Electroplated Ni/Ni-Co multilayer coatings for higher corrosion-erosion resistance

P. Hasanpour, P. Salehikahrizsangi, K. Raeissi, M. Santamaria, L. Calabrese, E. Proverbio

Erosion-corrosion behaviour of hierarchical structured hydrophobic nickel-cobalt coating, obtained by electrodeposition, was assessed. In situ electrochemical measurements were carried out to study the corrosion resistance and stability during erosion tests. The electrochemical behaviour was related to surface hydrophobicity and its hierarchical structure nature as well as its modification. The pure Ni showed the lowest erosion-corrosion resistance. A smoothing of the hierarchical structure and thus a reduction the hydrophobicity was highlighted. On the other hand, Ni-Co coating even if associated to a lower electrochemical stability showed a more stable hierarchical structure also at high erosion times.

KEYWORD: ELECTRODEPOSITION; COATING; ROUGHNESS; HYDROPHOBICITY; EROSION-CORROSION.

INTRODUCTION

In the recent years, increasing consideration have been gained by highly hydrophobic bio-inspired surfaces to obtain specific surface properties such as water repellence, anticorrosion and self-cleaning properties [1]. Several approaches can be used to obtain hierarchical textured hydrophobic surfaces including chemical etching, plasma etching, sol-gel, chemical vapour deposition and electrodeposition [2]. In such a context, the electrodeposition can be considered a promising technology to produce corrosion resistance hydrophobic coatings since to cost-effective, flexibility, easy scale up, manufacturing control capabilities [3]. However, the great part of the research activities have been mainly aimed at assessing the coating durability and performances under dry or static wet conditions. Only few studies were aimed to evaluate coating erosion resistance and how such resistance can be influenced by surface hydrophobicity and surface texture structure [4]. In the present work, a specifically designed erosion/corrosion test set-up [5] was used in order to assess the durability in an erosive-corrosive medium of hierarchically structured nickel-based coatings with the aim to develop underwater hydrophobic metallic surfaces suitable for corrosion resistance in marine environments. In particular the effect of performance improvement in erosion corrosion behaviour of cobalt in nickel electroplated layer was evaluated. Secondary Ni and Ni-Co alloy layers were deposited on primary layers of Ni using a two-step electrodeposition procedure. Surface morphology modification, wettability and corrosion resistance of highly hydrophobic Ni/Ni and Ni/Ni-Co coatings were investigated.

P. Hasanpour, P. Salehikahrizsangi*, K. Raeissi
Department of Materials Engineering, Isfahan University of Technology 84156-83111, Isfahan, Iran

M. Santamaria, K. Raeissi
Department of Engineering, University of Palermo, Viale delle Scienze, Ed.6, 90128, Palermo, Italy

L. Calabrese, E. Proverbio
Department of Engineering, University of Messina, Contrada di DioSant'Agata, 98166 Messina, Italy

EXPERIMENTAL PROCEDURE

The nickel plating bath for Ni was prepared according to [6]. The plating bath for composite Ni-Co layer deposition was prepared adding to the previous one $CoCl_2 \cdot 6H_2O$ (40 gL^{-1}) [7]. All electrodepositions were carried out in a 500 mL beaker (pH=4 and T=60 ± 0.1 °C). A copper substrate (14 mm diameter and 2 mm thickness) and a platinum plate, located at a distance of 1 cm, were used as working and reference electrode, respectively. A magnetic stirrer was placed in the middle of the two electrodes rotating at 300 rpm. Ni/Ni and Ni/Ni-Co coatings were obtained by a two-step electrodeposition process and coded NN and NC respectively. The first step able to deposit a nickel layer was performed at a constant current density of 20 mA cm^{-2} for 10 min. Afterwards, the second-step deposition (Ni or Ni-Co layer) was applied using a constant current density of 50 mA cm-2 for 3 min.

Surface morphology, thickness and chemical composition of the coatings were evaluated by Philips XL 30 scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscope (EDS). Water contact angles were evaluated using a goniometer equipped with an optical system and a CCD camera. A 4 µL water droplet of distilled water (conductivity<1 µS) was placed on the surface and the digital images taken using the CCD camera were immediately transferred to a personal computer for contact angle measurements using Image J software. Five droplets were put on each sample and the average contact angle was considered. The average roughness was assessed in the middle of each coating within 5 mm by using a Mitutoyo SJ 210 roughness meter. Erosion-corrosion behaviour of the coatings was evaluated in 1 L of a slurry solution containing 40 wt. % SiO2 sand +3.5 wt. % NaCl. The size of the SiO2 particles was in the range of 200-300 µm and the propeller rotational speed was set at 500 rpm. A three-electrode cell configuration was adopted with a shielded Ag/AgCl (KCl saturated) reference electrode and a wide surface activated titanium mesh as the counter electrode. A Biologic Science potentiostat (SP-300 model) was used for electrochemical measurements during the erosion test. A detailed description of the test set-up is reported in [8]. Periodically, during time, EIS tests were carried out in the frequency range of 10^{-2} to 10^{5} Hz with a 10 mV potential amplitude. After sample immersion in the solution, the first EIS cycle was performed in static condition. Then by running the propeller, the other cycles were performed in dynamic condition.

RESULTS AND DISCUSSION

Coating Characterization

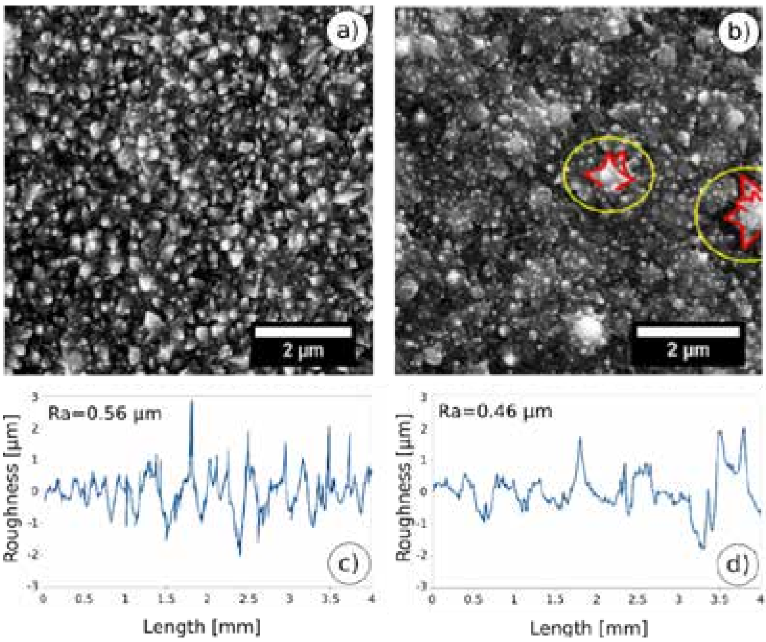

Fig. 1 - Surface morphology and linear roughness profile for NN (a,c) and NC (b, d,)) sample

Fig. 1a,b shows surface morphology of Ni/Ni and Ni/Ni-Co coatings. The microstructure of both electroplated coating is characterized by a rough morphology with several asperities (Ni or Ni/Co crystals). In pure Ni sample, Fig. 1a, randomly dispersed hierarchical structures with narrow peaks and valleys can be identified. Surface texture is jagged with sharp roughness. Several cones are well defined and aggregated in 1-2 µm size microcolonies. The formation of a conical structure in Ni coatings can be explained based on the Burton-Cabrera-Frank (BCF) theory. This theory suggests a step advancing mode of crystal growth to achieve equilibrium on the surface. In this case, cessation of growth on the smooth areas of the surface followed by adsorption and desorption of atoms at the step edges of screw dislocations was responsible for incipient island formation [9]. On Ni/Co sample, the Ni cones, generated during the first deposition, are fully covered by flower-like Ni-Co large deposits with height and width of about 300 nm and 200 nm, respectively (Fig. 1b). This micro and nano scale roughness was analogously observed in the literature [10]. The flower-like structure in NC sample can be explained according to the metal ion deficient layer (MIDL) theory [11]. Based to this theory, two steps are involved in the formation and growth of a flower- like structure. At the first, metal ions (Ni2+ and Co2+) and the crystal modifier molecules are absorbed on the metal substrate and some colonies of deposits are shaped. The Ni2+ and Co2+ ions flow to the tip of the nuclei to form nano-cones which then grow fast due to the tip discharge phenomena. Since the absorption of the crystal modifier molecules on the tip of the cones is higher than on the sidewalls, they block the path for growth of more metal deposits. Afterwards, the second step starts when the metal ions are reduced at the sidewalls of the conical structures favoring flower-like final shaping of the upper-structure [11].

A cross section evaluation of dual NC coatings allowed to observe an almost compact and homogeneous structure with a thickness a the first Ni layer and second Ni-Co layer of about 4 µm and 2 µm, respectively.

Further interesting information can be acquired analyzing the roughness profiles of both coatings (Fig. 1c,d). The profile of pure NN coating is constituted by narrow peaks and valleys with a maximum gap of about 5 µm. The observed average roughness (Ra) is 0.56 µm. Instead on electrodeposited sample characterized by a second Ni-Co layer deposition, NC, the roughness is reduced (Ra= 0.46 µm) confirming the smoothing contribute of the addition of cobalt ions in the deposition bath. The asperities are characterized by a maximum gap of 4 µm. At the same time the root diameter of the flower-like structure is larger than NN sample. That can be related to the secondary growth of Ni-Co flower-like upper-structure on the Ni nano-cones generated during the first deposition.

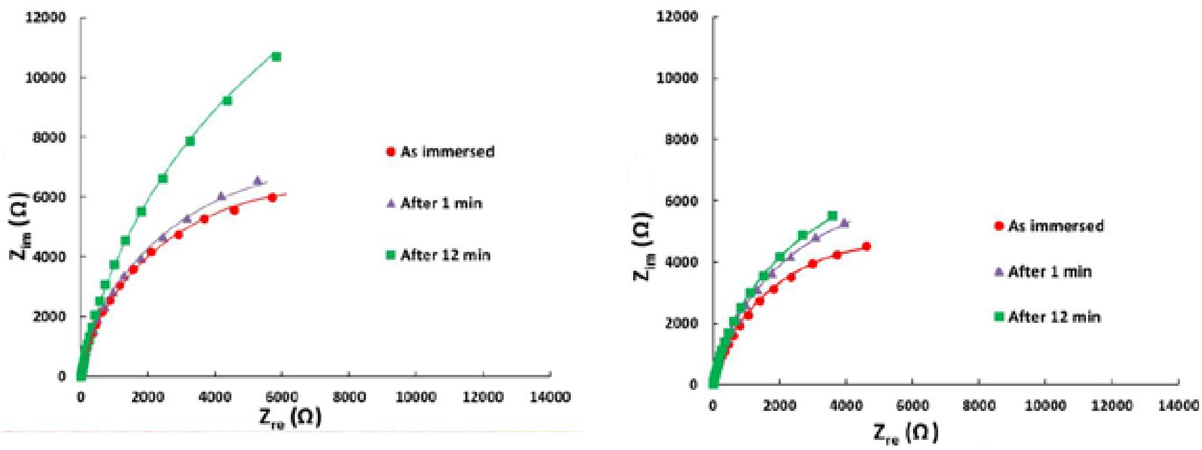

Fig. 2 - Nyquist plots of a) NN and b) NC sample at increasing erosion-corrosion time

Electrochemical impedance (EI) of the coatings was evaluated as immersed and in dynamic erosion-corrosion conditions. Nyquist plots of the coatings at increasing time are summarized in Fig 2. The impedance semicircle progressively enlarges at increasing ageing time. This indicates an increase of the polarization resistance and that the corrosion rate of all coatings should decrease during the erosion-corrosion tests. This anomalous behaviour can be justified as a consequence of the smoothing action, during the erosion-corrosion test, by the high speed impact of SiO2 particles on the coating sample. The reduction of surface roughness reduces the real area exposed to corrosive solution, and as a result, the calculated corrosion rate decreased [12] masking the effect of the increase in surface reactivity due to the removal of surface oxide and corrosion products. On the other hand, as expected, the open circuit corrosion potential was observed to reduce with increasing erosion time due to the exposure of new metal surface. Indeed in the static conditions, without erosion contribute, the corrosion resistance can be mainly ascribed to the coating composition. Considering that the cobalt has an anodic behaviour in Ni-Co galvanic coupling, it can be justified the lower corrosion resistance of NC sample compared to NN one. The EI of the coatings increases significantly after 12 min of erosion-corrosion, for pure Ni coating. This trend is less effective for composite NC coating. This behaviour can be related to the relevant roughness reduction in NN sample, cause of its lower hardness compared to Ni-Co alloy. In Fig. 3 SEM images before and after erosion-corrosion test for both samples are reported. The rough surface becomes clearly more smooth. The peak asperities, mainly in NN sample, are removed and the oxide components are formed on it (red circle in Fig. 3b). For NC sample, the original microstructure was preserved after erosion-corrosion test. Some local relevant smoothing of the crystal flower-like structure can be observed. Although, the beneficial effect of Co alloying element on Ni coating in erosion-corrosion resistance can be highlighted.

Furthermore, water contact angle (WCA) before and after erosion-corrosion test for all samples was measured. A decrease of WCA occurs both on NN and NC sample. The surfaces after erosion-corrosion tests are still hydrophobic despite of the roughness loss. However, in pure nickel coating a reduction of contact angle of about 14° can be observed. Instead a quite stable hydrophobic behaviour can be observed for Ni/Co coatings (Δθ about 8). Therefore, it can be argued that the addition of Cobalt alloying element had a positive effect both on erosion-corrosion resistance and in hydrophobic behaviour stability, making these results promising for further investigation and long erosion-corrosion ageing time

CONCLUSIONS

Ni/Ni (NN) and Ni/Ni-Co (NC) coatings were obtained by electrodeposition using chloride baths. Surface morphologies were characterized by hierarchical textured structures with well dispersed peaks and valleys. In NN samples, several cones are well defined and aggregated in 1-2 μm microcolonies. Instead, on NC samples, the Ni cones, generated during the first deposition, are fully covered by flower-like Ni-Co large deposits with height and width of about 300 nm and 200 nm, respectively. Both coatings sowed high hydrophobic behaviour with water contact angle above 130°. Furthermore, on site electrochemical impedance spectroscopy during a slurry erosion-corrosion test were carried out for coating characterizing. The results showed that the polarization resistance increases enhancing time. This behaviour was related to roughness loss and formation of partial corrosion products generated on the surface. The Ni/Ni coating in comparison with the dual Ni/Ni-Co coating (with same first deposition condition) showed a weaker erosion-corrosion resistance as well as a higher loss of contact angle. NC samples showed low surface morphology modification and good hydrophobicity stability during erosion-corrosion test.

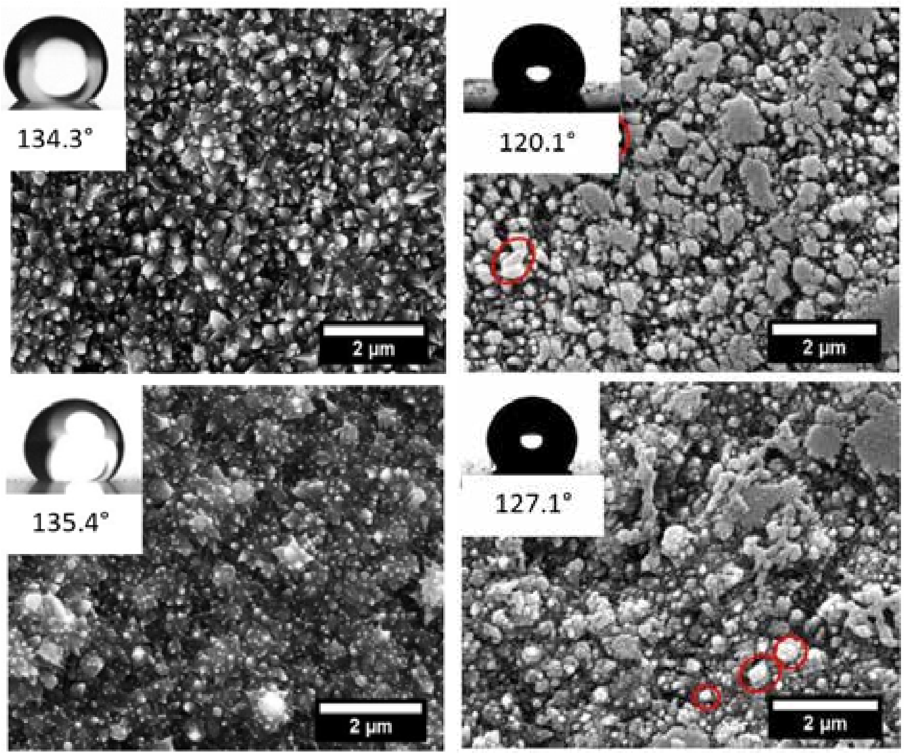

Fig. 3 - Surface morphology and WCA of the coatings before (a, c) and after (b, d) erosion- corrosion for: NN (a,b) and NC (c,d) sample

REFERENCES

[1] Yao X, Song Y, Jiang L. Applications of Bio-Inspired Special Wettable Surfaces. Adv. Mater. 2011; 23(6):719–734.

[2] Ma M, Hill RM. Superhydrophobic surfaces. Curr. Opin. Colloid Interface Sci. 2006; 11(4):193–202.

[3] Schlesinger M, Paunović M. Modern Electroplating, Hoboken NJ: John Wiley & Sons, 2011.

[4] Roach P, Shirtcliffe NJ, Newton MI. Progess in superhydrophobic surface development. Soft Matter 2008; 4(2):224–240.

[5] Salehikahrizsangi P, Raeissi K, Karimzadeh F et al. Erosion-corrosion behavior of highly hydrophobic hierarchical nickel coatings. Colloids Surfaces A Physicochem. Eng. Asp. 2018; 558:446–454.

[6] Salehikahrizsangi P, Raeissi K, Karimzadeh F et al. Highly hydrophobic Ni-W electrodeposited film with hierarchical structure. Surf. Coatings Technol. 2018; 344:626–635.

[7] Khorsand S, Raeissi K, Ashrafizadeh F. Corrosion resistance and long-term durability of super-hydrophobic nickel film prepared by electrodeposition process. Appl. Surf. Sci. 2014; 305:498–505.

[8] Hasanpour P, Salehikahrizsangi P, Raeissi K et al. Dual Ni/Ni-Co electrodeposited coatings for improved erosion-corrosion behaviour. Surf. Coatings Technol. 2019; 368:147–161.

[9] Myers-Beaghton AK, Vvedensky DD. Generalized Burton-Cabrera-Frank theory for growth and equilibration on stepped surfaces. Phys. Rev. A 1991; 44(4):2457–2468.

[10] Khorsand S, Raeissi K, Ashrafizadeh F, Arenas MA. Super-hydrophobic nickel–cobalt alloy coating with micro-nano flower-like structure. Chem. Eng. J. 2015; 273:638–646.

[11] Kong D, Chen Y, Wan P et al. Pre-plating of Bismuth film electrode with coexisted Sn2+ in electrolyte. Electrochim. Acta 2014; 125:573–579.

[12] Toloei AS, Stoilov V, Northwood DO. An electrochemical impedance spectroscopy and potentiodynamic polarization study of the effect of unidirectional roughness on the corrosion of nickel. Int. J. Comput. Methods Exp. Meas. 2014; 2(3):243–254.