

# Electrodeposition of Zn–Ni–Cu Coating layer to Protect low Carbon Steel Against Corrosion

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## Abstract

A new Zn–Ni–Cu plating process was developed which offers a unique way of controlling and optimizing the Ni contents in the final deposit. The selected system was considered as a replacement for cadmium and chromium plating system. zinc–nickel–copper alloy was deposited on carbon steel from ZnO, NiSO<sub>4</sub>·6H<sub>2</sub>O, CuSO<sub>4</sub>·5H<sub>2</sub>O, NaOH and C<sub>4</sub>H<sub>13</sub>N<sub>3</sub> as (chelating agent), by using potentiodynamic technique. Electrochemical and surface analysis indicated that the deposition took place with the formation of  $\gamma$  phase of zinc–nickel–copper alloy. The above mentioned coating showed high hardness, smooth, uniform and fine grain deposit as well as superior corrosion resistance against NaCl and sulphuric acid environments.

**Keywords:** Barrier Coating; Electrodeposition ; Zn–Ni Alloys ; Alkaline Bath ; Electrochemical Studies.

## Introduction

Electroplated zinc coatings has been the most widely used as a corrosion resistance coating for steel and other ferrous materials. Recently, the interest on Zn–Ni alloy coating has increased owing to its better mechanical and corrosion properties compared with pure zinc coatings [1,2,3 and 4], zinc coatings generally need to be thick (typically up to 25 $\mu$ m) in order to achieve good corrosion resistance because the zinc is consumed sacrificially at a relatively high rate while under exposure to corrosive conditions. Thick coatings are problematic, however, due their poor formability and weldability [5].

Its also difficult to obtain a high protective thick layer[6].This has prompted the search for techniques to further improve the corrosion resistance of zinc, thereby permitting the use of thinner coatings while still maintaining a high level of performance. Reduction in corrosion susceptibility by a factor of 5–7 times, for example, have been claimed for Zn

coatings alloyed with 9–17 wt.% Ni, as compared to those having no alloying additions at all [7].

Due to the attractive properties of Zn–Ni coatings, the introduction of this alloy into industrial practice has been extremely successful. Zn–Ni electrodeposits performance; however, the beneficial influence of alloying is not fully understood. Several hypothesis have been advanced assuming that corrosion inhibition may be related to the structural and/or electronic properties of the passive oxide film.

At this time, approximately 75% of market demand for zinc alloy coatings come from automotive industry [8], steel autobody panels[9], fuel tanks[10], and fasteners[11] are a few of the products that well suited to the thinner and lighter Zn–Ni coatings.

Zn–Ni coating has recently used to replace cadmium plating, which is widely used in the aerospace industry for the corrosion protection of steel [12]. Cadmium plating, is used to protect steel components on aircraft primarily because of its excellent corrosion resistance and its electrochemical compatibility with any of aluminium alloys used in aircraft construction [13]. Despite the advantages of cadmium plating, however, alternatives are required due to the toxicity of the metal and its compounds.

Chrome ( $\text{Cr}^{6+}$ ) is used, as a passivating layer on zinc alloys; the chromate layer offers good corrosion protection properties, because of the fact that chrome ( $\text{Cr}^{6+}$ ) is very active and can migrate over the surface, thus providing self-healing properties. Due to that reactivity, hexavalent chrome is also toxic and carcinogenic. When replacing hexavalent chrome with a chrome ( $\text{Cr}^{6+}$ ) free product, the passivating properties are reduced. One of the alternatives is to replace chrome ( $\text{Cr}^{6+}$ ) by using a coating of Zn–Ni alloys, this coating shows great promise from the corrosion resistance point of view.

Steady growth in the usage of Zn–Ni coatings has also been seen in the household appliance, electrical component, metal building, construction and HVAC (heating ventilation and air conditioning) industries. Potential exists, as well, for Zn–Ni to be used as electrodes for electrocatalytic water electrolysis.

This work i.e. Zn–Ni coatings represents an alternative for Ni–Zn coatings. This attempt is however, represents a real challenge.

## Experimental Procedure

The substrate metal used in this study was low carbon steel; the limiting chemical composition of base metal is shown in Table (1). The substrate samples were cut into circular cross sectional shape with dimensions (12mm in diameter. 1.5mm thickness). The surface, was grinded using 120,220,320,600,1000 and 1200 grit silicon carbide papers, then these followed by rinsing with distilled water, then polished using alumina powder to get a bright mirror finish as a final step.

These samples were degreased with acetone and then ultrasonically cleaned for two minutes using ethanol. After drying, these samples were examined using optical microscope to insure that the surface was free from any defect.

After that the samples were etched using hydrochloric acid with concentration 5.4% for 2 minutes followed by rinsing with distilled water, then stored in the desiccator.

The experimental apparatus used for the electrodeposition was made up of double-layered cylindrical glass container, with a capacity of 300 ml.

Electrochemical measurements were carried out using electrochemical cell with three electrodes. The working electrode (WE) to be coated was situated in special Teflon holder. Zn sheet of purity 99.79% was used as a counter electrode with a surface area considerably greater than that of the working electrode, the distance between the working and counter electrode was maintained at constant value of 3 cm.

The reference electrode was Ag/AgCl mounted in luggin capillary. The electrodeposition was performed by using the potenionstat interfaced to a personal computer. The potential scan rate was set at  $5\text{mVS}^{-1}$ , step potential  $25\text{mVS}^{-1}$  and covered the potential range from  $-2000\text{ mV}$  to  $-900\text{ mV Vs.Ag/AgCl}$ . Nitrogen of purity (99.99%) was purged through out the experiment in order to remove dissolved oxygen from the electrolyte.

Many experiments were carried out to investigate the feasibility of Zn-Ni-Cu using electroplating to reach demandable percentage for the first layer. All solutions were prepared with analytical grade reagents and distilled water, chemical dissolution occurs under alkaline conditions (Table 2).

Many experimental works were carried out to reach the optimum coating thickness approximately 10  $\mu\text{m}$  by controlling the time of electrodeposition.

The film composition was determined by X-Ray Fluorescence Spectrometer, The chemical composition of the coating material under scrutiny is represented by the average of at least four measurements at different points in each sample followed by a quantitative method, in order to confirm the result, Energy Dispersive X-Ray was used as an analytical method.

The morphology of surface deposits was observed by a scanning electron microscopy (SEM). Microhardness Vickers tester was used to measure the hardness distribution at the coated layer of Zn–Ni–Cu as well as base metal, with 10 g load and holding time of 26 seconds combined with optical microscopy to measure the diagonal length of Vickers impression.

5% NaCl was used as a corrosive environment in a salt spray chamber at 35°C, 24hrs for the Base Metal, Zn–Ni–Cu and Zn–Ni–Cu (after heat treatment).

The corrosion current,  $i_{\text{corr}}$ , is directly related to the corrosion rate and obtained from a Tafel plot by extrapolating computerize the linear portion of the curve to  $E_{\text{corr}}$ , this test was conducted using deaerated 1%  $\text{H}_2\text{SO}_4$  solution at 45°C, using the potenionstat.

## Results

Corrosion is a complicated phenomena due to the involvement of several factors in increasing the aggressiveness of the whole process as a result. The Factor governing the rate of corrosion may be related to the metal and/or the environment.

When referring to the effect of environment include, the acidity or alkalinity of the liquid, rate of supply and distribution of oxygen, rate of flow of liquid, relative humidity, presence of external stress, and presence of impurities in the atmosphere [14].

Electroplating technique has been used in these environments, but its corrosion resistance needs to be improved by surface modifications. The electrodeposition of Zn–Ni–Cu process show some unexpected effect, this effect is an agreement with the work of other researchers in which high zinc in Zn–Ni layer is not well understood [15]. Therefore, controlling the process is a big job.

Figure (1) shows the average polarization curves for potentiodynamic electrodeposition Zn–Ni–Cu, this curve is automatically plotted to describe the deposition process as in figure (2), the polarity is reversed at –1474 mV vs Ag/AgCl, this magnitude is different from

the deposition potential of zinc or nickel because the deposit is an alloy. If zinc deposited from bath containing only zinc ions starts at about  $-1000$  mV. Cathode surface analysis did not reveal the presence of zinc of more negative potentials, indicating that the current is due to hydrogen discharge. Alloy deposition is strongly inhibited by pure nickel, but it is enhanced by comparing it with a pure zinc deposition at potentials more negative than  $-1000$  mV vs Ag/AgCl [16].

These results show that zinc can be codeposited with nickel at potentials where it does not deposit in pure form, which could be explained by the formation of low cathodic polarization, of a mixed intermediate which catalyses by the induced codeposition, where a given element can be codeposited to form an alloy. Two different mechanisms depending on the potential have been hypothesized as follows [17]:

At low polarization, the production of Zn–Ni alloys is due to the underpotential discharge of Zn, driven by nickel ion reduction, in the potential range from  $-700$  to about  $-900$  mV vs Ag/AgCl. Therefore  $i_{\text{Zn}} / i_{\text{Ni}}$  ratio changes only slightly and does not depend on the bath composition.

At potential more negative than  $-900$  mV vs Ag/AgCl, corresponding to the equilibrium potential of zinc rich phase deposition, zinc and nickel reduction can occur separately, according to their respective exchange current densities.

But it can not be deposited in a pure form. However, interactions between the components in the deposit may shift the deposition potential of the less noble metal [18].

It is found in this work that when increasing the nickel bath concentration, the changes in composition of the deposits become gradually less dependent on the applied potential. When the deposition potential decreases, the slope of the curves increases because zinc can form composite with nickel–copper and anomalous deposition is often obtained.

The major alloying on the surface is zinc as indicated by X-Ray fluorescence Table (3). Several attempts were made to obtain a composition in such a way that it situated in the single phase of the phase diagram for Zn–Ni–Cu. On the other hand the results of (EDX) test for Zn–Ni–Cu is shown in figure (3) which shows the main peak for zinc metal.

Other researchers mentioned that such layers exhibited a top specification which was obtained when the deposited alloy contains about 12–15% Ni [19, 20]. Also it has been reported in the literature [21] that the enthalpy of  $\gamma$  phase of Zn–Ni deposits is lower and

hence has the highest thermodynamic stability when compared to other phases such as  $\alpha$  and  $\eta$  phase.

Figure (4&5) show (SEM) topography for Zn–Ni–Cu coating for X500 and X2000, significant change in topography of the coating layer is observed. Kirkendall voids may also formed but less than those observed in the Zn–Ni coating [22], due to inward diffusion flux of Zn, Ni and Cu.

The coating surface is covered by a number of submicron sized grains conglomerated together to form the "cauliflower like" structure as shown in figure (6).

The mechanical properties of base metal and Zn–Ni–Cu coatings were investigated by using microhardness testing; the average value of Zn–Ni–Cu is 482 VHN, this result shows significant difference value between coating and base metal. On the other hand slight change in hardness value of Zn–Ni–Cu after heat treatment at 200°C, 1hr for coated layer was observed in comparison with the value of hardness before heat treatment as shown in figure(7). This difference is due to enhancing stability of the coating which has been improved by temperature.

To evaluate the corrosion properties of the coated system and the base metal was tested, to provide a standard reference to compare its corrosion resistance. The corrosion resistance of Zn–Ni–Cu alloy is related to passivation layer for Ni and Cu content in the alloy. The growth of the Ni content induces a growth of the corrosion resistance. Nevertheless corrosion resistance of the Zn–Ni–Cu alloys is related to their anodic potential versus steel (sacrificial protection), which is controlled by the Ni content. The growth of the Ni content switches the corrosion potential towards less electronegative values, making it to become cathodic versus steel. It means that there is an optimum range of the Ni concentration in alloy to obtain the maximum corrosion resistance ranged between 8–14 % Ni [23].

The corrosion kinetics of the base metal , base metal coated with Zn–Ni–Cu and base metal coated with Zn–Ni–Cu (after heat treatment) was investigated in 5% NaCl using salt spray chamber at 35°C for 24hrs as shown in Table (4).

The corrosion rate results of the base metal ,base metal coated with Zn–Ni–Cu and base metal coated with Zn–Ni–Cu (after heat treatment) was 1.2258 mm/y, 0.3799 mm/y and 0.4568 mm/y respectively.

These results explain the good corrosion resistance when coated by Zn–Ni–Cu, because it acts as a good barrier layer between metals and environment. There wasn't any significant



role for heat treatment on improving the corrosion properties of Zn–Ni–Cu alloy as shown in the corrosion rates given in Table (4).

Figure(8,9 and 10) show a great difference in the surface topography due to the corrosion phenomena among the base metal , base metal coated with Zn–Ni–Cu and base metal coated with Zn–Ni–Cu (after heat treatment).These figures showed clearly a change in the topography of the outer layer. The layer is enriched in Ni and Cu particle forming a diffusion barrier which prevents further reaction.

The base metal coated with Zn–Ni–Cu and base metal coated with Zn–Ni–Cu (after heat treatment) showed better corrosion resistance when exposed to acidic media ( i.e. 1 % sulfuric acid ) than the base metal as shown in Figures ( 11,12 and 13 ). It is obvious from the corrosion current densities of the base metal coated with Zn–Ni–Cu and base metal coated with Zn–Ni–Cu (after heat treatment) ( i.e. 24.66& 12.00 A/m<sup>2</sup>) in comparison with the base metal ( i.e. 107.8 A/m<sup>2</sup>)

The values for corrosion current  $I_{corr}$ . only 2.466E–3 A/cm<sup>2</sup> and 1.2E–3 A/cm<sup>2</sup> corresponding Zn–Ni–Cu and Zn–Ni–Cu (heat treatment) with the base metal value 1.078E–2 A/cm<sup>2</sup>.

## Conclusion

- 1–The Zn–Ni–Cu alloy before and after heat treatment worked as an excellent passivation layer to protect the base metals from the aggressive corrosion environments (5% NaCl and 1% H<sub>2</sub>SO<sub>4</sub>).
- 2–The use of the potentiodynamic electrodeposition of Zn–Ni–Cu helped in an efficient way to reach the optimum coating thickness (i.e. 10 µm).
- 3– The average codeposition potential of Zn–Ni–Cu coating layer was –1474 mV vs Ag/AgCl.
- 4– Kirkendall voids and cauliflower like structure were formed on the surface of the Zn–Ni–Cu coating layer.
- 5– Significant improvement in hardness was observed on the base metal after adding the coating layer (i.e. Zn–Ni–Cu).

Table1. Chemical composition of the base metal

Al	Cu	Cr	Mn	Mo	Ni
0.0910%	0.0692%	0.0386%	0.5351%	0.0000%	0.0250%
P	Si	V	S	C	Fe
0.0284%	0.3458%	0.0026%	0.01081%	0.18283%	Rem.

Table2. Electroplating bath composition

Depositing Conditions	Chemical Composition	Bath
Anode Plate: Zn (99.79%)  pH:12.5  Plating Time: 60 min  17 Run  Dull Appearance	ZnO 20 g/l  NiSO <sub>4</sub> .6H <sub>2</sub> O 2g/l  CuSO <sub>4</sub> .5H <sub>2</sub> O 0.66g/L  NaOH 150 g/l  C <sub>4</sub> H <sub>13</sub> N <sub>3</sub> Diethylentriamin 3.33ml/l  (Chelating Agent )	Zn-Ni-Cu

Table3. X-RAY fluorescence for ZN-Ni-Cu

System	Composition element for first layer	Weight percentage for first layer
Zn-Ni-Cu	Zn	81.0505%
	Ni	15.3172%
	Cu	3.6323%



Table4. Corrosion rate after exposure 5%NaCl at 35°C, 24hrs.  
In salt spray chamber

Metal	Base Metal	Zn-Ni-Cu	Zn-Ni-Cu (After Heat Treatment)
mm/y	1.2258	0.3799	0.4568

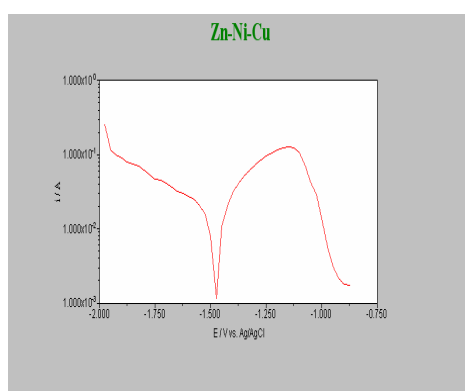


Fig.1 Average polarization curve for deposition  
Zn-Ni-Cu

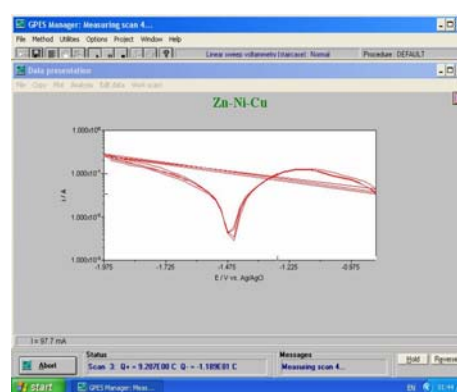


Fig.2 Multilayer scan for electroplating  
Zn-Ni-Cu

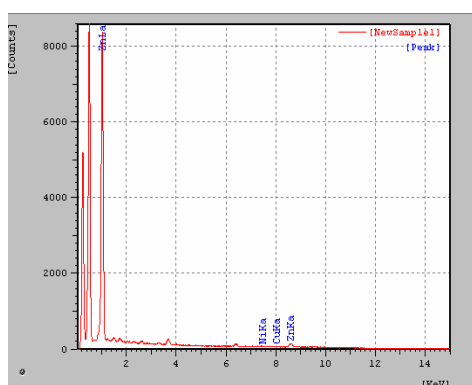


Fig.3 EDX for Zn-Ni-Cu

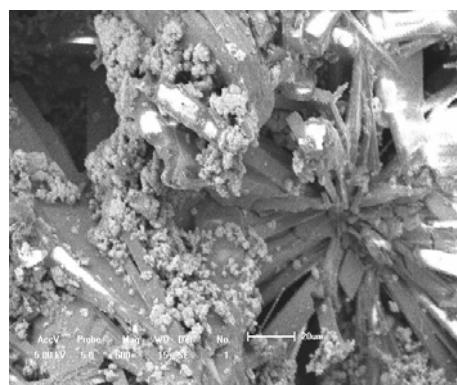
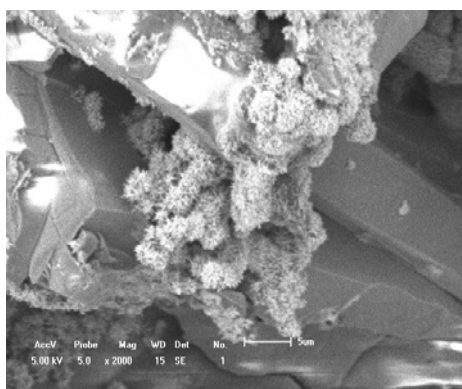
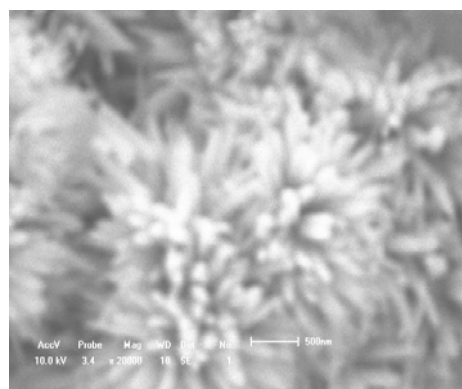


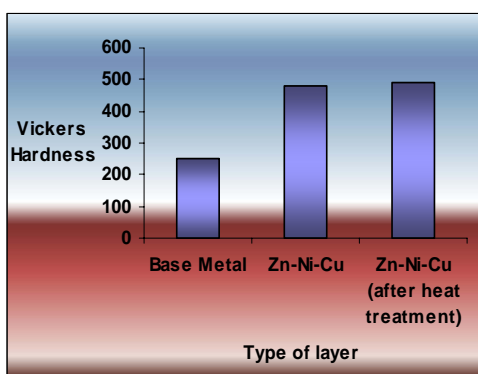
Fig.4 SEM of Zn-Ni-Cu coating (X500)



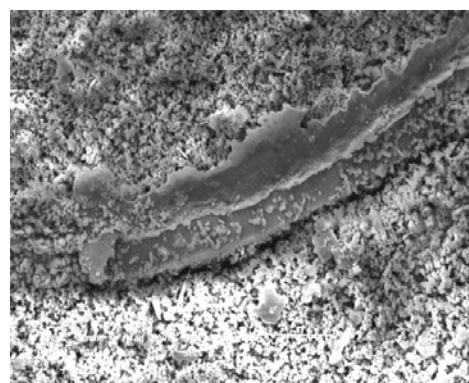
**Fig.5** SEM of Zn-Ni-Cu coating (X2000)



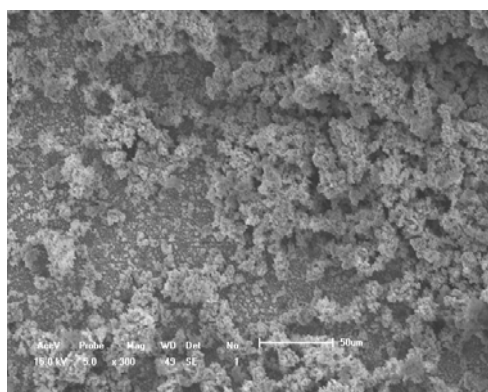
**Fig.6** SEM of Zn-Ni-SiO<sub>2</sub> coating (X20000)



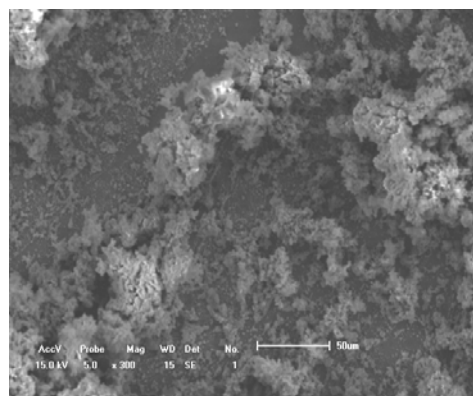
**Fig.7** Average Vickers hardness for Base Metal, Zn-Ni-Cu and Zn-Ni-Cu (after heat treatment)



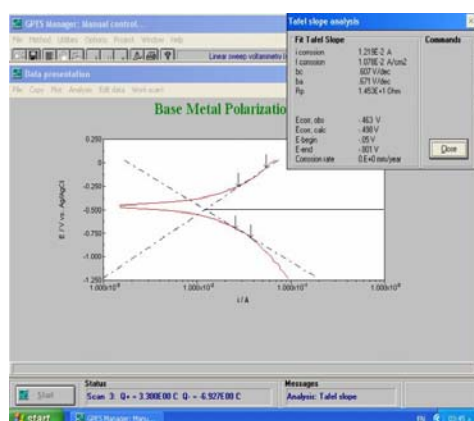
**Fig.8** SEM micrograph (X300)for Base Metal after exposure to salt spray chamber (5% NaCl at 35°C for 24hrs)



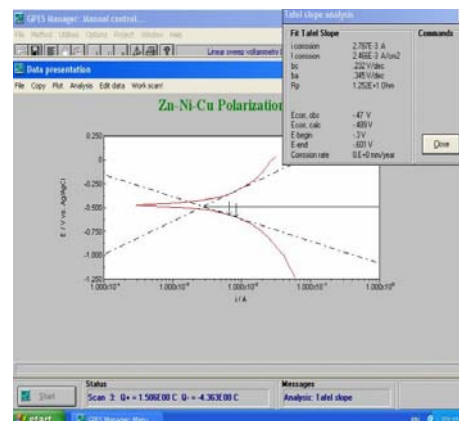
**Fig.9** SEM micrograph (X300) for Zn-Ni-Cu after exposure to 5%NaCl at 35°C for 24hrs (Salt Spray Chamber)



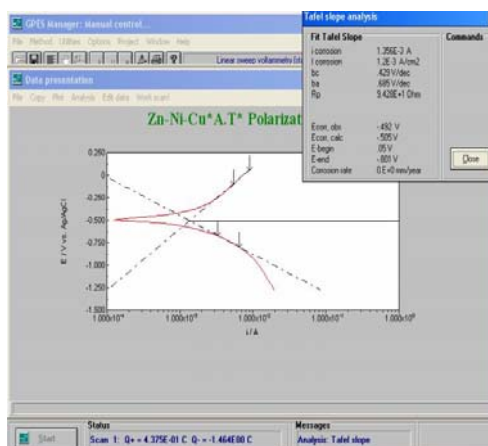
**Fig.10** SEM micrographs(X300) for Zn-Ni-Cu (heat treatment) after exposure to 5% NaCl 35°C for 24hrs (Salt Spray Chamber)



**Fig.11** Tafel slope analysis for Base Metal in 1% sulfuric acid



**Fig.12** Tafel slope analysis for Zn-Ni-Cu in 1% sulfuric acid



**Fig.13** Tafel slope analysis for Zn-Ni-Cu (heat treatment) in 1% sulfuric acid

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