

MORPHOLOGY AND PROPERTIES OF ELECTRODEPOSITED ZN-NI ALLOY COATINGS ON MILD STEEL

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Abstract: Zinc-nickel alloys electrochemically deposited on mild steel under various deposition conditions were investigated. The effect of plating variables (bath composition, pH, current density) on the coating composition, morphology, corrosion property and microhardness were investigated. Modified morphology with perfect crystal growth, uniform arrangement of crystals, refinement in crystal size and hence bright deposit was obtained from sulfate Bath-3 containing 30 g/l H_3BO_3 at a current density of 75 mA/cm². Corrosion resistance as well as microhardness of Zn-Ni alloy coatings increased with the increase of %Ni in the deposit for all the sulphate baths studied. Optimum conditions for good deposition are also discussed.

Keywords: Zn-Ni alloy, electrodeposition, morphology, corrosion resistance.

INTRODUCTION

Zinc is widely used as metallic coatings applied to steel surfaces to protect them from corrosion which can be obtained either hot dipping or electroplating process. Electroplated Zn produce thinner coating as compared to hot dipping suitable for the subsequent forming process to be used in the automotive industry, but thin pure Zn coating shows very poor corrosion resistance. Zinc alloys are able to provide higher corrosion resistance than that of a pure zinc¹⁻³. This is obtained by alloying Zn with more noble metals of in the iron group (Ni, Co and Fe)^{4,5}. Recently electrodeposited Zn-Ni alloy coatings have attracted a great deal of attention because they can offer a high degree of corrosion resistance and mechanical properties e.g. micro-hardness, wear resistance, ductility, strength, decorative properties etc. than pure zinc coating^{6,7}. Zinc-nickel alloy may also serve as at less toxic substitute for cadmium⁸. Substantial improvements are obtained even with small percentage of the more expensive Ni. Consequently potential advantages in using Zn-Ni alloy have been recognized.

The deposited Zn-Ni alloy is always richer in Zn than Ni when electrodeposited from the solution containing Ni²⁺ and Zn²⁺. The electrodeposition of Zn–Ni alloys is classified by Brenner as an anomalous codeposition where Zn is a less noble metal which is preferentially deposited⁹. Many studies have been carried out to understand the characteristics of the deposition process of Zn–Ni alloy. It is found that the characteristics of the deposited coating depend on the applied voltage, current density, pH, bath composition, additives and temperature etc.¹⁰. The phases and microstructure of the surface of the deposited Zn-Ni alloys is another important characteristic which controls the corrosion resistance and other mechanical properties¹¹. One serious drawback of the electrodeposition process is the generation of internal stresses resulting in the formation of microcracks¹². However, the internal stress level can be reduced by heat treatment or the addition of

inhibitors¹³. Limited information is available in the open literature on the coating surface morphology deposited using a wide range of current density.

The objective of the present study is to develop the plating baths with suitable compositions and establish the optimum electrodepositing conditions (bath composition, pH, current density etc.) for obtaining good quality Zn-Ni alloy deposition. Finally detailed investigation on the morphology of the surface of coatings deposited at different current density and bath composition has been done.

EXPERIMENTAL

The electrodeposition of Zn-Ni alloy was performed in an electrochemical cell of three electrodes where commercial mild steel (50mm x 15mm x 1mm) sheet was used as substrate and platinum sheets (35mm x 15mm x 0.4mm) were used as anodes. Before electrodeposition the substrate was polished with successively finer grades of emery paper, cleaned with Na₂CO₃ solution, descaled by acid pickling operation in 20% HCl at 70°C and finally activated by dipping in 10% HCl solution at room temperature for 15 seconds followed by rinsing in distilled water. Anode and cathode were connected to the D.C. power supply via a multimeter. Two anodes were used on both sides of the cathode for uniform deposition on both sides of the cathode (Fig.1).

Three sulfate baths were prepared by dissolving different relative amounts of NiSO₄.7H₂O, ZnSO₄.7H₂O, Na₂SO₄ and H₃BO₃ (Table 1). Deposition was carried out at constant current densities ranging from 25 to 275 mA/cm² with the bath pH ranging from 1 to 4.1 at 45°C. All the depositions were continued for a predetermined time period of 30 minutes. The pH value of the solution before and after electrodeposition was measured and the change of pH was recorded. The pH range required for the good deposition was determined from the physical

appearance of the deposited alloy coating at different current densities.

Composition of the deposited Zn-Ni alloy coatings was determined by the conventional wet chemical analysis method. Surface morphology of the Zn-Ni alloy coating deposited at different current densities from all

three baths was investigated using Scanning Electron Microscope (SEM) (Philips XL30). The corrosion resistance of the deposited Zn-Ni alloy coatings was investigated by exposure technique which is the salt-water immersion test. The samples were immersed

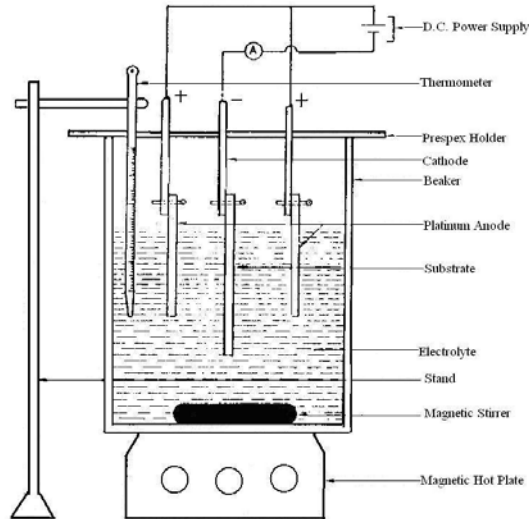


Figure 1. Schematic diagram of electrodeposition unit

in salt-water (3% NaCl) solution for 48 hours. The corrosion attack of the coatings was evaluated by visual inspection and weight loss measurement which consists of an original and final weighing of the coatings. Microhardness (VHN) of all the coatings deposited at varying current densities and bath compositions was measured by using a Shimadzu Microhardness Tester under an application of 100 g load.

RESULTS AND DISCUSSION

Electrodeposition of Zn-Ni alloy coating

The bath pH and applied current density ranges to obtain good deposition from the three baths in the present study are summarized in Table 2. The deposit quality is identified by visual examination. Uniform and adherent coatings from three baths are obtained at higher pH range with lower current density (25-75 mA/cm²) and at lower pH range with higher current density (200-250 mA/cm²). Higher current density range for good deposition is 125-200 mA/cm² in Bath-1. No deposition is seen when the p^H

value is below 0.8 for all the baths. At baths of pH < 0.8, deposit could form only near the edges while major portion of the substrate surface remained bare. At this low pH Zn-Ni plating baths become too corrosive and therefore the newly deposited Zn-Ni alloy is chemically attacked and dissolved. At the mid portion of the sample where current density is lower than the average, rate of this chemical attack is higher than the deposition rate. On the other hand, at areas near the edges which receive more current than the average, the deposition rate is higher than the rate of chemical attack. As a result, significant amount of deposit could only be seen near the edges at pH lower than 0.8¹⁴. In almost all baths no good deposition was obtained at a current density of 250-275 mA/cm². At these current densities deposited coatings tend to peeling due to developing of stress and some times curved surface was observed. Thus no electrodeposition was carried out at any current density > 275 mA/cm² for all the baths.

Table 1. Plating bath composition for the electrodeposition of various Zn-Ni alloy coatings

| Bath ingredient | Concentrations (g/l) | | |
|--------------------------------------|----------------------|--------|--------|
| | Bath-1 | Bath-2 | Bath-3 |
| NiSO ₄ ·7H ₂ O | 285 | 350 | 150 |
| ZnSO ₄ ·7H ₂ O | 150 | 150 | 290 |
| Na ₂ SO ₄ | 150 | 150 | – |
| H ₃ BO ₃ | – | – | 30 |

Table 2. p^H and current density range for uniform and adherent deposition from the experimental baths

| Bath type | Bath p^H range | Current density range (mA/cm ²) |
|-----------|------------------|---|
| Bath-1 | 4.1-2.5 | 25-75 |
| | 2.0-1.1 | 125-200 |
| Bath-2 | 3.7-2 | 25-75 |
| | 1.75-1.3 | 200-250 |
| Bath-3 | 3.4-2 | 25-75 |
| | 1.75-1 | 200-250 |

Chemical Analysis

Nickel content in the deposited coatings obtained from the wet chemical analysis as a function of applied current density is shown in Fig. 2. Different Ni/Zn ratio in different baths is also shown in the figure. It is seen that Ni content in the coatings deposited from Bath-2 is the highest while that from Bath-3 is the lowest. Nickel content in the deposited coating varies with the Ni concentration of the electrolyte in baths i.e. higher amount of Ni is deposited from the bath which consists of higher percentage of Ni containing electrolyte. This is supported by the alloy deposition principle that an increase in the metal percentage (or ratio) of a parent metal in an alloy plating bath results in an increase in its percentage (or ratio) in the deposit⁹.

Deposit composition can also be influenced by bath contents. Table 1 shows that Bath-1 and Bath-2 contains sodium sulfate (Na₂SO₄) while Bath-3 contains boric acid (H₃BO₃) and these have an influence on the %Ni in deposit. Sodium sulfate increases the conductance of the bath solution⁸. The presence of Na₂SO₄ in the Bath-1 and Bath-2 significantly increases the amount of Ni in the deposit. The role of boric acid has been of great interest in the electrodeposition of Ni¹⁵ and Zn-Ni alloy¹⁶. It is now believed that boric acid either complexes with Ni²⁺, acting as a homogeneous catalyst, or adsorbs on the electrode surface, and has a significant role in morphology and compositional characteristics. The presence of boric acid results in an increase of Zn in the deposited alloy¹⁶. These

effects have been attributed to the adsorptive interactions of boric acid at the electrode surface. Also, boric acid acts as a buffer to maintain pH of the electrolyte bath¹⁷. Similar effects of boric acid are observed in the present work during Zn-Ni deposition from Bath-3. The addition of boric acid to Bath-3 without Na₂SO₄ increases the Zn content in the deposited alloy (Fig. 2).

It is also seen from Fig. 2 that in case of Bath-1 the Ni content in the deposit initially decreases to some extent with increase in current density but it increases with further increase in current density. In Bath-2 Ni content increases almost linearly with the increase in current density. In Bath-3 the trend of change of Ni content with current density is same as is the case of Bath-1 but the Ni content decreased at a current density of 150 mA/cm² and then starts to increase with further increase in current density. Ni content in the deposited coating increases with the increase in the current density for each bath at higher current densities. The reason for increasing Ni in the deposits with current density is thought that preferential deposition occurs during deposition at higher current densities. Since Zn is less noble as compared to Ni, during very early stage of electrodeposition Zn deposits at a higher percent following anomalous deposition and produces its depletion in the diffusion layer, and results higher concentration of Ni in this layer. The Zn depletion in the diffusion layer continues during the rest of the electrodeposition process and consequently Ni deposition rate increases at higher current densities¹⁸.

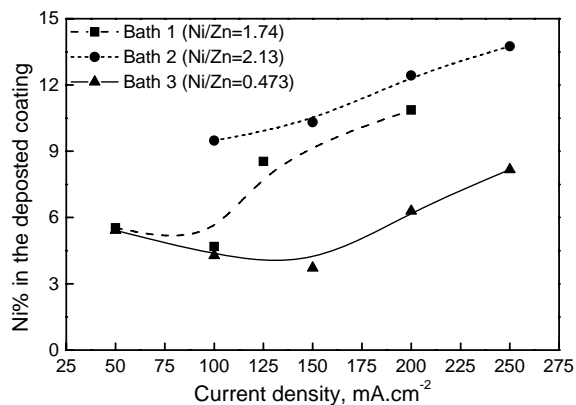


Figure 2. Effect of current density on chemical composition of electrodeposited Zn-Ni alloy coatings.

Surface morphology

Surface morphology of the Zn-Ni alloy coating electrodeposited at different current densities was investigated under scanning electron microscope (SEM). The morphology of deposited Zn-Ni alloy coating in terms of its uniformity, presence of porosity onto it, grain size, stress developed etc. changes with the current density and bath composition. The SEM images of the coatings deposited from Bath-1 at different current densities are shown in Fig. 3.

All the images are taken at the same magnification. At low current density (25, 50 mA/cm²) grain of the deposits is smaller, regular and no porosity is found in the coatings. Thus the nature of the deposit is found to be uniform, adherent and dense (Fig. 3a and 3b). With increasing current density, coarse-grained deposit having irregular crystal size results and at the same time numerous porosities become visible in the coating.

For electrodeposition process, the crystallization of the electrodeposited layer is a very important step for the electrogrowth, since it influences directly the structure of the deposit and therefore its properties. Crystallization occurs either by the buildup of old crystals or by the formation and growth of new ones. These two processes are in competition and can be influenced by different factors. Since the deposition rate is slow at low current density, at the beginning of the electrolysis, alloy deposits as a large number of tiny particles on almost all over the cathode surface which acts as nucleation for further deposition at the preferential sites. A high nuclei renewal rate results leading to an increase in nucleation number and hence smaller grain size. It is noteworthy to mention the porous-free nature of the coating due to smaller grain size of the coatings at low current density. On the contrary, a large number of tiny particles deposits on the cathode surface at the initial stage due to the high deposition rate at higher current density. All these particles can not provide preferential nucleation sites for the subsequent layer deposition. Limited number of new tiny particles can only form at the preferential sites. Crystallization occurs mostly

by the buildup of old crystals. Thus coarse grain structure results with some cracks in it due to formation of stress. All the gas produced at the cathode surface during electrolysis process can not escape rather they are trapped by the fast growing deposit. Moreover, these gases may grow as nucleation and growth mechanism like the deposited alloy and finally, when escape by their own accord, can create porosity.

Figure 4 shows the morphology of the coatings deposited from Bath-2. Similar structures are observed as the coatings deposited from Bath-1. The current density effect on coating structure is also found to be the same as Bath-1 i.e. the grain size and porosity increase as the current density increases.

When compared, the coating from Bath-1 is more uniform and densely packed than from Bath-2 at low current density ranging from 25 to 75 mA/cm². Only difference between Bath-1 and Bath-2 is the NiSO₄.7H₂O which is 285 g/l in Bath-1 and 350 g/l in Bath-2. Thus major morphological changes are not observed between the two sets of coatings.

SEM images of the deposited Zn-Ni alloy coating from Bath-3 (with boric acid and without sodium sulfate) at different current density are shown in Fig. 5. It is observed that the deposited coating is very smooth at a low current density of 75 mA/cm² (Fig. 5b). Surface of this coating is the most smooth one among all the coatings so far deposited in the present study. The grains become coarser at some higher current density ranges (125-200 mA/cm²). When current density is increased further to 250 mA/cm², grain size becomes smaller (Fig. 5f). Grains of wider size ranges are found here. But unlike the other baths there is almost no porosity in the coating surface among the grains. Smoothness of the coating surface deposited at higher current density is not as good as that obtained from Bath-1 and Bath-2. Thus the SEM photomicrograph (Fig. 5b) of the deposit obtained from Bath-3 at 75 mA/cm² shows perfect crystal growth, uniform arrangement of crystals, refinement in crystal size and hence bright deposit.

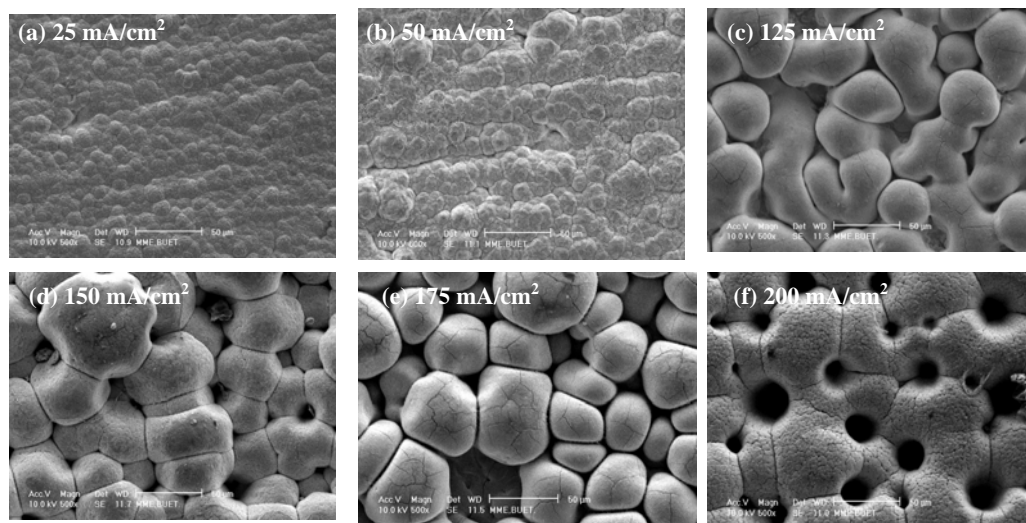


Figure 3. SEM micrographs of the deposits obtained from Bath-1 at different current density

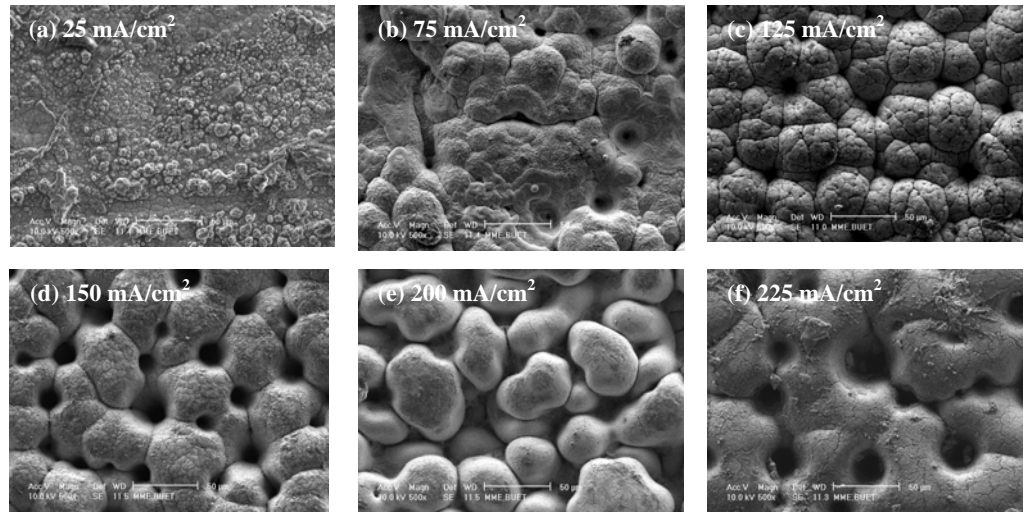


Figure 4. SEM micrographs of the deposits obtained from Bath-2 at different current density.

Corrosion property

The corrosion property of the Zn-Ni alloy coatings was evaluated both qualitatively and quantitatively in the immersion test. For qualitative evaluation, the immersed samples were taken out of 3% NaCl solution and observed visually for the identification of formation any white rust on the coated substrates. When Zn-Ni alloy coatings are exposed to salt solutions, hydroxide of zinc is found to form as corrosion product⁸. This product is known as white rust which bears the indication of corrosion.

For quantitative evaluation, the results of corrosion test are summarized in Fig. 6. Here, corrosion rate, expressed in mpy (*mils per year*), of Zn-Ni alloy coating as a function of %Ni in deposit is shown. It is observed from the curves that the corrosion rate of Zn-Ni alloy coating decreases with increase in the % of Ni in the deposit for each bath. In case of Bath-1 the corrosion rate decreases almost sharply with increase in %Ni in deposit. In Bath-2 the corrosion rate decreases linearly with Ni percentage. In

case of Bath-3 the corrosion rate decreases at a faster rate up to about 6.2% Ni and then at higher %Ni in deposit it decreases at very slower rate. So, these phenomena show that the Ni content in the deposited alloy increases the corrosion resistance of the coatings which follows the standard practice and supports the theoretical considerations as well as Ni is more noble element than Zn.

It is already mentioned that grain size and porosity of the coating increases with the increase in current density and Ni deposition also increases as well. Corrosion resistance is also found to increase with increase of Ni content in the deposit. Thus less effect of the microstructure of deposited coating on the corrosion resistance is found while from practical point of view, there should have effect of the morphology of coating on its corrosion resistance. In the present study, the corrosion medium used was less severe (3% NaCl solution at room temperature) and the corrosion test continued for a short

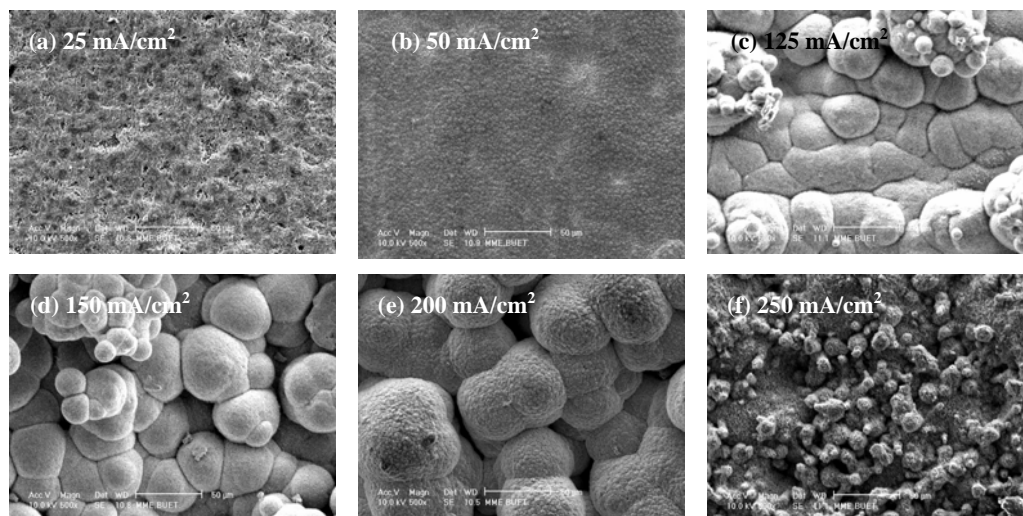


Figure 5. SEM micrographs of the deposits obtained from Bath-3 at different current density.

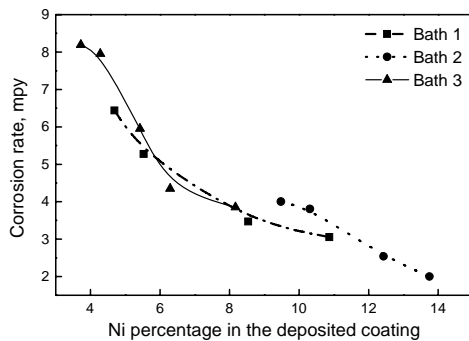


Figure 6. Corrosion rate of Zn-Ni alloy coating in 3% NaCl solution.

duration of 48 hours. It is supposed that if corrosion study could be carried out in a high corrosive medium with harsh environment for a time period of at least 72 hours, the effect of coating morphology on the corrosion properties might have been revealed. This requires further study in details and will be carried out in the next investigation.

Figure 7 shows the microhardness (VHN) change of the deposited coatings with %Ni in deposit for each different bath of Zn-Ni alloy coatings. Here, microhardness of the Zn-Ni alloy coating increases with the increases in the %Ni. In case of Bath-1 and Bath-2, the hardness increases almost in a straight way with the Ni content. In Bath-3 the microhardness increases at a slower rate at lower and higher percentage of nickel and it increases at a faster rate when %Ni varies from about 5.4 to 6.3 in the deposit.

CONCLUSIONS

Uniform and adherent Zn-Ni alloy coatings can be deposited from simple sulphate bath at higher pH range for lower current density (25-75 mA/cm²) and at lower pH range for higher current density (200-250 mA/cm²) at temperature 45^o C. Nickel content in the deposit increases with the increase in current density in all sulfate baths. At low current density, fine grained deposit is obtained for all the baths. With the increase in current density grains become coarser and porosity is introduced in the deposits. With the addition of boric acid in Bath-3, perfect crystal growth, uniform arrangement of crystals, refinement in crystal size and hence bright deposit is obtained at a current density of 75 mA/cm². The corrosion resistance as well as microhardness of Zn-Ni alloy coatings increases with the increase of %Ni in the deposit for all the sulphate baths studied.

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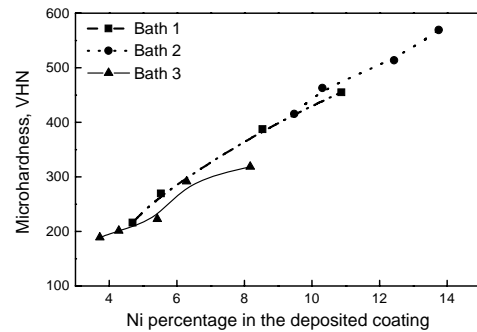


Figure 7. Microhardness (VHN) of deposited Zn-Ni alloy coating as a function of %Ni in it.

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