machine. The micro-hardness of the sample was investigated by pyramid shaped diamond indenter, 200gf load for loading time 10 second at room temperature using Vicker's hardness tester.

Results and Discussion

Table 1 shows the deposited mass of the Zn-Co-Ni alloys calculated before and after deposition on mild steel substrate by electrochemical deposition. The difference in the masses and thickness of Zn-Co-Ni alloy at different Co concentration is as shown in Table 1 [7].

Table 1: Mass difference before and after deposition of Zn-Co-Ni alloy

Samples	Co Concentration (g)	Deposited Mass (g)	Thickness (μm)
Zn-Ni	0.00	0.02	27.949
Zn-Co-Ni	2.09	0.02	24.620
Zn-Co-Ni	4.19	0.02	24.391
Zn-Co-Ni	6.29	0.02	24.207

The graph draws between the concentration of cobalt and the thickness of Zn-Co-Ni alloy coating is presented in Fig. 1. The graph shows that the dependence of the thickness of Zn-Co-Ni alloy coating on the concentration of the cobalt. It is seen from the curve of graph the thickness of Zn-Co-Ni coating initially decreases rapidly from about 28 μm at 0 g Co concentration to about 25 μm at 2.09 g Co concentration, after that the thickness of the coating approaches the 24.21 μm at 6.29 g Co concentration. As a result, the Co concentration increases the thickness of the coating decreases.

It is seen from the graph, when adding the 0 g Co concentration the decrease in thickness is rapid after that the decrease in thickness become slow. So, the decrease in thickness may be due to decrease in grain size which make the film smooth.

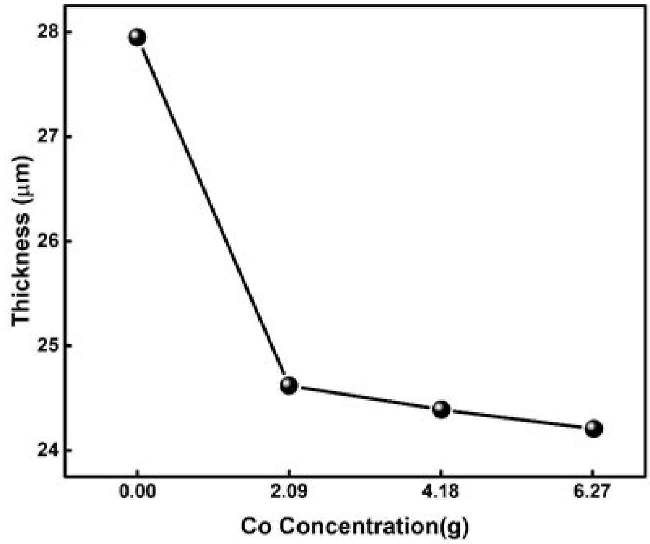

Figure 1: Thickness of Zn-Co-Ni alloy coatings at different Co concentration

The X ray diffraction pattern of the Zn-Co-Ni alloy film at different Co concentration on mild steel substrate by electrochemical deposition are as shown in Fig. 2. The three peaks of Zn-Co-Ni alloys have miller indices of (111), (200) and (220) which shows that all the crystal structure of sample is face centered cubic structure (fcc). The calculated average crystallite size of these peaks are 42, 20, 19 and 22 nm. The crystallite size is calculated by using Scherrer formula [8].

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where, D is the crystallite size (nm), λ is the X ray wavelength, β is the full width at half maximum of the XRD peaks (radian) and θ is the Bragg's angle (radian). The miller indices of these peaks are calculated by Bragg's law combining with plane spacing equation. The crystal structure is pure face centered cubic (fcc) which is known by using the common cubic lattice type sequence of diffraction lines [9]. An increase in first peak is observed when the Co concentration is increase at 6.29 g. At the same time, the intensity of peak for plane (220) decreased. The decrease of this peak due to the decrease of the thickness of Zn-Co-Ni alloy coatings obtained when the Co concentration increased [10].

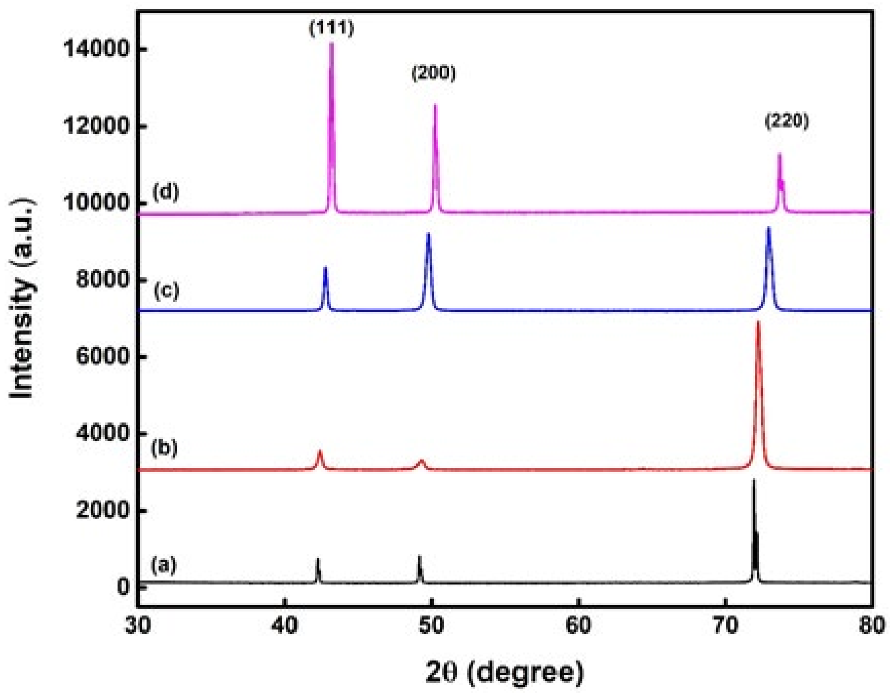

Figure 2: XRD pattern of Zn-Co-Ni alloy at different concentration of Co (a) 0 g; (b) 2.09 g; (c) 4.19 g and (d) 6.29 g on mild steel substrate

Crystallite size depends on nucleation rate and the growth in processing, it may different for different materials because different materials have different temperature sensitivity and melting point. Lattice parameter is the physical dimension of unit cells in a crystal lattice. Table 2 shows that, the crystallite size decrease at 4.19 g Co concentration after that the crystallite size increase at 6.29 g Co concentration and the lattice parameter decrease when increase the Co concentration.

Table 2: Crystallite size and lattice parameter of Zn-Co-Ni alloy coatings

Samples	Co Concentration (g)	Crystallite Size (nm)	Lattice Parameter (Å)
Zn-Ni	0	42.87	3.34
Zn-Co-Ni	2.09	20.80	3.33
Zn-Co-Ni	4.19	19.44	3.29
Zn-Co-Ni	6.29	22.23	3.23

The graph is drawn between the Co concentration and crystallite size as shown in Fig. 3. The graph shows that the dependence of the crystallite size on the Co concentration. The Fig. 3 shows that the crystallite size of the Zn-Co-Ni alloy decreases rapidly from about 42.87 nm at 0 g Co concentration to about 20.80 nm at 2 g Co concentration and then at 6 g Co concentration it become increase about 22.23 nm. By increasing the Co concentration, the crystallite grain size decrease from 42.87 nm at 0 g to 19.44 nm at 4 g. An increasing the Co concentration increases the nucleation rate and decrease the crystallite size [11]. But for last sample crystallite size is increased, this anomaly may be due to the decrease in nucleation rate at high Co concentration.

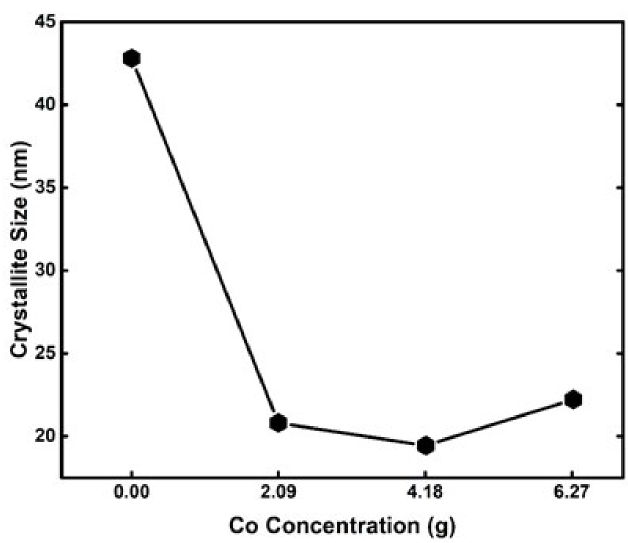

Figure 3: Effect of Co concentration on Crystallite size in Zn-Co-Ni alloy coatings

The graph is drawn between the Co concentration and lattice parameter shown in Fig. 4. The graph shows that the dependence of the lattice parameter on the Co concentration. The Fig. 4 shows that the lattice parameter of the Zn-Co-Ni alloy decreases with increasing the Co concentration. It is clear that at 0 g Co concentration the lattice parameter is 3.34 (Å) and at 6.29 g it reaches 2.27 (Å). The decrease in lattice parameter due to incorporating cobalt atom into the lattice of the film which shrink the lattice and reduce the lattice parameter [12].

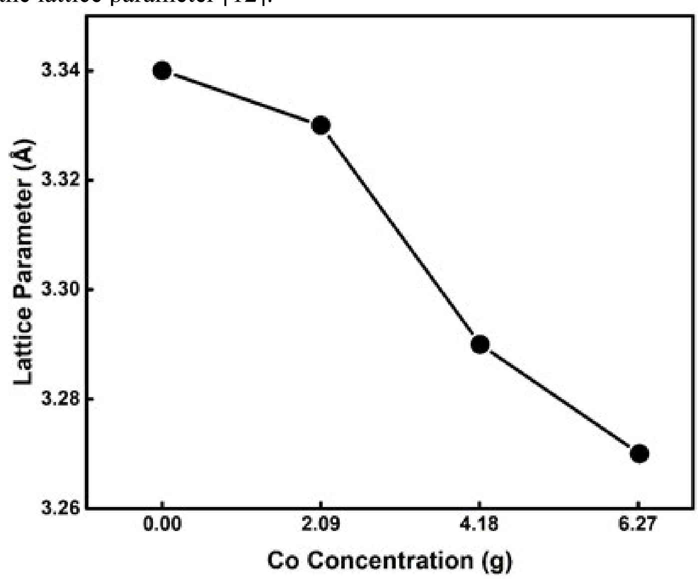

Figure 4: Effect of Co concentration on lattice parameter

The surface morphology of Zn-Co-Ni is observed by scanning electron microscopy. The surface morphology of Zn-Co-Ni is strongly dependent on their composition. The surface morphology and structure were observed by SEM at potential energy 5 Kv, different magnification of and different resolution. Fig. 5 shows the surface morphology of Zn-Co-Ni alloy at 0 g Co concentration in the presence of magnetic field had coarse grain size. Globular like morphology of Zn-Ni alloy coating at 20 mA/cm2 can be seen in Fig. 5 The SEM images with higher magnification show that rougher surface of coating. The average grain size of Zn-Co-Ni alloy coating at 0 g is 22 µm.

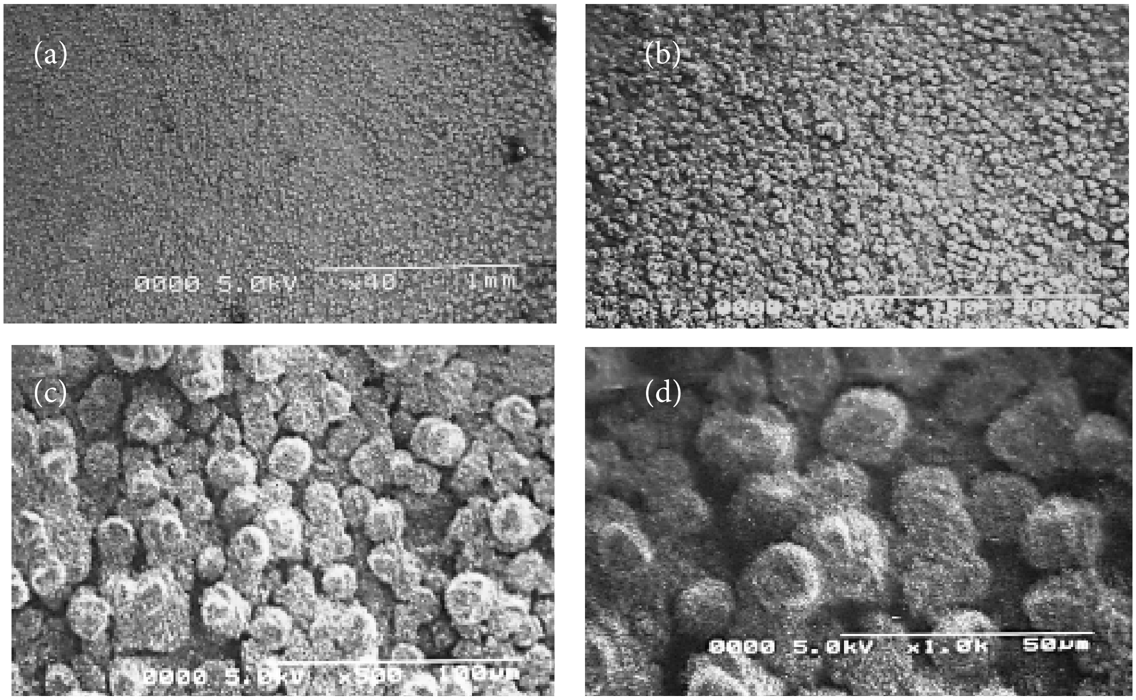

Figure 5: SEM images of Zn-Co-Ni alloy coating at 0 g Co concentration at potential energy 5 Kv, different magnification and different resolution

Fig. 6 shows the surface morphology of Zn-Co-Ni alloy at 6.29 g Co concentration in the presence of magnetic field had finer grain size. The SEM micrograph with higher magnification show that the coating surface is smooth and has no cracks. Increasing the Co concentration in the coating which affect the surface morphology. It can be seen that from Fig. 5 and 6, when increasing the Co concentration, the grain size decreases and the give more compact and smoother surface morphology. The grain size of Zn-Co-Ni alloy coating at 6.29 g is 18 µm. As seen in Fig 1, the thickness of Zn-Co-Ni alloy coating is decreases with increasing the Co concentration, so the grain size of Zn-Co-Ni alloy is decreases.

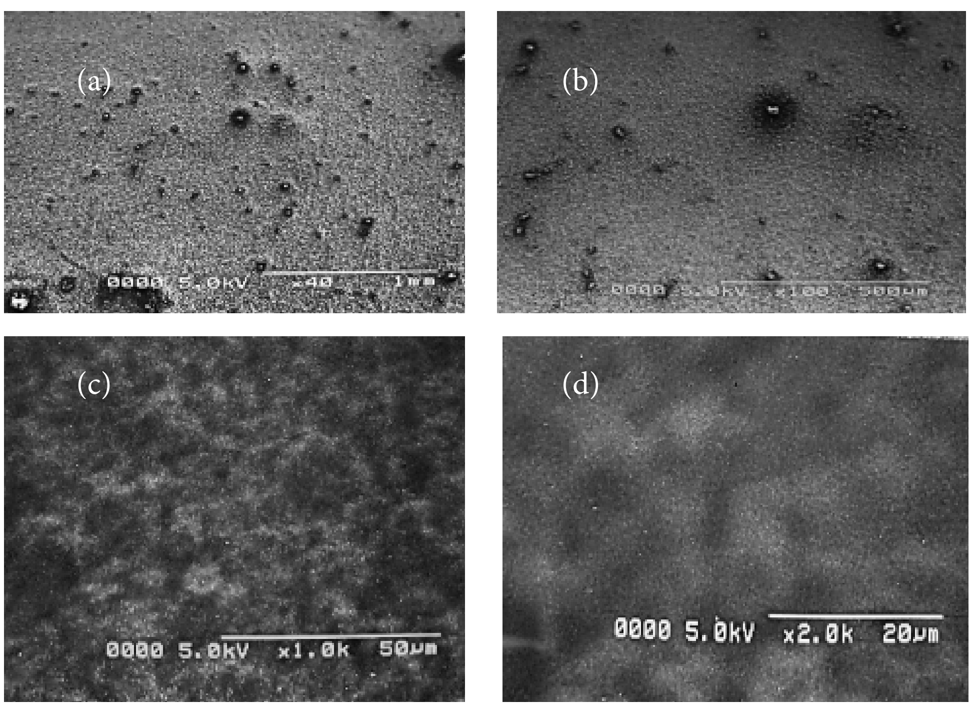

Figure 6: SEM images of Zn-Co-Ni alloy coating at 6.29 g Co concentration at potential energy 5 Kv, different magnification and different resolution

Table 3 shows that, when increase the Co concentration the microhardness of Zn-Co-Ni alloy increases. The micro hardness of Zn-Co-Ni alloy before deposition of mild steel substrate is 255.502 HVN. The values of microhardness before and after deposition are shown in Table 3.

Table 3: Microhardness of of mild steel with and without deposition

Samples	Co Concentration (g)	Microhardness	
		Before deposition (HVN)	After deposition (HVN)
Zn-Ni	0	255.502	517.704
Zn-Co-Ni	2.09	255.502	642.079
Zn-Co-Ni	4.19	255.502	665.593
Zn-Co-Ni	6.29	255.502	683.230

A graph is drawn between the concentration of cobalt and the micro hardness is shown in Fig. 7. The graph shows that the dependence of the micro hardness on the Co concentration. The Fig. 7 shows that the micro hardness of the Zn-Co-Ni alloy coating increase with increasing the Co concentration. It is clear that at 0 g Co concentration the micro hardness of the coating is 102% and at 6.29 g it reaches 167%. So, the percentage of micro hardness is increases with increase the concentration of Co. The increase in micro hardness may be due to reduction in grain size and solid solution strengthening of cobalt in alloy coating [13].

It is clear that part of the increase in micro hardness is due to the harsh effect of the solid solution by increasing the Co concentration of the coating [14]. The mechanical properties of metallic and polycrystalline alloys have been recognized to be highly sensitive to grain size. In many cases, the hardness depends on the grain size according to the Hall–Petch relationship. It is clear that the micro hardness of metallic substances increases significantly as the grain size decreases [15].

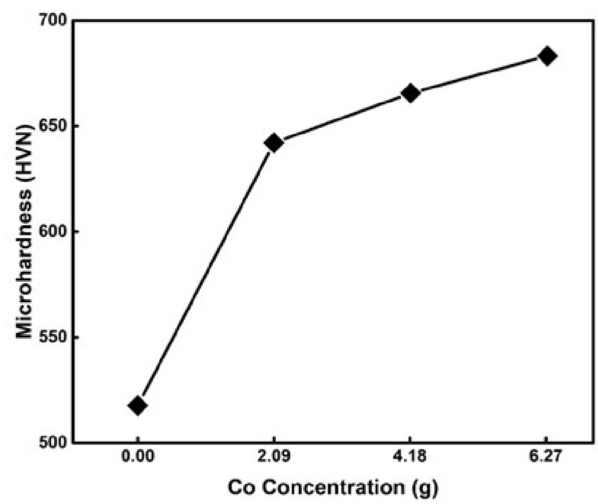

Figure 7: Effect of Co concentration on micro hardness in Zn-Co-Ni alloy coatings

Table 4 shows that, when increase the Co concentration the elastic modulus of Zn-Co-Ni alloy increases and elongation of Zn-Co-Ni alloys decreases. The elastic modulus and elongation of mild steel substrate before deposition is 200.323 and 18.009, respectively. The values of elastic modulus and elongation before and after deposition are shown in Table 4.

Table 4: Elastic modulus and Elongation of Zn-Co-Ni coatings at different concentration of Co

Samples	Co Concentration (g)	Elastic Modulus		Elongation	
		Before deposition (GPa)	After deposition (GPa)	Before deposition (%)	After deposition (%)
Zn-Ni	0	200.323	232.576	18.009	36.789
Zn-Co-Ni	2.09	200.323	250.450	18.009	35.282
Zn-Co-Ni	4.19	200.323	261.587	18.009	34.009
Zn-Co-Ni	6.29	200.323	266.897	18.009	33.231

A graph is draws between the elastic modulus, elongation and the concentration of cobalt is presented in Fig 8. The dependence of the elastic modulus and elongation on the concentration of the cobalt. As a result, when increase the Co concentration the elastic modulus increases and elongation is decreases. It is clear that at 0 g Co concentration the elastic modulus is 16% and at 6.29 g Co concentration the elastic modulus is 33% and the elongation is 84% of the coating. It can be seen that, with the variation of Co concentration the percentage of elastic modulus is increases and the elongation is decreases. The increase in elastic modulus due to decrease in grain size and solid solution strengthening of cobalt in alloy coating [8].

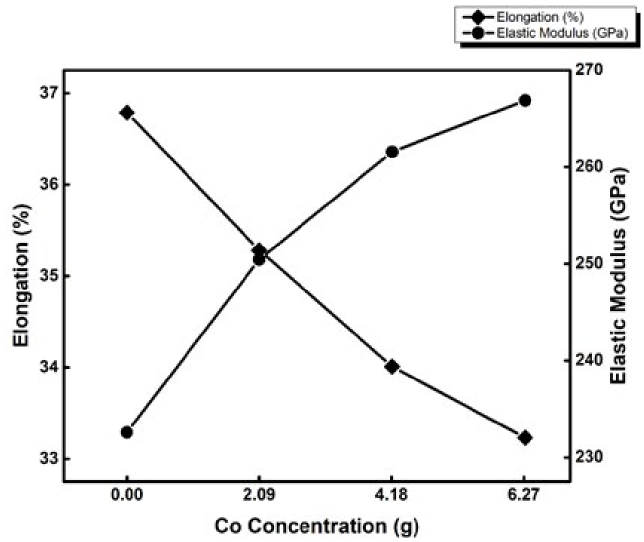

Figure 8: Effect of Co concentration on elastic modulus and elongation in Zn-Co-Ni alloy coatings

Table 5 shows that, when increase the Co concentration the ultimate tensile strength and yield stress of Zn-Co-Ni alloy increases. The ultimate tensile strength and yield stress of mild steel substrate without deposition is 336.789 MPa and 240.876 MPa, respectively. The values of ultimate tensile strength and yield stress before and after deposition are shown in Table 5.

Table 5: Ultimate tensile strength of Zn-Co-Ni alloy coatings at different concentration of Co

Samples	Co Concentratio (g)	Ultimate Tensile Strength		Yield Stress	
		Before deposition (MPa)	Before deposition (MPa)	After deposition (MPa)	After deposition (MPa)
Zn-Ni	0	336.789	240.76	254.231	347.982
Zn-Co-Ni	2.09	336.789	240.876	262.987	545.237
Zn-Co-Ni	4.19	336.789	240.876	274.783	574.072
Zn-Co-Ni	6.29	336.789	240.876	285.253	591.672

A graph is drawn between the concentration of cobalt and the ultimate tensile strength (UTS) and the yield stress is presented in Fig 9. The dependence of the ultimate tensile strength and the yield stress on the concentration of the cobalt. As a result, the Co concentration increases the ultimate tensile strength and yield stress also increases. It can clear that at 0 g Co concentration the ultimate tensile strength of the coating is 3% which increase rapidly approach 61% at 2.09 g Co concentration and 0 g Co concentration the yield stress of the coating is 5% and at 6.29 g Co concentration it reaches 18%. So, when increasing the cobalt concentration, the percentage of ultimate tensile strength and yield stress is increased. The increase in tensile strength and yield stress due to decrease in grain size and solid solution strengthening of cobalt in alloy coating [8].

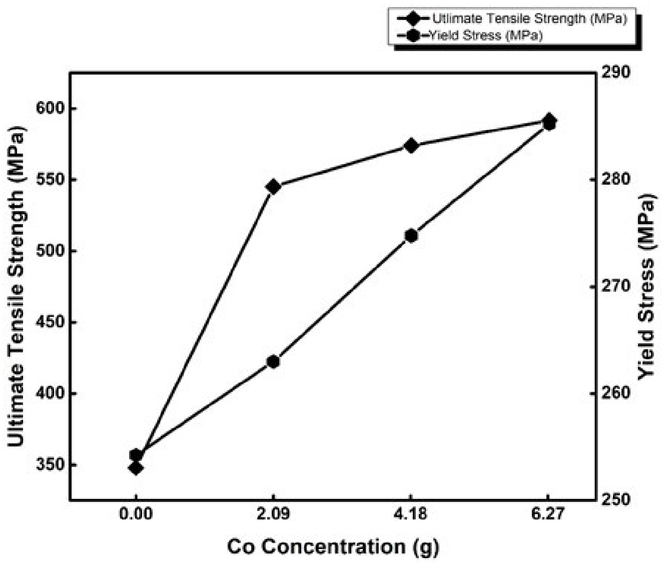

Figure 9: Effect of Co concentration on ultimate tensile strength and yield stress in Zn-Co-Ni alloy coatings

The graph draws between the hardness and elongation of Zn-Co-Ni alloy coating shows in Fig 10. The graph shows the dependence of elongation on hardness of Zn-Co-Ni alloy. It is clear that, the elongation initially decreases rapidly from about 104% at 102% hardness to about 95% at 151% hardness, after that the elongation of Zn-Ni-C alloy coating approaches the 84% at 176% hardness. So, increasing the hardness the percentage of elongation is decrease.

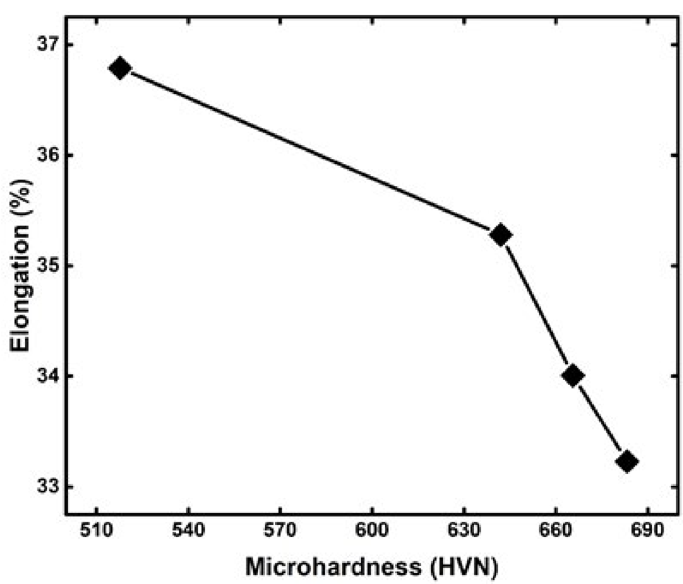

Figure 10: Effect of microhardness on elongation of Zn-Co-Ni alloys coatings

The mechanical behavior of Zn-Co-Ni alloy coating, the elastic modulus, yield stress, ultimate tensile strength and microhardness depends on the Co concentration. It is clear that from the Fig 11, the elastic modulus, yield stress, ultimate tensile strength and microhardness is increases when increase the Co concentration in Zn-Co-Ni alloy coating. Graph shows that, the elastic modulus, yield stress, ultimate tensile strength and microhardness of mild steel substrate without deposition is less than as compare to 0 g Co concentration of Zn-Co-Ni alloy coating. After that, when increases the Co concentration in Zn-Co-Ni alloy coating the percentage of elastic modulus, yield stress, ultimate tensile strength and microhardness is increases. This increase is due to decrease in grain size and solid solution of cobalt in alloy coating [8].

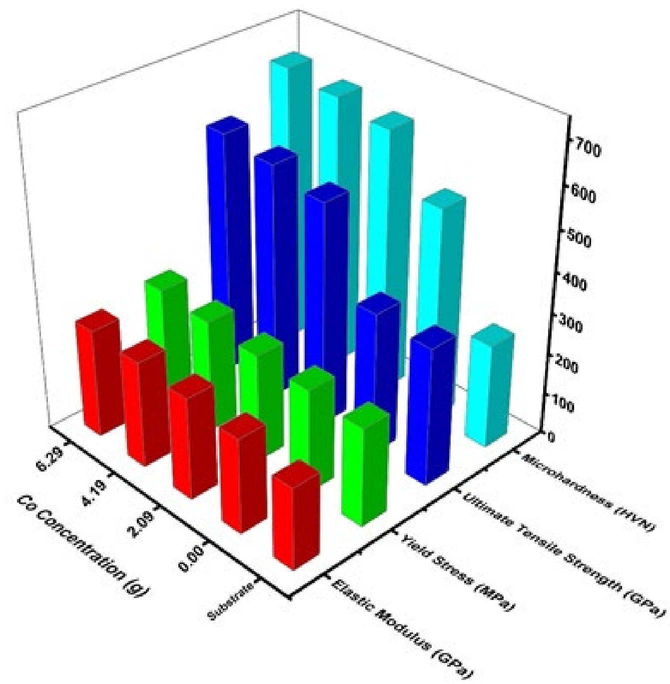

Figure 11: Mechanical behavior of Zn-Co-Ni alloy coatings at different Co concentration

Conclusion

The Zn-Co-Ni alloy is deposited on mild steel substrate prepared by electrochemical deposition method under constant magnetic field. The properties of mild steel are improved by variation of the cobalt. The pH was maintained at 3-4, the temperature of the bath kept at 45 °C and the current density was maintained at 20 mA/cm². X-ray diffraction, scanning electron microscopy and mechanical properties were used to investigate the surface morphology, phase structure, and microhardness. From result, it is concluded that the thickness of Zn-Co-Ni alloy is decreased by increasing the Co concentration. The microhardness, ultimate tensile strength, yield stress and elastic modulus of Zn-Co-Ni alloy is increased by increasing Co concentration. The elongation of Zn-Co-Ni alloy is decreased by increasing Co concentration. The SEM micrographs of Zn-Co-Ni alloy shows that, globular like morphology change into smooth morphology by increasing the Co concentration. The phase structure of Zn-Co-Ni alloy is face cubic centered structure. The lattice parameter is decreased by increasing the Co concentration due to shrinking the lattice.

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