EXPLORING THE IMPACT OF 2-BUTYNE-1,4-DIOL, AND PULSE PLATING ON Ni-MATRIX NANOCOMPOSITE COATINGS WITH ZrO_2

A. Nikolaou[1*], M. M. Dardavila[1], A. Tzanis[1], C. Kollia[1]

[1]Laboratory of General Chemistry, School of Chemical Engineering, Zografou Campus, National Technical University of Athens, 9, Iroon Polytechniou Str., 15780 Athens, Greece

(*aggelikh.nik90@gmail.com)

ABSTRACT

In this study, Ni-matrix nanocomposite coatings were developed via the co-electrodeposition technique under direct and pulse current regime, utilizing nano-ZrO_2 particles as the reinforcing phase. Our investigation focuses on the influence of the organic additive 2-butyne-1,4-diol, and of the variation of the duty cycle value (d.c.= 30%, 50%, 70%, and 90%) on the coatings' characteristics. The coatings' microstructure was examined with X-Ray diffractometry, while their surface morphology and composition with scanning electron microscopy and energy dispersive spectroscopy, respectively. Also, roughness measurements were conducted, and to study the coatings' microhardness the Vickers method was employed. The results show a decrease of the crystallite size that was attributed to 2-butyne-1,4-diol while the significant enhancement of the coatings' microhardness was correlated both with the organic additive and the nano-ZrO_2 particles. Furthermore, pulse parameters contributed further to the refinement of the nickel crystallites and significantly enhanced the Vickers microhardness.

Keywords: Nickel electroplating, ZrO_2 nanoparticles, 2-butyne-1,4-diol, pulse electrolysis, nanocomposite materials

INTRODUCTION

Electrodeposition stands out as a prominent technique for fabricating nanocoatings of metals/alloys and metal/alloy matrix composites due to its ability to finely regulate process parameters at a relatively low cost. Among the assortment of metals deposited through electrodeposition, nickel stands out as one of the most frequently utilized choices. Its application serves to enhance several properties of the substrate, among which are the corrosion resistance and the electrical conductivity. Ni electroplating is a versatile process used in the surface finishing industry with a broad spectrum of end use products for decorative, engineering, and electro-forming applications, among others [1].

When nanoparticles are introduced into metal matrices through the co-electrodeposition technique, the properties of the coatings can be markedly enhanced or even altered. The efficiency of this process can be further enhanced when composite coatings are developed using pulsed current (PC) [2]. For Ni matrix electrodeposits in particular, a great variety of particles have been used such as hard oxides (ZrO_2, SiO_2, Al_2O_3, TiO_2), carbides like WC and SiC, and carbon nanotubes [3, 4].

Zirconium, a durable transition metal, finds extensive application in its oxide form known as zirconia or zirconium oxide (ZrO_2). Renowned for its remarkable durability, hardness, high melting point, and resistance to abrasion, zirconia is often dubbed ceramic steel. This unique combination of properties has sparked significant interest within the scientific community, leading to extensive exploration of zirconia-based nanomaterials across diverse technological fields, such as catalysts, sensors, semiconductor devices, as well as structural materials such as coatings [5].

With the increasing availability of nanoparticles, the interest of the low-cost and low-temperature

composite electroplating is continuously growing, with major challenge being the achievement of high co-deposition rates and homogenous distribution of the particles in the metallic matrix [6].

Following our previous work in composite Ni coatings with micrometer-sized ZrO_2 particles [3, 4, 7], in the present study we introduce in the electrolytic solution nano-ZrO_2 particles in combination with the organic additive 2-butyne-1,4-diol. Furthermore, both direct current (DC) and pulse current conditions are applied, and the produced coatings are characterized morphologically and microstructurally, and evaluated as far as their microhardness and surface roughness are concerned.

METHODOLOGY

Brass cylinders with a diameter of 25 mm were used as substrates. Prior to the electrodeposition, they underwent meticulous pre-treatment involving grinding with SiC papers, polishing, and ultrasonic cleaning with acetone, and subsequently deionized water to eliminate impurities and oxides. The lateral surface of the substrate was isolated with a heat-shrinkable sleeve.

The electrodeposition of Ni-matrix nanocomposite coatings was successfully achieved potentiostatically under DC (Wenking ST 88, BANK Elektronic) and PC (Wenking DPC 72, BANK Elektronic) conditions, by employing a three-electrode setup, consisting of the brass substrate serving as the cathode, a semi-circular nickel foil (99.9%, Sigma Aldrich) serving as the anode, and a saturated calomel electrode used as a reference electrode.

A Watts-type electrolyte solution was utilized containing the usual concentrations of Ni (II) salts, *i.e.* hexahydrates of $NiSO_4$ (300 g/L) and $NiCl_2$ (35 g/L), alongside H_3BO_3 (40 g/L) serving as a pH buffering agent. The plating bath temperature was maintained at 50 °C, and the pH was adjusted to 4.5. The current density applied was j=5 A/dm^2, while under PC regime, the applied frequency was v=0.01 Hz. The effect of duty cycle on the Ni matrix composite coatings was explored by applying values of d.c.=30 %, 50 %, 70 %, and 90 %. In order to investigate the optimal concentration of the reinforcing phase, Ni/ZrO_2 coatings were produced under DC by altering the amount of ZrO_2 nanopowder (max 100 nm particle size, Sigma Aldrich) in the electrolyte. Zirconium oxide concentrations of 0.5, 1, 2, 4, 6, and 8 g/L, were tested. It was found that the addition of 8 g/L of the nano-ZrO_2 in the electrolyte led to the nanocomposite coating with the highest Vickers microhardness, hence this zirconia concentration was employed thereafter. The electrolytic bath was subjected to continuous magnetic stirring for a duration of one day prior to commencing the electroplating experiments. To ensure uniform dispersion of nanoparticles, and maintain homogeneous hydrodynamic conditions, mechanical stirring was employed at 600 rpm throughout the electrodeposition process. The organic additive 2-butyne-1,4-diol was added in the electrolytic bath at various concentrations, namely 0.5, 1, and 2 mmol/L, to improve the mechanical properties and performance of the depositions. [8].

The properties of the produced nanocomposite coatings were evaluated in terms of surface morphology and composition, microstructure, roughness, and microhardness. The morphology was studied by scanning electron microscopy (SEM, JEOL IT500LV), while the composition was analyzed with an energy dispersive X-ray spectrometer (EDS, Oxford X-Max Extreme) coupled on the SEM. The microstructural characteristics were evaluated with X-ray diffractometry (XRD, Bruker, D8 Advance), and the roughness measurements were carried out with a digital profilometer (Hommel Werke, Hommel Tester T1000). The microhardness was evaluated with the Vickers method, utilizing a Wolpert Wilson 402 MVD microhardness Tester.

RESULTS AND DISCUSSION

Figure 1 presents the X-Ray diffraction spectra of the prepared coatings. In Figure 1a, the preferred orientation [100] is clearly seen for the Ni-only coating, while in Figure 1b, the effect of the addition of the organic additive is depicted; with the increase of the additive's concentration a gradual transition in the preferred orientation is observed, shifting from the [100] to the [211] orientation.

Furthermore, in Figure 1c the texture of the samples can be observed when incorporating nano-ZrO_2 (without the organic additive). The preferred orientation directly shifts to [211] even at the minimum concentration of 0.5 g/L.

This evolution in preferred orientation highlights the intricate influence of both the organic additive and nano-ZrO_2 on the crystallographic structure of the coatings.
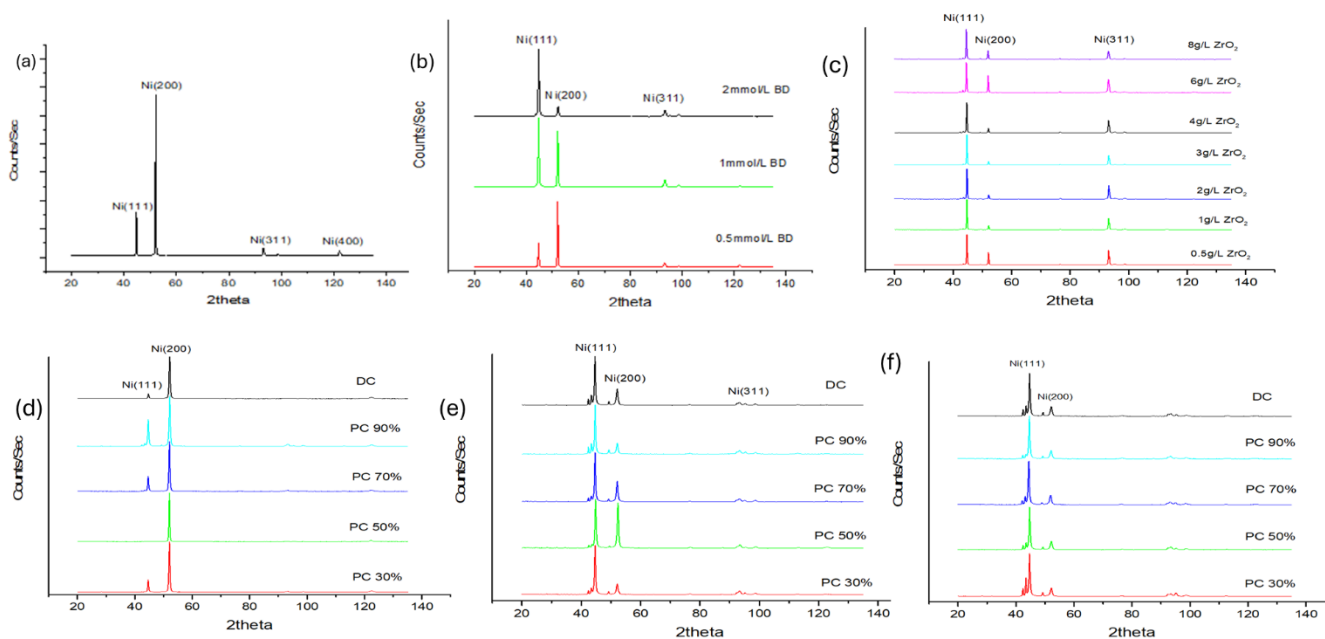

Figure 1. *(a)-(f) XRD patterns for samples: (a) only Ni, (b) addition of the organic additive at concentrations varying from 0.5 to 2 mmol/L, (c) addition of nano-ZrO_2 at concentrations varying from 0.5 to 8 g/L, (d) addition of both 8 g/L ZrO_2 and 0.5 mmol/L organic additive, (e) 8 g/L ZrO_2 1 mmol/L organic additive, (f) 8 g/L ZrO_2 and 2mmol/L organic additive.*

Figures 1d to 1f present the XRD diffractograms of the coatings when both ZrO_2 and 2-butyne-1,4-diol were introduced at the Watts solution, prepared under both DC and PC regime. The concentration of ZrO_2 was maintained constant at 8 g/L for all cases. For the samples prepared with 0.5 mmol/L 2-butyne-1,4-diol (Figure 1d), it can be deduced that Ni crystallites are orientated preferentially along [100] direction, indicating the competitive role of ZrO_2 and of the organic additive. By increasing the concentration of 2-butyne-1,4-diol to 1 mmol/L there is a notable shift of the Ni preferred orientation along [211] direction, which is more dominant at the concentration of 2 mmol/L (Figure 1f).
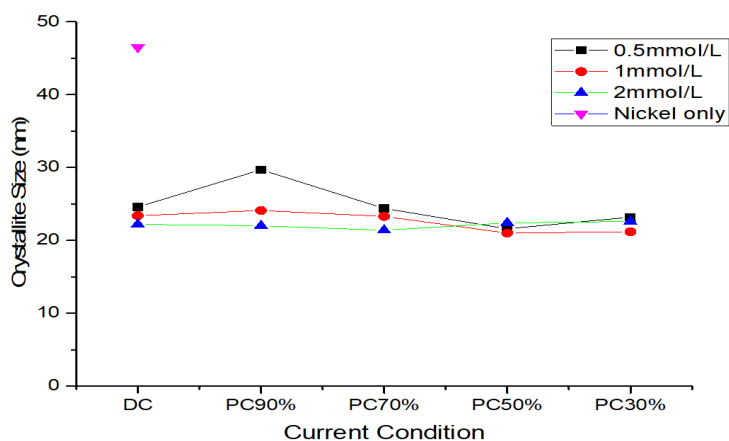
Figure 2: *Crystallite size of the deposits against the applied current condition.*

Figure 2 illustrates the evolution of the crystallite size as it was derived from the XRD measurements data, of the produced nanocomposite coatings from the electrolytic bath containing 8 g/L ZrO_2 and 2-butyne-1,4-diol at various concentrations (0.5, 1, and 2 mmol/L), as a function of the different current regimes. It is evident that the incorporation of the organic additive played a pivotal role in refining the size of Ni crystallites at the DC regime. The reduced crystallite size is attained also at PC regime, especially at the low duty cycles, such as 50% and 30%.

Roughness measurements showed that Ni-only coatings exhibited a mean roughness of 0.22 μm. When 2-butyne-1,4-diol was added to the electrolytic solution the mean roughness decreased to 0.10 μm, while when ZrO_2 was introduced at the bath the mean roughness exhibited values of 0.19 μm. Upon incorporation of both 2-butyne-1,4-diol and ZrO_2 at the Watts bath, roughness values spanned from 0.16 to 0.25 μm regardless of the current conditions, indicating that roughness is affected possibly by zirconia agglomerates formed at the surface, as confirmed by the following SEM micrographs and EDS analysis.

In Figure 3 indicative SEM micrographs of the surface morphology of the samples are presented, along with their corresponding Zr content (wt%) as detected by EDS.
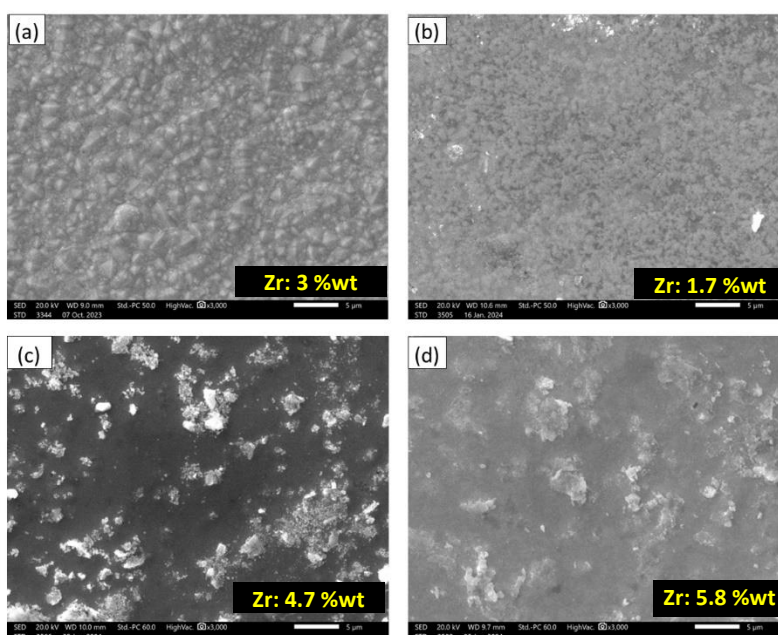

Figure 3: *SEM micrographs and Zr content for samples: (a) Ni/ZrO₂ (ZrO₂: 8 g/L, DC), (b) Ni/ZrO₂ + 0.5 mmol/L 2-butyne-1,4-diol (PC, duty cycle: 50%), (c) Ni/ZrO₂ + 1 mmol/L 2-butyne-1,4-diol (PC, duty cycle: 50%), (c) Ni/ZrO₂ + 2 mmol/L 2-butyne-1,4-diol (PC, duty cycle: 50%) [scale bar of 5 μm].*

In Figure 3a it is shown the surface morphology of the coating fabricated from the bath which contained only ZrO_2 at a concentration of 8 g/L. Nickel grains with the typical [211] texture can be observed on the surface[9].

With the introduction of the organic additive 2-butyne-1,4-diol it is evident that the surface of the coatings becomes notably more compact (Figures 3b-d), owing this feature to the nanocrystalline microstructure. Also, zirconia agglomerates can be observed protruding from the surface, as stoichiometrically identified by EDS. Furthermore, a crucial observation is the increased Zr content integrated into the coatings with the increased concentration of the organic additive, at almost every condition.

The mean values of the microhardness measurements are depicted in Figure 4. Particularly in Figure 4a, the microhardness values of the coatings produced at the DC regime are shown, while in Figure 4b for the ones prepared under PC.

It should be noted that the nanocomposite coating fabricated with the 8 g/L ZrO_2 (without the presence of 2-butyne-1,4-diol) demonstrated the highest microhardness mean value of 300.70 ± 24.75 HV, comparing with the lower ZrO_2 concentrations, unveiling the reason behind maintaining this ZrO_2 concentration for the afterward experiments.

Notably, across all current conditions, the Vickers microhardness demonstrates a consistent increase with the concentration of the organic additive.
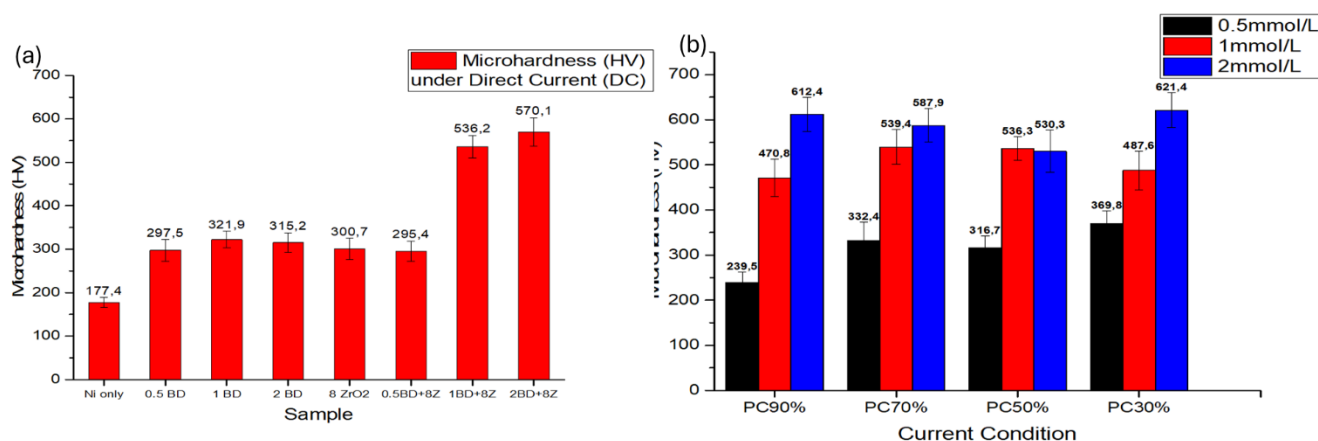

Figure 4:. *Microhardness measurements of the samples prepared at the (a) DC, and (b) PC regime.*

From Figure 4a it is clearly deduced that upon the incorporation at the electrolytic solution of both 8 g/L ZrO_2 and 2-butyne-1,4-diol, the microhardness is increased abruptly from 295.4 ± 23.3 HV for the 0.5 mmol/L 2-butyne-1,4-diol to 570.1 ± 32.7 HV for the 2 mmol/L 2-butyne-1,4-diol.

From the corresponding diagram at the PC regime (Figure 4b) it can be observed that at all duty cycles, the composite electrocoatingd prepared at the bath containing 8 g/L ZrO_2 and 2 mmol/L 2-butyne-1,4-diol manifested the highest microhardness values, and particularly the one fabricated at 30% duty cycle presented the value of 621.4 ± 38.3 HV.

The increased microhardness values are attributed to the increased ZrO_2 content of the coating,(3-5%) at the nanocrystalline microstructure, and at the lower duty cycle values.

CONCLUSIONS

Nickel nanocomposite coatings were successfully developed electrolytically from a Watts-type bath containing ZrO_2 nanopowder and 2-butyne-1,4-diol. The organic additive alone has demonstrated remarkable efficacy, particularly by increasing the microhardness of the coatings, while simultaneously refining the nickel grains resulting in smaller crystallite sizes. The incorporation of

both the 2-butyne-1,4-diol and the reinforcing agent nano-ZrO_2 has led to the development of Ni nanocomposite coatings exhibiting further enhanced microhardness. Moreover, the application of pulse current conditions has proven to yield coatings of even increased microhardness, especially evident at the 30% duty cycle (621.4 ± 38.3 HV), comparing with the samples prepared at the direct current regime (570.1 ± 32.7 HV). Roughness measurements revealed a decrease from 0.22 μm to 0.10 μm with the addition of 2-butyne-1,4-diol, and a slight increase to 0.19 μm with ZrO_2 incorporation. When both the additive and the strengthening phase were introduced, roughness ranged from 0.16 to 0.25 μm regardless of the type of current applied.

ACKNOWLEDGEMENTS

REFERENCES

[1] Agboola O. (2012), *International Journal of the Physical Sciences*, 7, 349-360.

[2] Chronopoulou N., Vozios D., Schinas P., Pavlatou E.A. (2018), *Materials Today: Proceedings*, 5, 27653-27661.

[3] Dardavila M.M., Hamilakis S., Loizos Z., Kollia C. (2015), *Journal of Applied Electrochemistry*, 45, 503-514.

[4] Kollia C., Deligkiozi I., Dardavila M.M. (2010), *Defect and Diffusion Forum*, 297-301, 930-935.

[5] Chitoria A.K., Mir A., Shah M.A. (2023), *Ceramics International*, 49, 32343-32358.

[6] Gyftou P., Pavlatou E.A., Spyrellis N. (2008), *Applied Surface Science*, 254, 5910-5916.

[7] Dardavila M.M., Kollia C. (2011), *Defect and Diffusion Forum*, 312-315, 235-239.

[8] Sun M., Zhang C., Ya R., He H., Li Z., Tian W. (2023), *Materials*, 16, 3598.

[9] Atanassov N., Vitkova St. and Rashkov St. (1980), *Surface Technology*, 13, 215-223.