Engineering and Technology Journal
Journal homepage: engtechjournal.org

Fabrication of Ni-ZrO_2 Nanocomposite Coating by Electroless Deposition Technique

Hiba M. Algailani [a*], Adel K. Mahmoud [b], Hanaa A. Al-Kaisy [c]

[a] Materials Engineering Department, University of Technology, Baghdad, Iraq. hiba82algailani@gmail.com

[b] Collage of Engineering, University of Diyala, Diyala, Iraq, adelalkayali@yahoo.com

[c] Materials Engineering Department, University of Technology, Baghdad, Iraq. 130011@uotechnology.edu.iq

*Corresponding author.

Submitted: 26/07/2019 Accepted: 17/10/2019 Published: 25/05/2020

K E Y W O R D S

Electroless deposition technique, Ni-ZrO_2 nanocomposite coating, ZrO_2 nanoparticles.

A B S T R A C T

This work aims preparation of Ni-based nanocomposite coating by electroless deposition method onto stainless steel (316L) substrate, the present work will compare the effects of incorporation of ZrO_2 nanoparticles at different percentages (1.25 wt %, 2.25 wt %, and 4.25 wt %) Ni-based electroless deposition coating of the bath nanocomposite on the phase structure, microhardness, and corrosion resistance is studied. Where the structure and chemical composition of nanocomposite coatings were studied by using (X-ray), (SEM) and (EDS). of Ni - ZrO_2 nanocomposite coating exhibits much-increased microhardness and remarkably improved corrosion resistance.

How to cite this article: H. M. Algailani, A. K. Mahmoud, and H. A. Al-Kaisy, "Fabrication of Ni-ZrO_2 nanocomposite coating by electroless deposition technique," Engineering and Technology Journal, Vol. 38, Part A, No. 05, pp. 649-655, 2020.
DOI: https://doi.org/10.30684/etj.v38i5A.491

1. Introduction

Nano zirconia (ZrO_2) is a bio-inert ceramic material with high mechanical properties and fracture toughness [1]. Nano Zirconia ceramics have several advantages has generated a lot of interest in recent years due to its specific optical, thermal, chemical and electrical properties and potential applications including biomedical application, transparent optical devices, and electrochemical capacitor electrodes, sensors, synthetic gemstone, fuel cells, catalysts including photocatalysts and advanced ceramics [2,3]. That the addition of zirconium oxide (ZrO_2) nanoparticles improves properties such as hardness, fracture toughness, wear & corrosion and chemical resistance [4, 5]. A novel technique has been developed to produce nano-ceramic reinforced materials coatings. This electroless deposition nanocomposite coating is a popular method used in advanced and scientific in the industrial field. Due to its ability to produce hard, wear-resistant, and corrosion-resistant surface, its recently the electroless nanocomposite coatings technique have gained wide currency in

Tribology, corrosion, biomedical aerospace applications [6]. Nickel electroless matrix nanocomposite coatings represent an alternative technique to obtain coatings on the various substrates with high thickness of the coating for all surfaces, including complex and edges interior geometry [7]. The present work aims to compare the effects of incorporation of ZrO_2 nanoparticles and its concentration on the phase structure, microstructure, morphological of electroless Ni- matrix nanocomposite coatings.

2. Experimental

Stainless steel alloy (316L) substrate material with dimension (20mm x 20 mm x 2mm) is used for Ni- ZrO_2 nanocomposite coatings. All surface samples are grinding process with emery paper 400, 500, 600 grades. After that the stainless steel surface is cleaned from any rust and corrosion products then washings with distilled water, acetone and dried it by a heater. Stimulation of the sample surface by using the dipping method into $PbCl_2$ for a short time duration to start the coating on the substrate inside the chemical bath. The stimulation surface substrate is then immersed into the chemical bath at 85ºC for a period of three hours to complete the nickel deposition process. After several experiments, operating conditions and bath chemical composition of electroless Ni- nanocomposite coating reinforced by ZrO_2 nanoparticle is selected. Operating conditions and bath chemical composition for electroless Ni– ZrO_2 nanocomposite coatings used as shown in Table 1. To have better dispersion of the second phase nanoceramic powder without any agglomeration of particles, add of 0.025g/l surfactant from Sodium Dodecyl Sulphate to the bath. Then take about 300 ml of solution reinforced with ZrO_2 nanoparticle and mixed using a magnetic stirrer to get the best uniform and thoroughly homogeneous suspension ZrO_2 nanoparticle powder in the bath. At first stage, a nickel layer is deposited in the first time to prevent consistent porosity in the coating layer and then the nickel bath reinforced with ZrO_2 nanoparticle is founded into the same Ni bath the subsequences in order to achieve Ni– ZrO_2 nanoparticle co-deposition. After complete the electroless coating process, the samples are cleaned with distilled water.

Table 1: Electroless Ni–ZrO_2 nanocomposite coatings bath operating conditions and chemical composition [8, 9]

Composition of Ni-Bath	Con	Condition
Sulphate of the Nickel	10g/l	pH (5.5-6)
Sodium Hypophosphite	5g/l	Temp. 85±3ºC
ZrO2 nanoparticle	(1.25, 2.25, 4.25%) g/l	Bath Volume 300 ml
Tri Sodium Citrate	5g/l	Deposition Time: 3hr.
Sodium Dodecyl Sulphate (SDS)	0.025g/l	Stirrer Speed: 150 rpm
Soduim Acetate	5g/l	
Lead Acetate	2 mg/L	
Sulphate of the Nickel	10g/l	pH (5.5-6)

3. Results and Discussion

I. X-ray Diffraction (XRD) Results

The XRD pattern of electroless process Figure 1 A shows the pure Ni-peak at (111), (200) crystallographic plane with low-intensity peak for ZrO_2 was observed. It is observed from the figure 1 B, pure Ni peaks have shifted towards the higher angle values on the addition of ZrO2 nanoparticle, it can be observed that Ni and Ni- ZrO_2 nanoparticle preferentially at (200) plane due to the uniform growth of the coating. Figure 1B shows angles at approximately 44.8 and 52 respectively, which nickel peaks appear from the diffraction pattern of the Ni film. From the result of the XRD Ni-ZrO_2 spectrum, the peak of Zirconia represents that layer of Zirconia are regularly growth and the crystalline phase exists in the coating film.

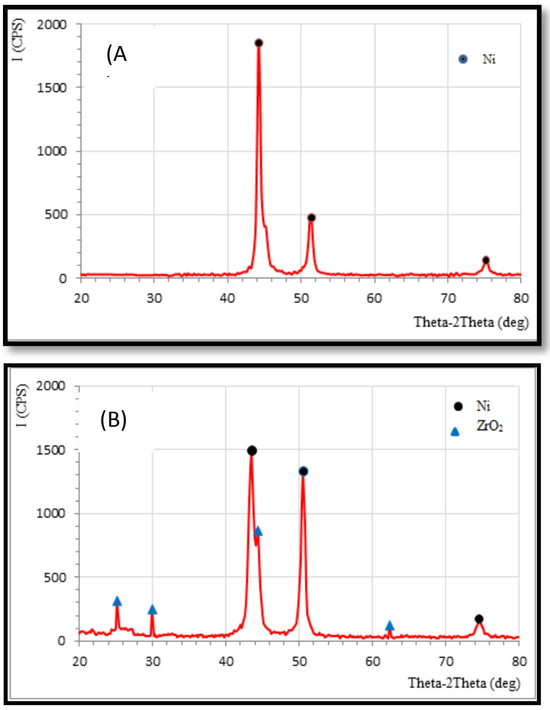


Figure 1: XRD pattern of (A) Ni pure and (B) Ni-ZrO_2 nanocomposite coating by the electroless method.

The XRD analysis results indicated that the Ni - (cubic ZrO_2) phases of nanocomposite coating are crystalline structures. Table 2 shows the crystallite size of nanocomposite coating is calculated for pure Ni matrix coating compared with Ni-ZrO_2 nanocomposite coating grains of stainless steel 316L substrate at a different weight percentage of nanoparticles utilized Debye-Scherrer's equation, given by [10].

$$D = \frac{K * \lambda}{\Delta red \cos\theta} \quad (1)$$

Where:

Δred: Full width at half maximum of this peak that determines (D) at 2θ degree.

D= Crystallite size in nano-meter.

K= 0.94 (constant).

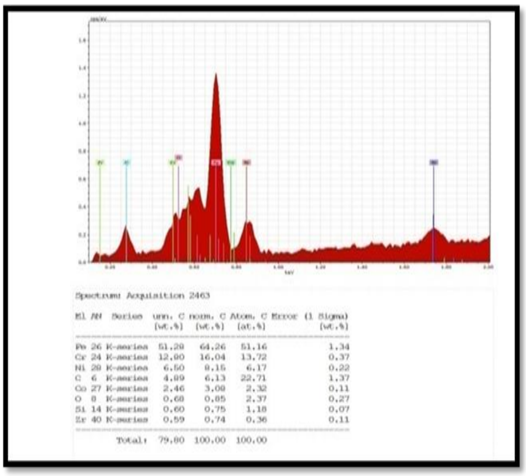
λ = 1.54 ° is the wavelength of Cu Kα radiation.

Table 2: Crystallite Sizes of nanocomposite coating grains of stainless steel 316L substrate

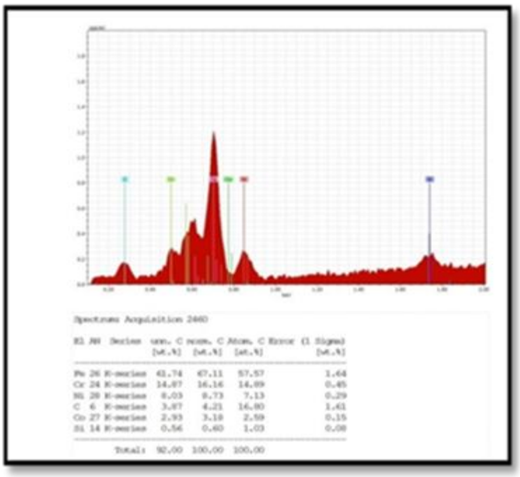
Category of coating	In. of most peak	FWHM (Rad)	Crystallite Size (nm)
pure Ni coating	496	0.0117	13.126
Ni- 4.25 wt % ZrO_2	875.6	0.0115	13.238
Ni - 2.25 wt % ZrO_2	717	0.0114	13.479
Ni - 1.25 wt% ZrO_2	926.6	0.0105	15.173

II. Microstructural and Composition Analysis Results

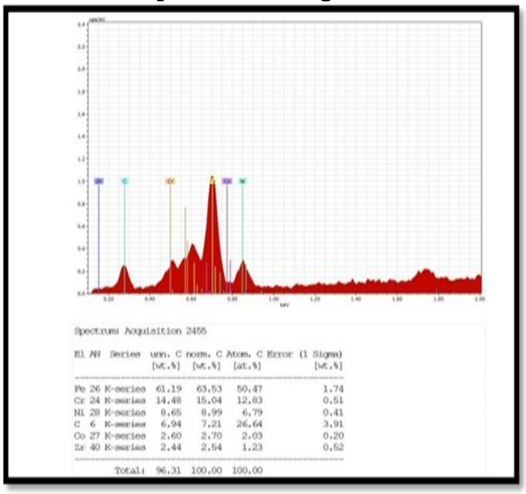
The SEM/EDX surface morphology and composition analysis examinations for the Ni–ZrO_2 nanocomposite coating by using the EDS spectroscopy for the verification of the ZrO_2 combination with pure nickel film, as shown in Figure 2 A, the Zirconia peak indicates the founded of the ZrO_2 nanoparticles in a Ni- metal matrix is embedded. The results analysis confirms that the presence of ZrO_2 nanoceramic in nickel matrix increase with the increase in the amount of ZrO_2 nanoparticles in the coating, this result led to enhance mechanical properties. The analysis from EDX shows the presence of mainly Ni (8.03%) on a stainless steel substrate after applying coating. Figures B, C, and D are shown the examinations of chemical composition coatings; the EDX analysis indicates the presence of mainly Ni along with the significant amount of Zr and O in the matrix. Higher amounts of Zr (0.74%), (2.54%), and (4.53%) and amounts of O (0.085), (0), and (18.57) were detected along with Ni (8.15%), (8.99%) and (0.14%) respectively.



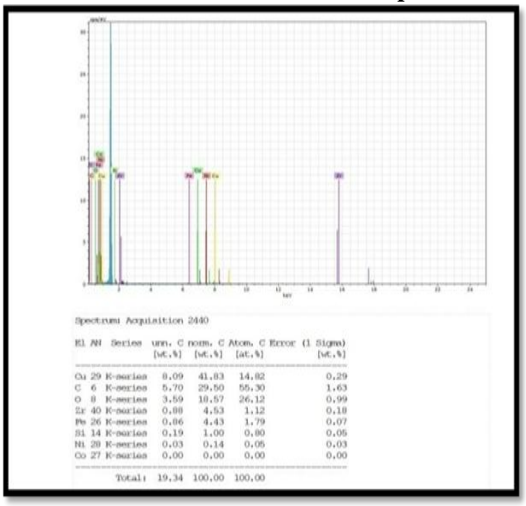
A: pure Ni coating



B: Ni-1.25wt % ZrO_2 nanocomposite coating.



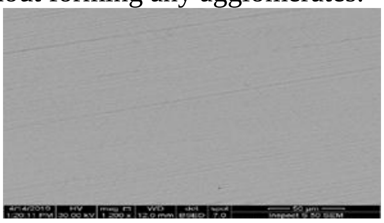
C: Ni -2.25 wt % ZrO_2 nanocomposite coating.



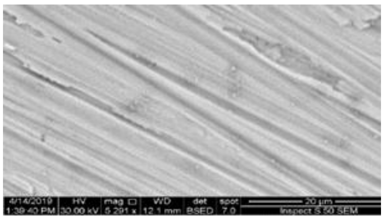
D: Ni-4.25 wt % ZrO_2 nanocomposite coating.

Figure 2: EDS of Ni- ZrO_2 nanocomposite coatings at different weight percentages of ZrO_2 nanoparticles.

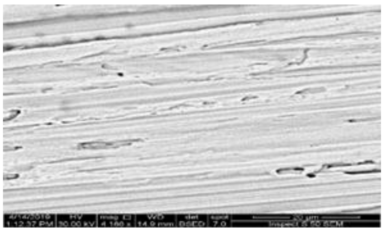
Figure 3 is shown the SEM examinations for the electroless of Ni- ZrO_2 nanocomposite coating on a metal substrate. Figure 3 B, C, and D show the nickel with ZrO_2 coating surface by the electroless deposition technique. ZrO_2 nanoparticles are distributed with fully dispersed in Ni-base coating to be dense, uniform and highly adhesive surface and continuous with a well homogenous mixture of ZrO_2 nanoparticle without forming any agglomerates.



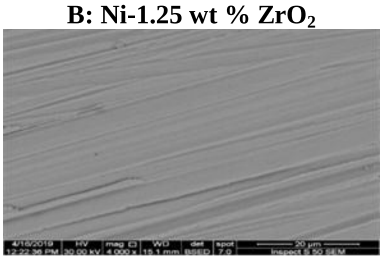
A: Ni pure



B: Ni-1.25 wt % ZrO_2



C: Ni- 2.25 wt % ZrO_2



D: Ni- 4.25 wt % ZrO2

Figure 3: SEM micrograph of nanocomposite coating by electroless deposition of (A) pure Ni coating (B) Ni-1.25 wt % ZrO_2, (C) Ni-2.25 wt % ZrO_2 and (D) Ni-4.25wt% ZrO_2.

A cross-sectional SEM image of Ni-based nanocomposites coating at the interface for the estimation of coating thickness is shown in Figure 4.

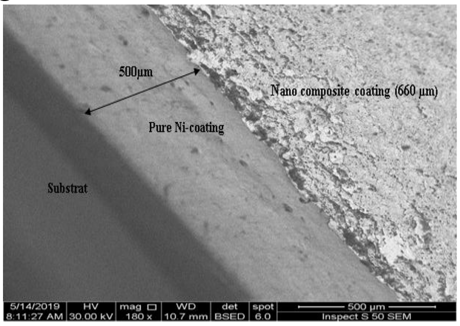


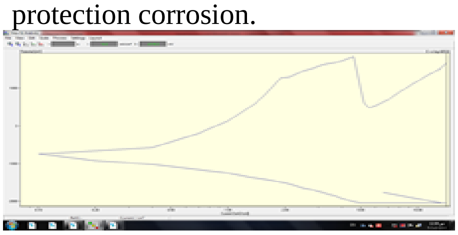
Figure 4: SEM micrograph at the interface of Ni-based nanocomposite coating by the electroless deposition technique

III. Corrosion results

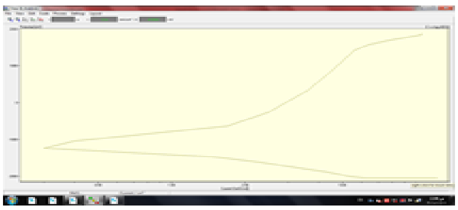
Reinforced nanoparticles act as physical barriers to the corrosion attack process of filling in micron holes or crevices and protect the surface due to best embedded occur, especially for ZrO_2 nanoparticles reinforcement Ni-based nanocomposite coating significantly lead to increase corrosion resistance value. The good barrier properties of the coating systems can be improved with nano-sized fillers have superior barrier properties even at low, reinforced, due to their higher surface area among these nanoparticles and excellent barrier resistance, nano-ceramic particles are one of the most promising types of fillers because of its advantages, such as high chemical stability in extreme environments, corrosion resistance, and fracture toughness. ZrO_2 nanoparticles are performed significant benefit to reinforcement in metallic coatings [11]. The corrosion rate (CR) in a given environment is directly proportional to its corrosion current density (Icorr) in accordance with the relation [12]:

$$CR = 0.13 \times Icorr \times (e / p) \quad (2)$$

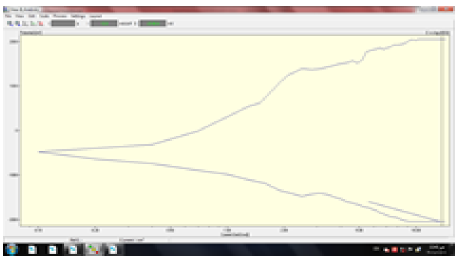
This equation relates to calculate CR in mil per year (mpy), where (e) and (ρ) are equal weight and density of elements of the coating, respectively. The test was conducted in the Material Engineering Department / University of Technology, The Figure 5 and Table 3 shown corrosion parameters for coating electroless of Ni-ZrO_2 nanocomposites coating calculated by Tafel extrapolation method in ringer solution and temperature 37°C. These parameters include potential (E corr), corrosion current density (Icorr) and Tafel slopes (bc & ba) and corrosion rate. The corrosion rate of coated specimen electroless Ni-ZrO_2 nanocomposite coatings on the different amount of ZrO_2 nanoparticles was Corrosion rate was enhanced for the coatings with 4.25 wt %, and 1.25 wt%, nano-ZrO_2 contents. The Zirconia coated acts as a good barrier that reduces effectively both anodic and cathode current densities at the 4.25 wt % Zirconia nanoparticle enhance coating performance showed the best protection corrosion.



A: Ni pure



B: Ni-1.25 wt % ZrO_2



C: Ni-4.25 wt % ZrO_2

Figure 5: Tafel plot for the sample of Ni-based ZrO_2 nanocomposite coating (500 ml) Ringer's solution at body human temperature 37°C.

Table 3: Effect of varying concentrations of nanoparticles on the corrosion behavior of pure Ni- matrix coating compared with ($Ni-ZrO_2$) nanocomposite coatings in (500 ml) Ringer's solution at body human temperature 37°C which evaluated by Tafel extrapolation method.

Type of coating	pure Ni coating	$Ni-ZrO_2$ (4.25wt %)	$Ni-ZrO_2$ (1.25 wt %)
Type Solution	Ringer's solution		
-Ecorr	744.3	393.7	453.6
Icorr ($\mu A.cm^{-2}$)	280	251	265
CR(mpy)	254	143	190
-bc	976.3	851.67	1338
-ba	1832.4	280.5	1695

IV. Microhardness of coatings

The microhardness test was used to measure the microhardness values for different ZrO_2 nanoparticles percentages using in the bath coating of the electroless $Ni-ZrO_2$ nanocomposite coatings in the as-deposited shows in Figure 6 shows sample coated nickel lowest value of microhardness when compared with others samples values of the coatings a little increased by coating at concentration ZrO_2 nanoparticle at (4.25 wt%). The microhardness of electroless Ni- (4.25 wt%) ZrO_2 nanocomposite reached HV= 428.2, increase compared with that of pure nickel Hv= 366.2, this means that higher content of ZrO_2 nanoparticles may affect the Ni crystal structures leading to favorable performance of the nanocomposite coatings.

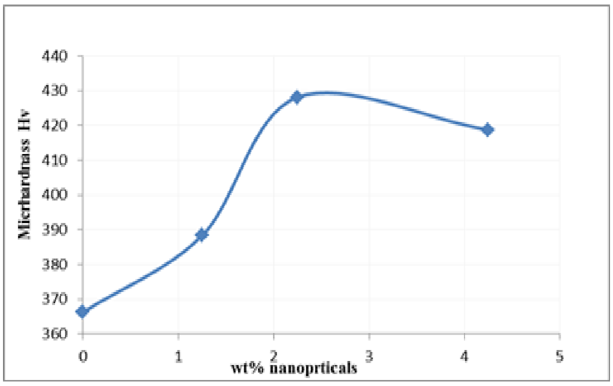


Figure 6: Variation of microhardness of electroless Ni-based coatings with ZrO2 nanoparticle content in the bath.

4. Conclusions

Through the present work, the following conclusions can be drawn:

1. Using the electroless deposition technique may be synthesised ZrO_2 nanoparticles reinforced Ni-matrix nanocomposite coating successfully.
2. The EDX micrograph analysis showed that the deposited nanocomposite $Ni-ZrO_2$ coating is fully dispersed in Ni-base coating to be dense, uniform and highly adhesive surface and continuous with a well homogenous mixture of the ZrO_2 nanoparticle coating without forming any agglomerates.
3. The XRD analysis results revealed that the $Ni-ZrO_2$ nanocomposite coating is a crystalline structure.
4. The microhardness increase with increasing second phase concentration reinforcement phase ZrO_2 nanoparticles.

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