Investigation of corrosion behavior of galvanized mild steel by improved Zn acidic bath containing ZnO nanoparticles

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ABSTRACT

In this study, ZnO nano particles were deposited on mild steel sheets from an acidic zinc bath. These particles were synthesized by using an auto combustion technique. The effect of concentration of ZnO nano particles on the corrosion behavior of depositions was investigated. The results of salt spray tests and electrochemical measurements showed that corrosion resistance is improved by addition of ZnO nano particles to the acidic zinc bath. Based on the results, the coating containing 0.5g of zinc oxide nanoparticles had the lowest corrosion rate (1.022mpy) and high corrosion resistance. Scanning electron microscopy (SEM) and X- ray diffraction (XRD) were used for studying the surface morphology and crystal structure of the zinc deposit. SEM observations showed that zinc oxide nano-particles acted as a barrier against corrosive environment by absorbing the corrosive agents. The XRD pattern showed that the addition of nano ZnO decreased the amount of corrosion products, which indicated a higher corrosion resistance compared to the sample without any nano-particles.

1. Introduction

Zinc coatings are widely used for corrosion prevention on ferrous metals, acting not only as a barrier layer from corrosive media, but also as a sacrificial anodic layer for protection [1]. Zinc by virtue of its low standard electrode potential (E°= -0.76 V vs NHE) acts as a sacrificial coating on steel [2]. These types of coatings are prepared by the plating treatment named galvanization, cold and hot [3]. Cold galvanization is based on the electroplating process of zinc, which has been widely used for the corrosion protection of steel [4, 5]. The deposition of zinc has been obtained from various types of baths like chloride, sulphate, sulphate-chloride and alkaline [6-8]. Among these, chloride baths are preferred because of their high- conductivity, low-cost and non-polluting nature [9].

Nano-materials due to their size in compared with other similar materials with larger size show unusual behavior [10]. These unusual behavior causes to appearance new properties in corrosion-resistant coatings, soft magnetic materials for magnetic recorders and also in electro-catalysts for hydrogen evolution and oxidation reactions [11]. Recently, the adding of nano-powders to the electroplating bathes has been done by means of fabrication of composite coatings. It has been further shown that electrodeposited zinc-ceramic composite coatings containing SiO_2 [12], TiO_2 [13] or Al_2O_3 [14] have increased wear and corrosion resistance versus pure zinc coatings. The electroplating process of metal-ceramic coatings

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requires the use of stable suspensions of positively charged ceramic particles. Sedimentation process depends on several parameters such as electrolyte acidity, sedimentation method, current density, type of materials used and amount of additives into electrolyte [15]. Existence of organic compounds in the electroplating bath can improve deposition characteristics such as structure, morphology, porosity and grain size [16]. In this study, ZnO nano-powders were added to the chloride bath of zinc electroplating and the structure and corrosion behavior of fabricated composite coatings were investigated. The effect of the zinc oxide nano-particles content on corrosion behavior of coating solutions in NaCl 3.5wt% were evaluated by polarization tests. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were employed for investigating of the surface morphology and phase structure of coatings, respectively.

2. Materials and Methods

2.1. Synthesis of nano-zinc oxide and galvanization treatment

Details of nano ZnO powder has been published elsewhere [17, 18]. In brief, in a porcelain crucible were mixed 4 gr of zinc nitrate with 2.99 gr of glycine, and then exactly 15 mL deionized water (DI) added. By adding ammonia to solution, the pH was reached to 6. The porcelain crucible was placed in water bath with 60°C for 7 hours, while during this period, mechanical agitator was working. When the solution became as gel form, the mechanical agitator was pull out and allowed keeping time be completed. After this stage, the porcelain crucible placed on flame with 400°C until auto combustion process be done. Then the porcelain crucible for 2 hours was transferred to the furnace until calcination reaction in 600°C was done. Using scanning electron microscopy (SEM), nano-particles size about 38 nm was determined that in Fig. 1 is shown.

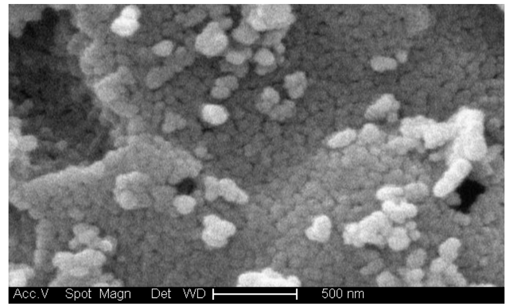

Fig 1. SEM image of zinc oxide nano-particles

To galvanization of mild steel from zinc chloride bath according to Table 1 was used.

Table 1. Details of zinc chloride bath

Materials	Concentration(g/L)
Zinc Chloride	60
Ammonium chloride	170
Boric acid	20
addetives	110

The pH value of solution and the current density was adjusted to 5 and 0.35A/cm^2 respectively. It should be mentioned that the time of electroplating were considered 30 minutes. Samples with dimensions 50×30×1 mm of mild steel were created. The samples were firstly washed with detergent solution and warm water and then were placed in 15% potash solution in an ultrasonic cleaner for 2 minutes. After this step, samples were washed in deionized (DI) water and placed for 2 minutes in a solution of HCl 10%. Then samples were washed in DI water and were placed in electroplating cell. The concentration of zinc oxide nano particles in the baths was adjusted between 0 to 1 g/L.

2.2. Microstructure characterization

Crystal structure of the plated samples was studied by X-ray diffractometer (Philips PW-3040, 40kV and 30mA) using monochromatized Cu Kα radiation (λ = 0.1506 nm). XRD spectra of the films were recorded by scanning 2θ at the range of 10–90°.

2.3. Corrosion behavior characterization

The corrosion behavior of the specimens was tested in an electrolyte of 3.5%wt NaCl solution using an Autolab PGSTAT 30 Electrochemical

Measurement System. The electrochemical corrosion test was carried out in a flat cell with the specimen-exposed area of 1 cm². The flat cell included a stainless steel auxiliary electrode, a saturated calomel reference electrode (SCE) and the specimens as working electrodes. The scans were carried out at a rate of 0.1 mV/ sec from – 0.25 V to +0.5 V relative to the open-circuit potential. Before starting test, the samples were kept in the OCP for 30 minutes until equilibrium situation was reached. For characterization of polarization curves and determining of the slope of cathodic (β_c), anodic (β_a) sections of curves and the polarization resistance (R_p), Corrview software was employed. This software evaluates R_p by Stern and Geary relationship, according to the following equation:

$$R_p = \frac{\beta_a . \beta_c}{2.3 i_c \quad .(\beta_a + \beta_c)}$$

where i_{corr} is corrosion current density, β_c is cathodic Tafel slopes, and β_a is anodic Tafel slopes.

3. Results and discussion

3.1. Electrochemical measurements

With applying of potentiodynamic and Tafel polarization methods in NaCl 3.5wt% solution (as shown in Fig. 2 for simple galvanized sample and galvanized coating containing ZnO nano-powders), results according to available results in Table 2 were obtained. Optimum amount of nano oxide concentration was obtained in the sample No.5 with 0.5 g/L nano-zinc oxide.

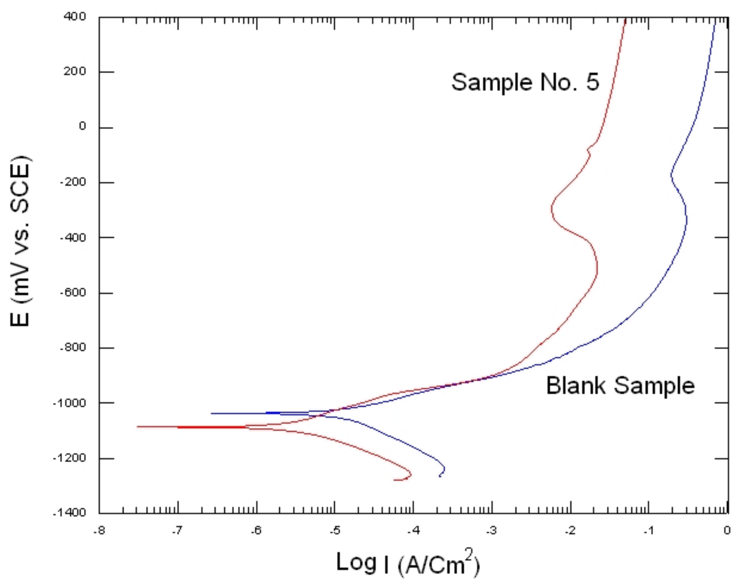

Fig 2. Tafel polarization tests for blank sample and sample No. 5 (galvanized with 0.5 g/L nano ZnO)

Table 2. Results of Tafel tests

Item	Smaple Name	Mean of Corrosion Rate(mpy) [±SD]	E_{corr} (mV) (vs. SCE)	I_{corr} (μA/cm^2)
1	Galvanized Steel	4.18[±0.55]	-1087	15.5
2	Galvanized Steel + 0.05g nano ZnO	1.78[±0.02]	-1216	6.1
3	Galvanized Steel + 0.1g nano ZnO	1.42[±0.04]	-1306	4.9
4	Galvanized Steel + 0.25g nano ZnO	1.31[±0.03]	-1334	4.3
5	Galvanized Steel + 0. 5g nano ZnO	0.98[±0.20]	-1432	3.5
6	Galvanized Steel + 0.75g nano ZnO	2.1[±0.72]	-1420	7.4
7	Galvanized Steel +1g nano ZnO	2.2[±0.04]	-1430	7.6

SD : Standard Deviation

A notable difference in Fig. 2 is that the curves of the fabricated composite coating containing ZnO nano-particles shift to the left-hand side over the entire potential range in comparison with those of the conventional Zn coating, which means that the fabricated composite coating containing ZnO nano-particles had lower both anodic and cathodic reaction rates during corrosion process than the conventional Zn coating. The improvement in corrosion resistance of the composite coating arises from two effects of the ZnO nano-particles: (i) as inert and insulating materials, the ZnO particles protect the underlying zinc matrix against corrosion attack, essentially forming a localized barrier film and (ii) the incorporated ZnO particles could also support corrosion products and slow down subsequent corrosion [19].

Table 3 shows one way Analysis of Variance (ANOVA) results of Table 2. Considering that the amount of p-value smaller than 05 / 0. Between results in different crime ZnO nano-particles added to each liter of plating solution is a significant difference.

Table 3. one way ANOVA results in Table 2

	Sum of Squares	df	Mean Square	F	p-value
Between Groups	14.924	6	2.487	72.097	0.000
Within Groups	0.310	9	0.034		
Total	15.234	15			

Fig. 3 shows corrosion rate changes versus the adding amount of the ZnO nanoparticles to the electroplating solution. As is seen in Fig. 3, the fabricated composite coating that its plating solution contains 0.5g nano-particle per liter has the lowest corrosion rate between all coatings.

In addition, it is observed that the use of ZnO nano-particles in the plating baths improves the corrosion resistance of the coatings in comparing with the coating without any nano-particles. It is worth to say that the adding of ZnO nano-particle to the plating baths reduces corrosion potential of the coatings which means the protection power of the coatings has improved. Based on the cathodic protection theory, the coating with the lower corrosion potential can protect substrate better than the coating with higher corrosion potential.

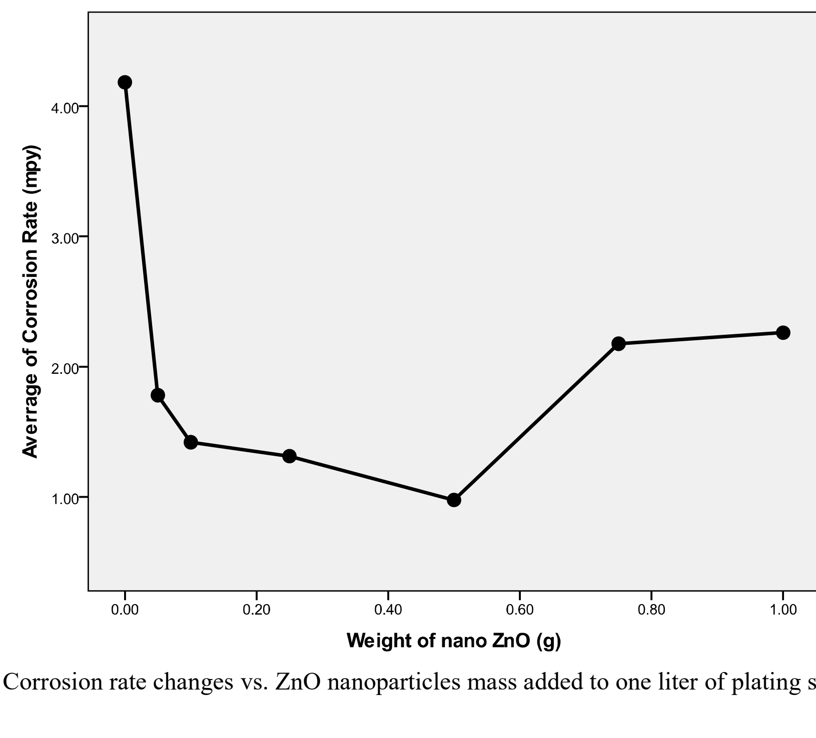

Fig 3. Corrosion rate changes vs. ZnO nanoparticles mass added to one liter of plating solution

3.2. Salt Spray Test

The salt spray test was carried out as per ASTM B 117 by following the standard procedure [20]. For corrosion behavior assessment of sample without any nano-particles and sample containing zinc-oxide nano-particles, these samples were placed in a salt spray test chamber. On both samples after 8 days, white rust was observed, but the red rusting was observed on sample without any nano-particles after 1023 hours and on galvanized sample with zinc-oxide nano-particles after 1320 hours.

3.3. Studies of surface morphology

3.3.1. The results of SEM images

In the following can see SEM images of tested sample without any nano-particles and samples including 0.5 g nano-zinc oxide:

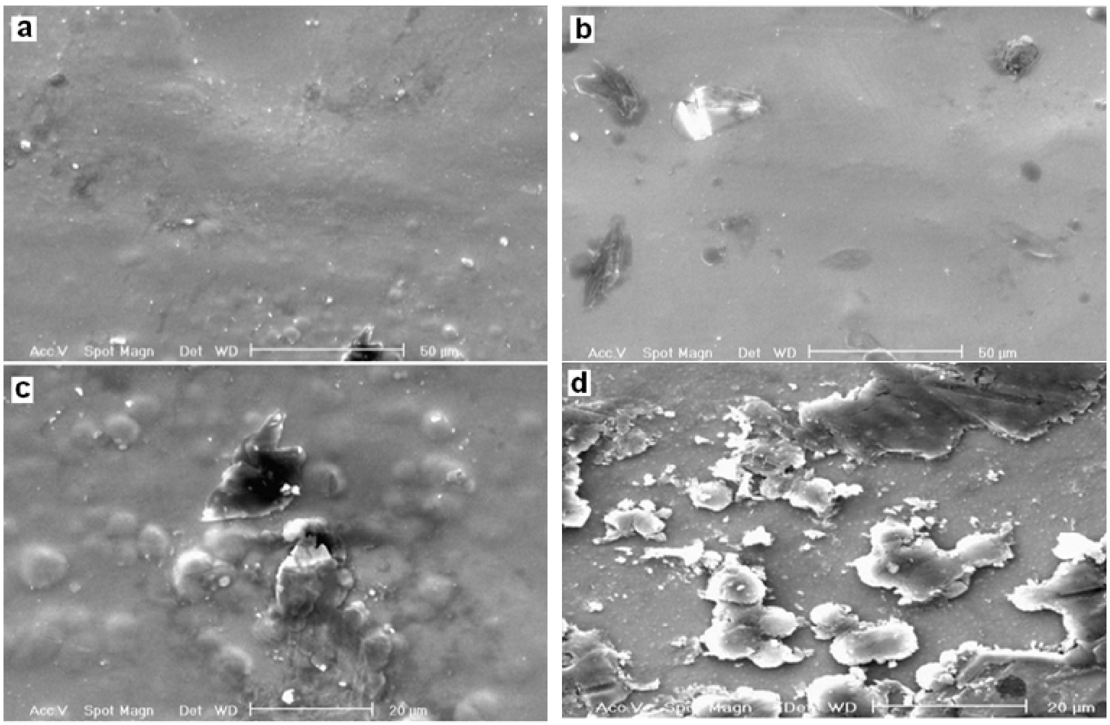

Fig 4. Galvanized coating before and after the corrosion test in the NaCl 3.5wt% solution with presence 0.5g/L zinc oxide nano-particles and without it. (a) sample before testing, (b) sample with 0.5g of zinc oxide nano-particles before test, (c) sample without any nano-particles after testing, (d) sample with 0.5g of zinc oxide nano-particles after test

As in Fig. 4a has been shown, before corrosion test the sample of conventional galvanized steel has been smooth and uniform surface, while in the Fig. 4c that is connected to the end of corrosion test, the bed of sample surface in addition to corrosion, has been blistered. Fig. 4b is referring to the surface of galvanized steel with nano-particles of zinc oxide. It should be noted that before corrosion tests by ocular inspection the surfaces of both galvanized steel were completely smooth and homogeneous. After the corrosion test as in Fig. 4d has been shown, zinc oxide nano-particles by absorption of the corrosive agents have action as a barrier against corrosive environment. As shown in this Figure, the original surface of galvanized steel is smooth and homogeneous without any blisters. The use of nano particles of zinc oxide also creates a uniform surface by SEM is shown.

3.3.2. XRD pattern

Fig. 5 to Fig. 8 show XRD diffraction patterns before and after corrosion tests in NaCl 3.5wt% solution with presence of zinc-oxide nano-particles or their absence in coating.

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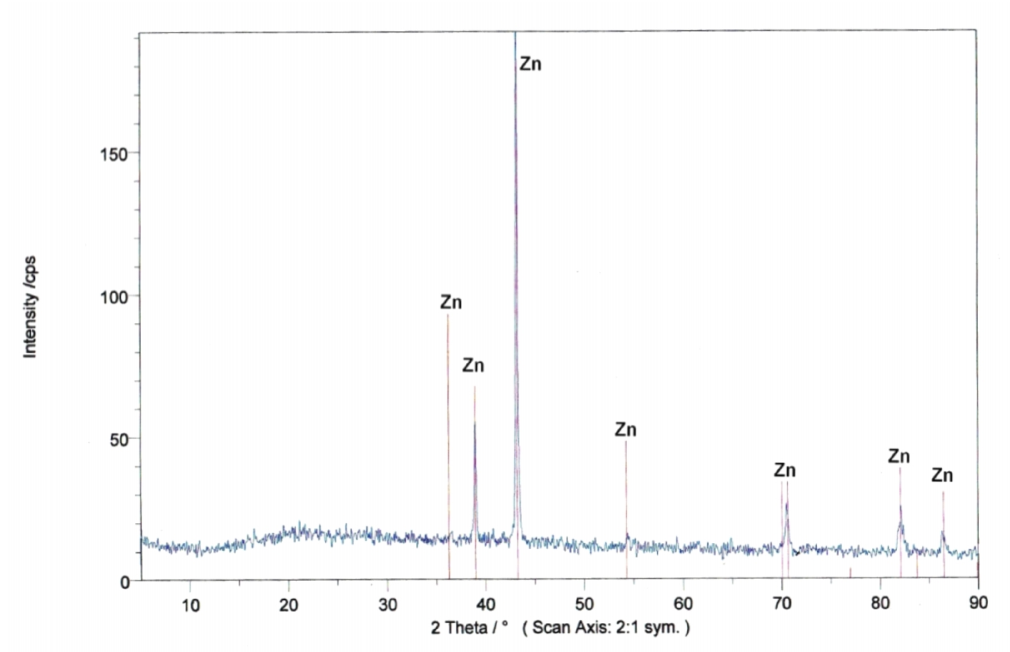

Fig 5. XRD patterns of sample without any nano-particles, before testing

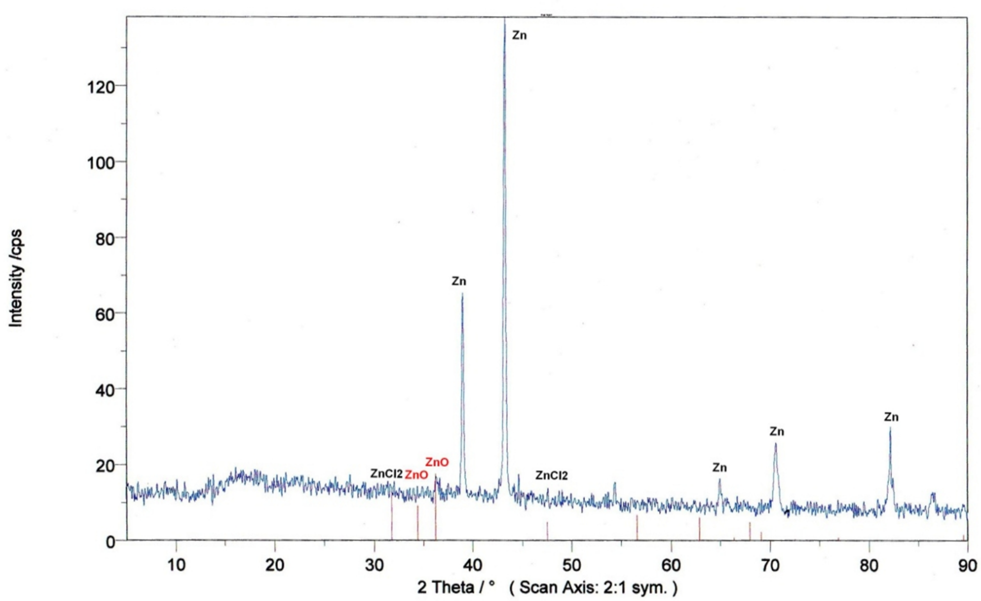

Fig 6. XRD pattern of sample without any nano-particles, after testing

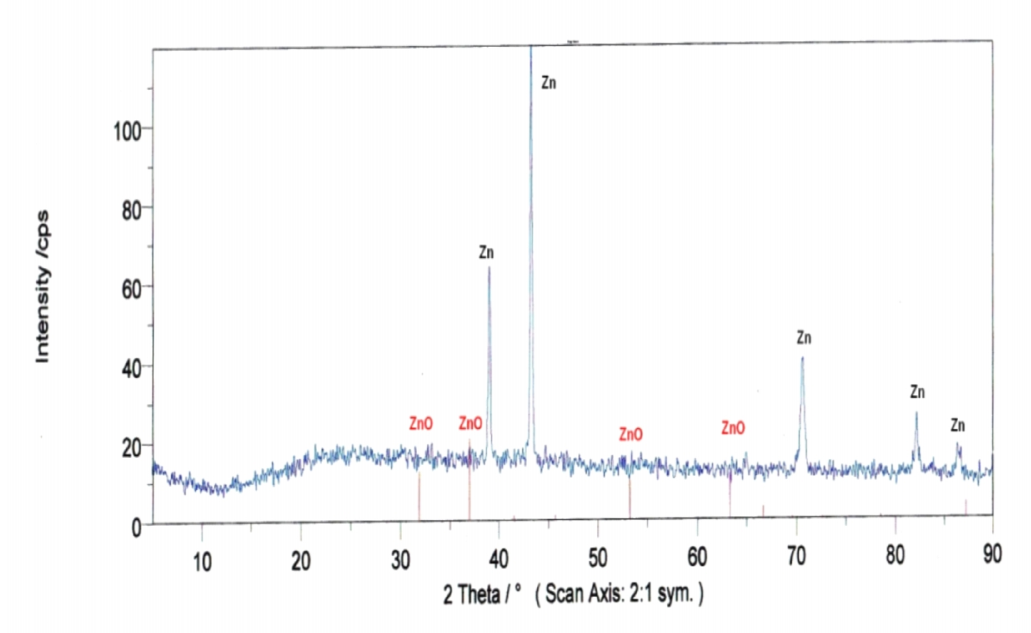

Fig 7. XRD Pattern Sample galvanized with zinc oxide nano-particles, before testing

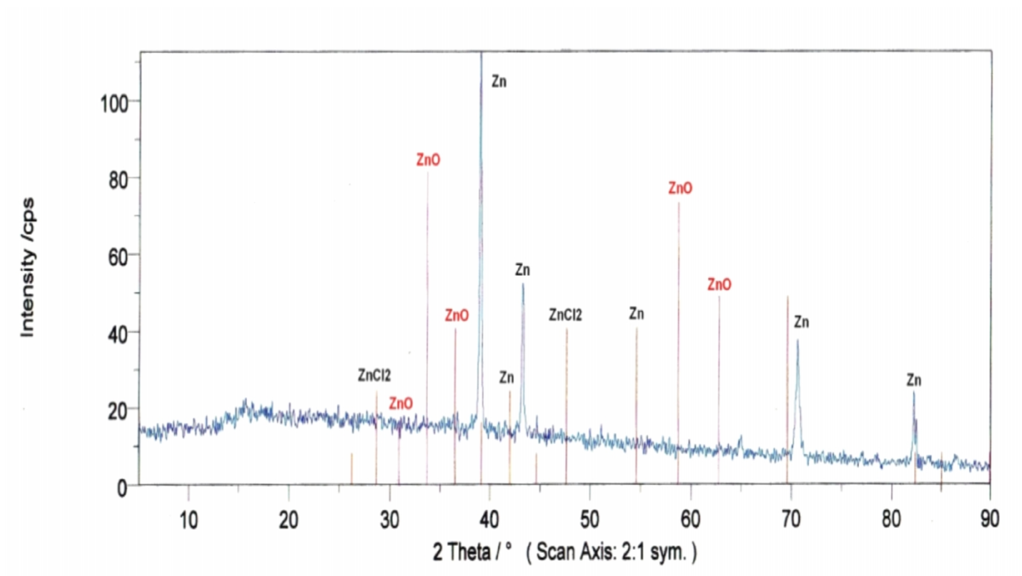

Fig 8. XRD pattern of samples with galvanized zinc oxide nano-particles, after testing

As in Fig. 5 is seen, before corrosion test the spectrum of sample without any nano-particles only exists Zn peaks. After testing in the sample without any nano-particles spectrum (Fig. 6) in addition to Zn peaks, also peaks connected to $ZnCl_2$ and ZnO are seen. These two matters are most commonly detected corrosion products on zinc surface corroded in choloride-containing environments [21, 22]. There are maybe other corrosion products such as $Zn(OH)_2$, which are sometimes difficult to be found by XRD [23, 24]. Galvanized sample spectrum with zinc oxide nano-particles, in addition to peaks of Zn, also having ZnO peaks that indicate the presence of zinc oxide nano-particles in coating (Fig. 7). In the next figure (Fig. 8) the spectrum of galvanized sample with zinc oxide nano-particles after testing is shown that in addition to Zn and ZnO peaks, also $ZnCl_2$ peaks are seen. By comparison of Fig. 6 and Fig. 8 is seen that in the sample without any nano-particles surface, the amount of corrosion products are more than of galvanized sample with zinc-oxide nano-particles, which indicates a higher corrosion resistance than the sample without any nanoparticles.

Conclusion

- In the present research, the galvanized coatings in which nano-ZnO was added were deposited on mild steel and the effect of the added amount of ZnO on the coatings morphology and its corrosion behavior were studied.
- Based on results, the use of nano-particles of zinc oxide improved the corrosion resistance of coatings. The fabricated composite coating that its plating solution contains 0.5g nano-particle per liter has the lowest corrosion rate between all coatings..
- SEM observations showed that before corrosion tests the surfaces of both galvanized steel were completely smooth and homogeneous and after the corrosion test zinc-oxide nano-particles by absorption of the corrosive agents had action as a barrier against corrosive environment. The use of nano-particles of zinc oxide also created a uniform surface.
- The study of XRD pattern showed that in the sample without any nano-particles surface, the amount of corrosion products were more than of galvanized sample with zinc-oxide nano-particles, which indicated a higher corrosion resistance than the sample without any nano-particles.

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