Corrosion behavior of Ni/WC nano-structured composite layers synthesized by electrochemical method

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Abstract. Ni/WC nano-structured composite coatings were developed by electrodeposition method from a nickel plating electrolyte containing WC nanoparticles (diameter size of ~60 nm). The corrosion behavior of Ni/WC nano-structured composite coatings and pure Ni coating were comparatively investigated in wet conditions in the solution that simulates the primary water of Pressurized Water Reactors (PWRs). The morphology and chemical composition of the obtained coatings before was observed through scanning electron microscopy (SEM) connected to an energy dispersive X-ray system (EDX). The open circuit potential (OCP) and Electrochemical Impedance Spectroscopy (EIS) methods were used to evaluate the corrosion behavior, at room temperature. The nanohardness of pure Ni and Ni/WC nanocomposite coatings was tested by nanoindentation technique. SEM-EDX analyze proved that WC nanoparticles were successfully incorporated into Ni matrix. Presence of WC nanoparticles in the nickel matrix transforms surface morphology from regular pyramidal to irregular global and changes the crystallizations of nickel matrix to smaller and thinner crystallites. Ni/WC nanocomposite coating revealed a higher nanohardness value in comparison with pure Ni coating. The corrosion resistance of Ni/WC nanocomposite coating is higher under similar experimental conditions as compared with pure nickel layers, proving an enhancement of corrosion resistance.

1. Introduction
A first challenge in the nuclear power plant sector is the need to operate these plants as long as possible in a safe and cost-effective way. And to accomplish this task, the aging of materials, components and structures must be kept under control.

Over the years, nuclear power plants have suffered several failures, the main cause being corrosion, costing the industry billions of euro’s, although their design was made of corrosion-resistant alloys, including stainless steel.

In any case, using only these alloys in the literature is rich in examples of corrosion failure of these alloys.

Although a great deal of knowledge has been gained about the corrosion behavior of metallic materials over several thousand years, this has to be further developed by depositing other materials to improve corrosion behavior [1].

In metal matrix composites, the properties can be modified by presence of a second phase [2].

The second phase can be so hard like oxide or carbide particles (WC) reinforced composite Ni coatings, improving the coating properties [3, 4].
The interest in corrosion resistant of nickel coatings was traced back to the promising results of other nanocrystalline materials and the possibility to decrease the nickel grain size due to the incorporation of nanoparticles, the growth of WC grains is concerned. It is essential to make sure that good anti-corrosion properties of coatings are preserved, especially if they are to work in aggressive media [4-6].

The WC is a type of hard particle with superior physical and chemical properties, it can be used in many field, while the incorporation of WC nanoparticles was reported to improve fretting and wear behaviors [7] structure and hardness [8]. However, in the published paper [7-9], the mechanical properties of this type of coating was fully discussed, limited reports are available in its corrosion behavior [6].

The purpose of this study was to evaluate the corrosion resistance of Ni/WC nano-structured composite layers synthesized by electro-codeposition process. The corrosion resistance is evaluated in simulated pressurized water reactor (mixed boric acid and lithium hydroxide). The used electrochemical methods were: open circuit potential (OCP) and Electrochemical Impedance Spectroscopy (EIS) monitored during 24 hours.

The presence of WC nanoparticles embedded into nickel matrix was proved by SEM-EDX analysis and SEM-EDX mapping for W element.

The results show that the corrosion resistance of Ni/nano-WC nanostructured layers is higher and increases during immersion period, proving an enhancement of corrosion resistance due to embedded WC nanoparticles into nickel matrix.

2. Experimental procedures

2.1. Materials and methods

2.1.1. Preparation of Ni/nano-WC nanocomposite layers on 304L steel support. The electrodeposition of Ni/nano-WC composite layers is carried out galvanostatically with a potentiostat/galvanostat and a two electrode cell as it is shown schematically in Figure 1, where (a) represents the potentiostat/galvanostat, (b) is the electrolytic cell with cathode, anode and nickel plating solution with dispersed WC nanoparticles, (c) shows the mean size of nano–WC particles, (d) represents the schematic Ni/nano-WC layer on (e) 304L steel support and (f) SEM micrograph of the Ni/nano–WC nanocomposite layer obtained.

The Ni/nano–WC layer is electrodeposited from an additive-free standard nickel Watts plating bath to which the WC nanoparticles with a concentration of 10 gL−1 were added, as presented in Figure 1(a) [10].

The composition of nickel aqueous electrolyte is: 200 gL−1 nickel sulphate, 50 gL−1 nickel chloride and 30gL−1 boric acid. The resulting pH of nickel plating electrolyte is 4.04 [10].

The mean diameter size of WC nanoparticles is 60 nm, purchased from Hefei Kaier Nanometer Technology & Development Co. Ltd. The nanoparticles were used as received, their morphology being presented in Figure 1(c). In order to ensure the uniform dispersion of nanoparticles, the nickel plating electrolyt is stirred using a magnetic stirrer.

To obtain electro–codeposited layerss, a 304L stainless steel plate support was used as the cathode (working electrode – WE). Before electrodeposition, the steel substrate is first cleaned in alkaline solution, washed, acid etched, washed and dried. A pure nickel plate was used as a counter electrode (CE).

Electrodeposition took place in the plating dispersion electrolyte at 45±1 °C. A double walled electrochemical cell containing the two electrodes (WE, CE) was used to maintain the desired temperature. The electrodes were positioned vertically and parallel to one another, distanced equally for each measurement.
Figure 1. Schematic electro-codeposition of WC nanoparticles into nickel matrix.

The schematic presentation of the electrolytic cell is indicated in Figure 1(b), where the cathode (WE, as support for layers) is on the right (−), the anode (CE, as nickel plate in order to maintain a constant content of nickel ions into nickel plating electrolyte) on the left (+).

2.1.2. Characterization of Ni/nano–WC nanocomposite layers. The surface morphology and the chemical composition of the Ni/nano–WC nanocomposite layers obtained electrochemically is analyzed by scanning electron microscopy (SEM – Philips XL 30 FEG) and by energy dispersive X-ray spectroscopy (EDX). Also, the embedded WC nanoparticle into Ni matrix is estimated by EDX analysis. For corrosion investigation, Ni/nano-WC nanocomposite layers with a mean value of WC inclusion at 2.92 wt % (calculated using the W element content from EDX analyses).

A three–electrode set–up is employed for the corrosion investigation by electrochemical measurements. An Ag/AgCl electrode with KCl saturated solution (E = 200 mV vs. standard hydrogen electrode – SHE) is used as reference electrode (RE) and a plan Pt–Rh grid as counter electrode (CE).

Figure 2. Schematic representation of experimental protocol showing the electrochemical measurement steps for open circuit potential and electrochemical impedance spectroscopy.

2.1.3. Experimental protocol. The experimental protocol is illustrated schematically in Figure 2 and consisted of the following steps: (a) measuring the open circuit potential (OCP1), for 60 minutes till a stable open circuit potential, OCP 1 value of the test sample is obtained; (b) performing an electrochemical impedance measurement (EIS1) at open circuit potential; (c) measuring the open circuit potential (120 min. – OCP2) and also performing an electrochemical impedance measurement (EIS2) at open circuit potential; (d) measuring the open circuit potential (OCP3) for 180 minutes till a stable open circuit potential, OCP3 value of the tested sample is obtained and (e) performing an electrochemical impedance measurement (EIS3) at open circuit potential, (f) measuring the open circuit potential (360 min. – OCP4) and also performing an electrochemical impedance measurement (EIS4) at open circuit potential and so on until OCP6.
All EIS measurements were made at the open circuit potential, performed in the frequency range between 10 kHz and 1 mHz, with an AC sine wave amplitude of 10 mV, frequency per decade equal to 10 Hz. The resulting data were recorded using ZView software and each experiment was repeated three times to check the reproducibility.

3. Results and discussion

3.1. SEM surface morphology of electrodeposited coatings
Figures 3(a) and (b) show the SEM morphology and SEM-EDX mapping for W element of Ni/nano-WC deposited layers prepared by electrochemical deposition. The SEM micrograph of Ni/nano-WC layers from Figure 3(a) is a small magnification in order to obtain a better response EDX analyse and mapping of W element on composite surfac...
The addition of WC nanoparticles into the nickel plating electrolyte leads to a Ni/nano-WC nanocomposite layer with characteristic cauliflower surface morphology revealed in Figure 4(a). WC nanoparticles show a distinct tendency to disturb nickel electrocrystallization and to form spherical agglomerates uniformly distributed over the whole surface of the composite layer.

3.2. Corrosion behavior of Ni/nano-WC nanocomposite layers

3.2.1. Evolution of open circuit potential. The measurement of open circuit potential gives information on the electrochemical state of a material, for example active or passive state in the case of passivable metals and alloys. However, open circuit potential measurements provide limited information on the mechanism and kinetic of surface reactions.

In Figure 5 is shown the open circuit potential measured during 24 hours of immersion period. The open circuit potential reveals a positive value at immersion time in Water + B + Li solution. After a very slow decreasing the open circuit potential becomes stable at a positive and constant value of 0.048 V vs. Ag/AgCl, proving a passive surface layer. The constant value of open circuit potential is reached after 12 hours from immersion time being stable during 24 hours of monitoring.

3.2.2. Electrochemical Impedance Spectroscopy measurements. The impedance diagrams corresponding to first hour of immersion to the impedance diagram measured after 24 hours of immersion in Nyquist presentation are shown in Figure 6. The size of the impedance diagrams differs by several orders of magnitude, particularly in the low frequency range (typically < 0.1 Hz). Usually an interpretation of the impedance diagrams consists in relating the corrosion current, \( I_c \), on a given area, \( A \), to the charge transfer resistance, \( R_{ct} \) \[11, 12\], which is a parameter of the electrochemical impedance that can be deduced from the experimental diagrams:

\[
I_c = \frac{B}{R_{ct}}
\]

Where: B is a constant factor related to the corrosion or passivation mechanism (value between 25 and 50 mV) \[12\]. In the case of diagrams consisting of a single arc of circle, the charge transfer resistance \( R_{ct} \) is also the polarization resistance, \( R_p \) (\( R_{ct} = R_p \)), defined as the limit of the impedance \( Z_i \) of metal-electrolyte system when the frequency tends to zero.
\[ R_{pol} = \lim_{\omega \to 0} Z_i \] (2)

The impedance diagrams recorded for Ni/nano-WC, from Figure 6 show an increased trend proving once again a passivation process ongoing on nanocomposite surface during immersion period, from the first diagram (EIS1) to the last one (EIS5).

Figure 6. Evolution of Electrochemical Impedance Spectroscopy Nyquist plots measured during immersion period of Ni/nano-WC nanocomposite layers in water + B + Li solution.

In order to obtain the polarization resistance values the EIS data are fitted with a simple electrical circuit shown in Figure 7, considering for impedance expression a constant phase element instead of capacitance, which explain the depressed semicircle of experimental Nyquist impedance due to inhomogeneous surface of Ni/nano-WC composite layers. CPE impedance can be written with the equation [13]:

\[ Z_{CPE} = \frac{1}{Q(f\omega)^n} \] (3)

Where: Q is a constant measured in \( F \cdot cm^2 \cdot s^{(n-1)} \), n is a value representing the deviation from purely capacitive behavior. When the n value is 1 pure capacitive behavior is observed and Q is the layer capacitance.

Figure 7. Electrical equivalent circuit used to fit the EIS experimental data.
The resulted values of polarization resistance from fitted diagrams are presented in Table 1.

| Nr. Crt. | EIS measurement      | Polarisation resistance [kohm·cm²] |
|---------|----------------------|----------------------------------|
| 1.      | EIS1 - after 1h      | 370.43                           |
| 2.      | EIS2 - after 3 h     | 435.28                           |
| 3.      | EIS3 - after 6h      | 950.0                            |
| 4.      | EIS4 - after 12 h    | 1150                             |
| 5.      | EIS5 - after 24 h    | 1700                             |

From the Table 1 it can be observed the increasing of polarization resistance during immersion period of Ni/nano-WC nanocomposite layer in water+B+Li solution, after 12 h and 24 h being almost constant in the same order of magnitude. The Bode diagrams of EIS experimental results are presented in Figure 8(a), as Z modulus versus frequency and (b) phase angle versus frequency.

![Bode diagrams](image)

Figure 8. Evolution of Electrochemical Impedance Spectroscopy Bode plots measured during immersion period of Ni/nano-WC nanocomposite layers in water + B + Li solution: (a) Z Modulus versus frequency; (b) Phase angle versus frequency.

From Figure 8(a) the higher impedance modulus reveals a higher corrosion resistance of Ni/nano-WC nanocomposite layers in water + B + Li solution and a good stability during EIS measurements steps.

The high impedance value obtained at low and medium frequency reveals a low reactivity or a good corrosion resistance for Ni/nano-WC electro-codeposited layers suggests the presence of protective passive film enhanced by presence of WC nanoparticles into nickel matrix.

From Figure 8(b) it can be observed that Ni/nano-WC layer exhibit a near capacitive response, illustrated by a phase angle close to 80° over a wide range of frequency. It indicates also a typical behavior of a thin passive film. This behavior suggests that the ion diffusion process could be reduced, which further can reduce the reactivity or corrosion rate of Ni/nano-WC nanocomposite layers in water +B + Li solution.

4. Conclusions
The research work demonstrates the possibility of obtaining Ni/nano-WC nanocomposite layers by electro-codeposition of dispersed WC nanoparticles into a nickel plating electrolyte.
SEM-EDX investigations show a specific surface morphology of Ni/nano-WC nanocomposite layers like cauliflower, WC nanoparticles having a distinct tendency to disturb nickel electrocrystallization and to form spherical agglomerates uniformly distributed over the whole surface of the composite layer.

EDX mapping analyze for W element on SEM micrograph reveals a uniform distribution of WC nanoparticles into the nickel matrix. EDX composition analyse could evaluate the WC content embedded into nickel matrix.

Open circuit potential value of Ni/nano-WC nanocomposite layer in water $+ \text{B}^+$ Li solution is reached after 12 hours from immersion time being stable during 24 hours of monitoring proving a passive surface layer.

From the EIS measurements can be conclude that the polarization resistance of Ni/nano-WC nanocomposite layer immersed in water $+ \text{B}^+$ Li solution increasing with immersion time.

5. References

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