Corrosion performance of nanocomposite coatings in moist SO_2 environment

Ashish K. Kasar[1], Muhammad U. Bhutta[2], Zulfiqar A Khan[2,]*, and Pradeep L. Menezes[1,]**
[1] Department of Mechanical Engineering, University of Nevada, Reno, NV 89557, USA
[2] NanoCorr, Energy and Modelling (NCEM) Research Group, Department of Design and Engineering, Bournemouth University Talbot Campus, Poole, Dorset, BH12 5BB, UK
*zkhan@bournemouth.ac.uk,**pmenezes@unr.edu

Abstract:

This paper presents a study of corrosion behavior of electrodeposited Ni, Ni-Al_2O_3, Ni-ZrO_2, and Ni-Graphene (Gr) coatings in moist SO_2 environment. Nanocomposite coatings were deposited on steel substrate by pulse electrodeposition technique with an average thickness of 9 ± 1 μm. Coatings were characterized by using nanoindentation and scratch tests to measure their mechanical properties prior to conducting corrosion tests. The corrosion resistance of coatings was evaluated according to G87-02 Method B, employing SO_2 cyclic spray in the presence of moisture followed by drying. The results indicated that the addition of nanoparticles is beneficial both for enhancing mechanical properties and improving the corrosion resistance of these coatings. Higher surface corrosion resistance was observed for Ni-Gr coating. Corrosion behavior of coating was also quantified by open circuit potential measurement in 0.5 M H_2SO_4 environment. The results suggest that the nanocomposite Ni coatings have improved corrosion resistance compared to pure Ni coating. This work will bring significant impacts in terms of industrial applications such as architectural, automotive and marine industries in the presence of S-pollutants because it can cause corrosion either due to acid rain or by the reaction of moisture with dry deposition of Sulfur.

Keywords: Electrodeposition, Ni coating, nanocomposite coating, moist SO_2 environment.

1. Introduction

Ni coatings are mainly applied for protection against corrosion, erosion, and abrasion. Ni coating by electrodeposition method is one of the most technologically and economically suitable techniques. Electrodeposition can be performed in three ways: (i) direct current (DC), (ii) pulse current (PC), and (iii) pulse reverse current (PRC) electrodeposition. The coating developed by DC electrodeposition suffers from poor adhesion, porosity, and undesirable microstructure defects, whereas PC and PRC provide better physical, mechanical, and corrosion properties [1-3]. Additionally, pulse electrodeposition technique can also be used for deposition of composite coatings. Electrodeposition of composite involves co-deposition of various micro or nano metallic, non-metallic or polymer particles within the electrolytic bath with suitable electroplating conditions. Quality of nanocoating is mainly governed by pulse physical parameters, nano constituents, substrate roughness, and coating thickness.

Corrosion failure of coatings combined with wear has been studied recently to develop synergistic wear-corrosion models for prediction of coating failures. Recently reported models[4] attempt to predict wear-corrosion in bulk materials or metals only; therefore, these models lack the capacity to predict the performance of nanocomposite coatings subject to wear and corrosion during their applications. It has been always remained the key issue to predict the precise role of Eigen-stresses, grainsize, porosity and thermal mismatch of nano-composites, as intrinsic nano-mechanics parameters in synergistic wear-corrosion phenomenon [4]. Following from the above rationale and its significance a unified Khan-Nazir II numerical model has been developed and reported [4]. Interfacial characteristics have been studied recently and have suggested that interfacial strength between Ni coating and the substrate can be obtained by controlling interface roughness and coating thickness [5]. The influence of Ni ion concentration has also been observed to evaluate its effects on the tribological and corrosion properties of pure Ni and Ni-Al_2O_3 composite coating due to surface roughness and wettability [6]. Some of the Ni composite coatings and their properties are listed in Table 1.

Table 1. Properties of electrodeposited Ni-nano composite coatings.

Coating	**Particle size**	**Mechanical properties**	**Electrochemical properties**	**Reference**
Ni-SiC	SiC: 1.2 μm	Knoop Hardness = 900 (4.5 times higher than the steel substrate)	-	[7]
Ni-SiC	SiC: 20 nm	Friction coefficient (μ) of composite coating = 0.25, μ of Ni = 0.35	Corrosion potential (E_{corr}) of composite coating = -212.5, (E_{corr} of pure Ni = -281.6) in 0.5M Na_2SO_4	[8]
Ni-SiC	SiC: 50 nm	Microhardness (HV) of composite coating = 720, HV of pure Ni = 540	E_{corr} of composite coating = ~0.35 V, E_{corr} of pure Ni = 0.45 V in 0.5 M NaCl solution	[9]
Ni-Al_2O_3	Al_2O_3: 0.6 μm	HV of composite coating ~ 525, HV of pure Ni ~375	-	[10]
Ni-carbon nano tube (CNT)	-	HV of composite coating = 600, HV of pure Ni = 300	-	[11]
Ni-CNT	-	-	E_{corr} of composite coating = -0.55 V, E_{corr} of Ni ~0.48 V in 3.5 wt.% NaCl	[12]
Ni-ZrO_2	ZrO_2: 10 μm	HV of composite coating ~ 1100, HV of pure Ni ~ 210.	E_{corr} of composite coating = -0.34 V in 0.5 M K_2SO_4	[13]
Ni-Graphene (Gr)	-	HV of composite coating ~ 375, HV of Ni ~ 275	E_{corr} of composite coating = -0.398 V, E_{corr} of pure Ni = -0.492 V in 3.5 wt.% NaCl	[14]
Ni- Al_2O_3, Ni-SiC and Ni-ZrO_2	-	HV for composites: Ni-Al_2O_3=380, Ni-	-	[15]

		SiC=500, ZrO_2=400 and for pure Ni = 450		

From Table 1, it can be seen that micro-nano particles improve both mechanical properties and enhance corrosion properties. Extensive work on nanocoating failure, prediction, and prognosis have been conducted at NanoCorr, Energy & Modelling Research Group, UK [16]. A comprehensive study of thin coating-substrate system deterioration enhanced by a combination of fracture and corrosion has been reported and modeled as Khan-Nazir I model [16,17]. This study provides an understanding of bi-material characteristics of coatings, mixed mode interfacial cracks, and combination of mechanics and diffusion concepts within the context of corrosive degradation. Wear-corrosion synergistic model Khan-Nazir II has been reported, which provides more accurate prediction compared to the conventional model, which were reported earlier [4]. Modeling of metal coating failure due to environmental factors has been published in [18]. Corrosion behavior of several Ni-based nanocomposite coating to include Ni-Al_2O_3, Ni-SiC, Ni-ZrO_2, and Ni-Graphene have been reported [19]. Recently, mathematical models have been developed for the prediction of uniform corrosion rate of structural steel subjected to acid rain, low pH conditions, the study investigated corrosion performance of steel in moist sulfur dioxide environment [20]. Lopez et al. [21] tested the electrodeposited Ni-Samarium (Sm) coating in NaCl environment as per ASTM B117 and ISO 10289 standards. Authors reported 6000 hours of salt spray exposure time without any corrosion in the presence of 34.6 mM of Sm^{3+}.

However, these coatings have not been tested in moist air containing SO_2, which is a major air pollutant and causes aggressive corrosion due to catalytic effect of iron oxide and hydroxide on the formation of H_2SO_4 from SO_2, H_2O, and O_2. Limited accelerated corrosion studies have been conducted to asses nanocoating in moist SO_2 environment. Therefore, it is important to study the corrosion behavior of Ni nanocomposite coatings in moist SO_2 environment for real world applications such as automotive, architecture and marine applications where S-pollutants can cause corrosion due to formation of sulfuric/sulfurous acids either by acid rain or by reaction between moisture and dry deposition of Sulfur.

The present work is aimed to evaluate the corrosion behavior of electrodeposited Ni-nano composite coatings in moist SO_2 environment. This paper presents a detailed experimental study of four various types of nanocomposite coatings: Ni, Ni/Al_2O_3, Ni/ZrO_2, and Ni/Graphene (Gr). ASTM Standard G87-02 Method B has been applied during the investigation of the nanocoatings mentioned above. Corrosion behavior of these coatings was also monitored by using Open Circuit Potential (OCP) in H_2SO_4 environment. These coatings were analyzed by using surface characterization methods, including Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDS) and nano-hardness testing.

2. Experimental Procedure

2.1 Coating preparation:

Pure Ni, Ni-Gr, Ni-ZrO_2, and Ni–Al_2O_3 nanocomposite coatings (9 ± 1 μm in thickness) were produced by pulse electrodeposition method. Prior to coating, steel substrates were conditioned with acetone by ultra-sonication for 5 min, followed by rinsing with deionized water. For electrodeposition, pulse current condition was controlled by using a Pulse Interface connected to pulse power supply. Pulse current conditions were kept as current density 3 A/dm^2, pulse on/off time (20–80 ms), and a duty cycle of 20%. An optimized Watt's bath chemical composition was used for the deposition process as listed in Table 2[6]. For the development of nano-enhanced composite coating, Gr platelets (6-8 nm), ZrO_2 (30-40 nm), Al_2O_3 (50-60 nm) nanoparticles were added into an electroplating bath that was under continuous magnetic stirring process. Moreover, to ensure better suspension of particles, the chemical solution was ultrasonically stirred during the deposition process. A nickel sheet of 99.9% purity was used as an anode, and a section of steel circular plate was coated while using it as a cathode. Standard surface conditioning was deployed before the coating development process. Flat plate samples with a surface area of 0.09 dm^2, was mechanically polished to an average roughness of 0.05 μm and ultrasonically conditioned with ethanol followed by acetone and then coating was conducted. Surface morphology of electrodeposited samples was studied by using a SEM. Elemental analysis was conducted by using an EDS.

Table 2. Chemical and nanoparticle composition of bath for electrodeposition of Ni and Ni nanocomposite coatings.

Coating	Chemical composition (g/L)			
	Nickel sulfate	Nickel chloride	Boric acid	Nanoparticles
Ni	265	48	31	-
Ni-Al_2O_3	265	48	31	20
Ni-ZrO_2	265	48	31	20
Ni-Gr	265	48	31	0.1

2.2 Nanoindentation and scratch test

To determine the hardness of Ni and Ni-nanocomposite thin coating, indentation hardness measurements were conducted. The tests were conducted using a diamond Berkovich tip in a nanoindentation system under depth-controlled setup with a maximum 1 μm displacement. The choice of indentation depth was to utilize 10% of the thickness of the coating to avoid the coating to substrate transitioning hardness measurement. The indentations were made with a dwell period of 10s at maximum load.

Nano-scratch tests were performed on the coating by using spherical indenter with a gradual increase in load from 0 to 150 mN, and total distance was 1500 μm as shown in Figure 1.

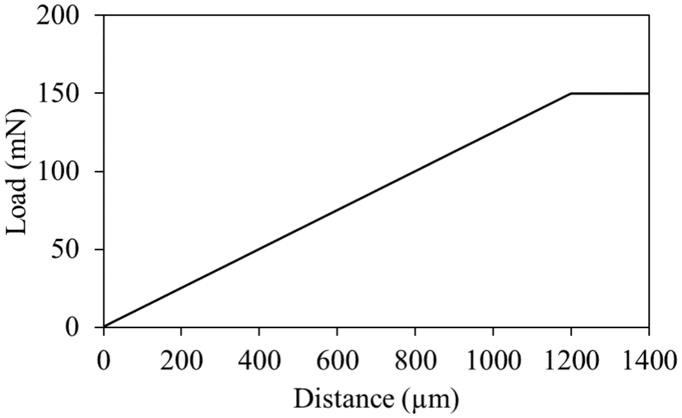

Figure 1. Loading profile during scratch tests on coatings using spherical indenter.

2.3 Corrosion tests

According to ASTM Standard G87-02 Method B alternating exposure[22], synthetic industrial atmosphere tests in moisture containing SO_2 were conducted to quantify the protection provided by the coating. This test is more correctly a porosity test because it finds (and sometimes creates) holes through the coating to the substrate. Testing was conducted in an alternating atmosphere by using a dosing volume of 2000 cm^3 of SO_2. The test duration was two cycles, each cycle consisting of 8 hours of SO_2 exposure at 40 °C +/- 3 °C followed by 16 hours under ambient conditions. Only the coated sections of the circular steel disc were exposed to a moist SO_2 environment, and the rest of the steel surface was covered with wax, as shown in Figure 2.

Corrosion behavior of Ni nanocomposite coatings was quantitatively measured by open circuit potential (OCP) in 0.5 M H_2SO_4 solution. The OCP was measured by using three electrode setup. A graphite electrode was employed as a counter electrode, and a saturated calomel reference electrode (SCE) was used as a reference electrode.

Figure 2. Ni and Ni-nanocomposite coated steel samples during moist SO_2 exposure tests.

3. Results and discussion

3.1 Nanoscale characterization

Hardness and elastic modulus measured by nanoindentation using a Berkovich indenter are plotted in Figure 3 and Figure 4, respectively. Due to the addition of the nanoparticles, the mean hardness and elastic modulus have increased significantly compared to pure Ni coating. Ni-Gr was observed to have 3.74 GPa mean hardness, which is the highest among all of the coatings and it is 19.9% higher than Ni coating. Similarly, mean elastic modulus was ~86% higher for Ni-Gr and Ni-Al_2O_3 as compared to Ni coating.

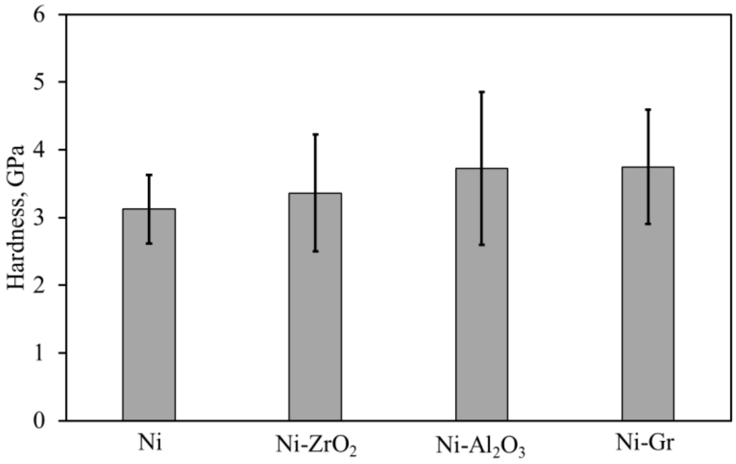

Figure 3. The hardness of the electrodeposited Ni and Ni-nano composite film by nanoindentation using Berkovich indenter.

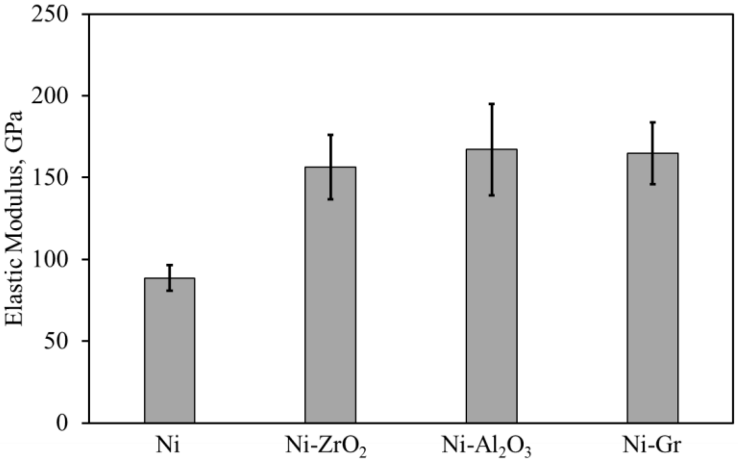

Figure 4. Elastic modulus of the electrodeposited Ni and Ni-nano composite film by nanoindentation using Berkovich indenter.

Scratch resistance of the coating was analyzed using a spherical indenter with a gradual increase in load up to 150 mN. All the four coatings showed a similar trend with ~ 2000 nm depth after 1500 μm scratch as presented in Figure 5. However, after two cycles of corrosion tests in moist SO_2 environment, the maximum scratch depth increased by one order of magnitude compared to non-corroded samples. This increase in scratch depth is due to the formation of corrosion products on the surface of the coatings. The maximum scratch depth on the corroded samples is shown in Figure 6. The maximum scratch depth of 32 μm was observed for pure Ni coating. Whereas nanocomposite Ni coatings yielded a maximum scratch depth of 24-25 μm.

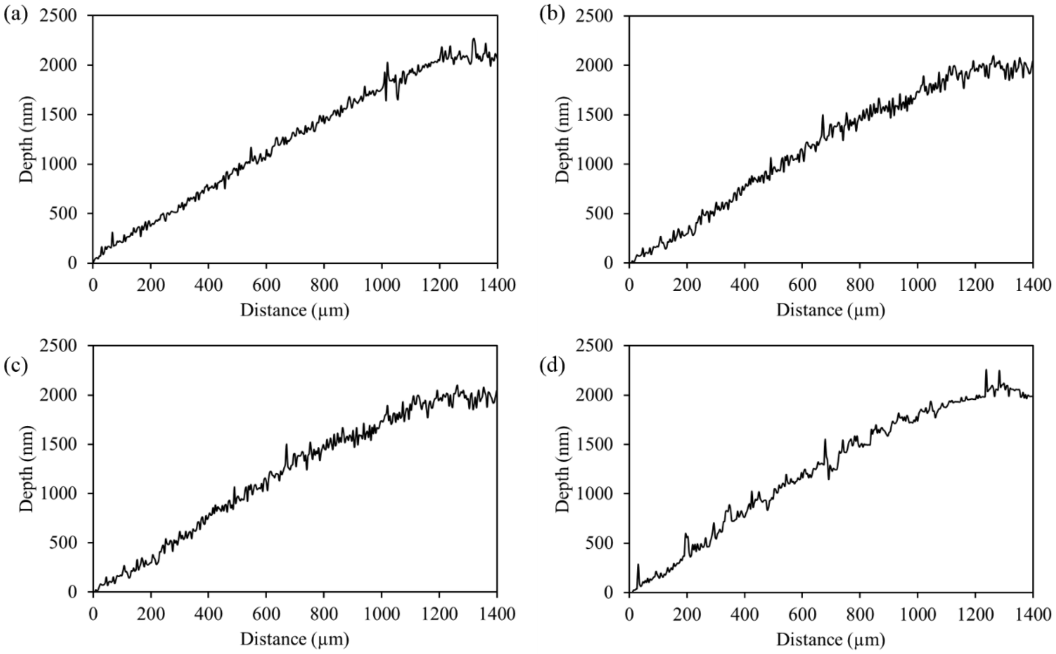

Figure 5. Scratch test profile on (a) Ni, (b) Ni-ZrO_2, (c) Ni-Al_2O_3 and (d) Ni-Gr using a spherical indenter with a gradual increase in load up to 150 mN

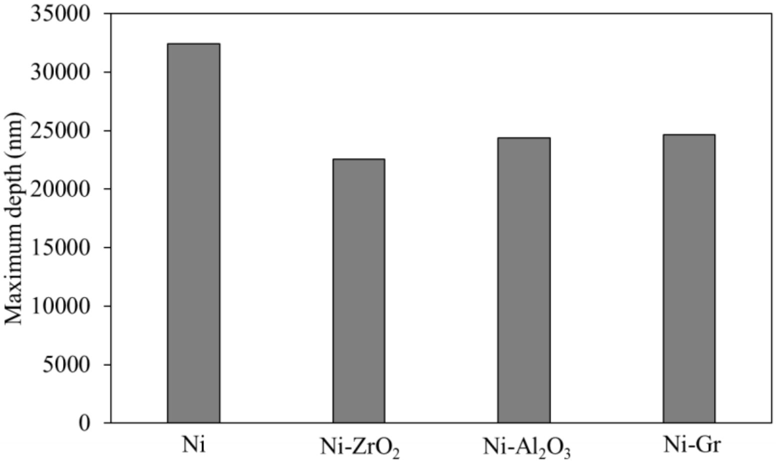

Figure 6. Maximum scratch depth on Ni-based coatings after two cycles of corrosion tests in moist SO_2 environment.

3.2 Surface corrosion

Figure 7 shows the corrosion status of bare steel, Ni, and Ni-nanocomposite coatings before and after two cycles of moist SO_2 exposure. The images of pre and post corrosion surface clearly show that the highest surface corrosion on the bare steel surface (Figure 7(a)), where Ni-ZrO_2 and Ni-Al_2O_3 were observed to have some brown spots that suggest ferrous corrosion. In the case of pure Ni and Ni-Gr coatings, no ferrous corrosion was observed. This behavior is also in good agreement with the accelerated corrosion on these coatings during salt spray testing of 450 h [19], where lowest surface corrosion was observed on Ni-Gr coating.

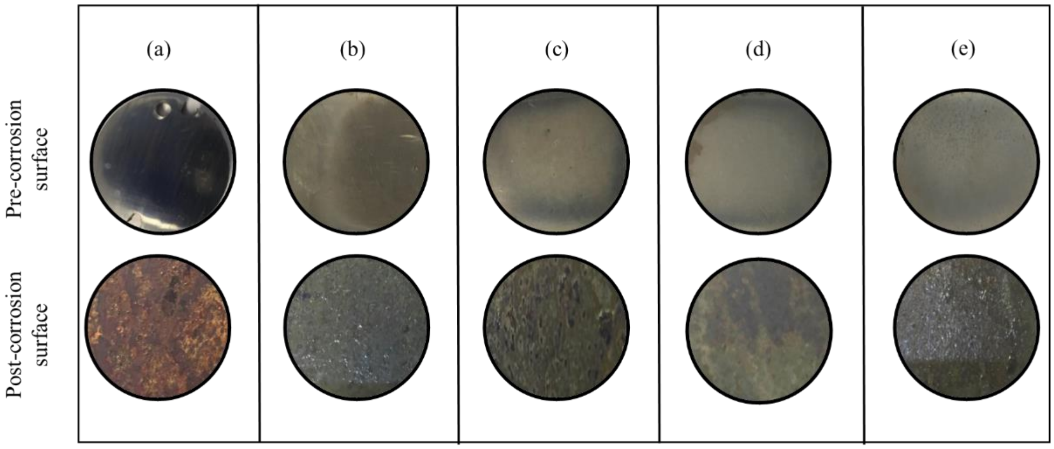

Figure 7. Pre and post corrosion status of (a) bare steel, (b) Ni, (c) Ni-ZrO_2, (d) Ni-Al_2O_3, and (e) Ni-Gr electrodeposited coatings.

Pre-corrosion SEM micrographs for all the coating surfaces are shown in Figure 8 along with their chemical compositions observed by EDS. The EDS spectrum confirms the presence of nanoparticles in the matrix. It also indicates that large particle size in Ni-Al_2O_3 (Figure 8 (e)) and Ni-ZrO_2 (Figure 8 (c)) coatings accounted for the large porous structure that can make the surface prone to ferrous corrosion. However, the Ni-Gr coating has the smallest particle size and formed a very smooth coating, which has also been observed in the previous study [19].

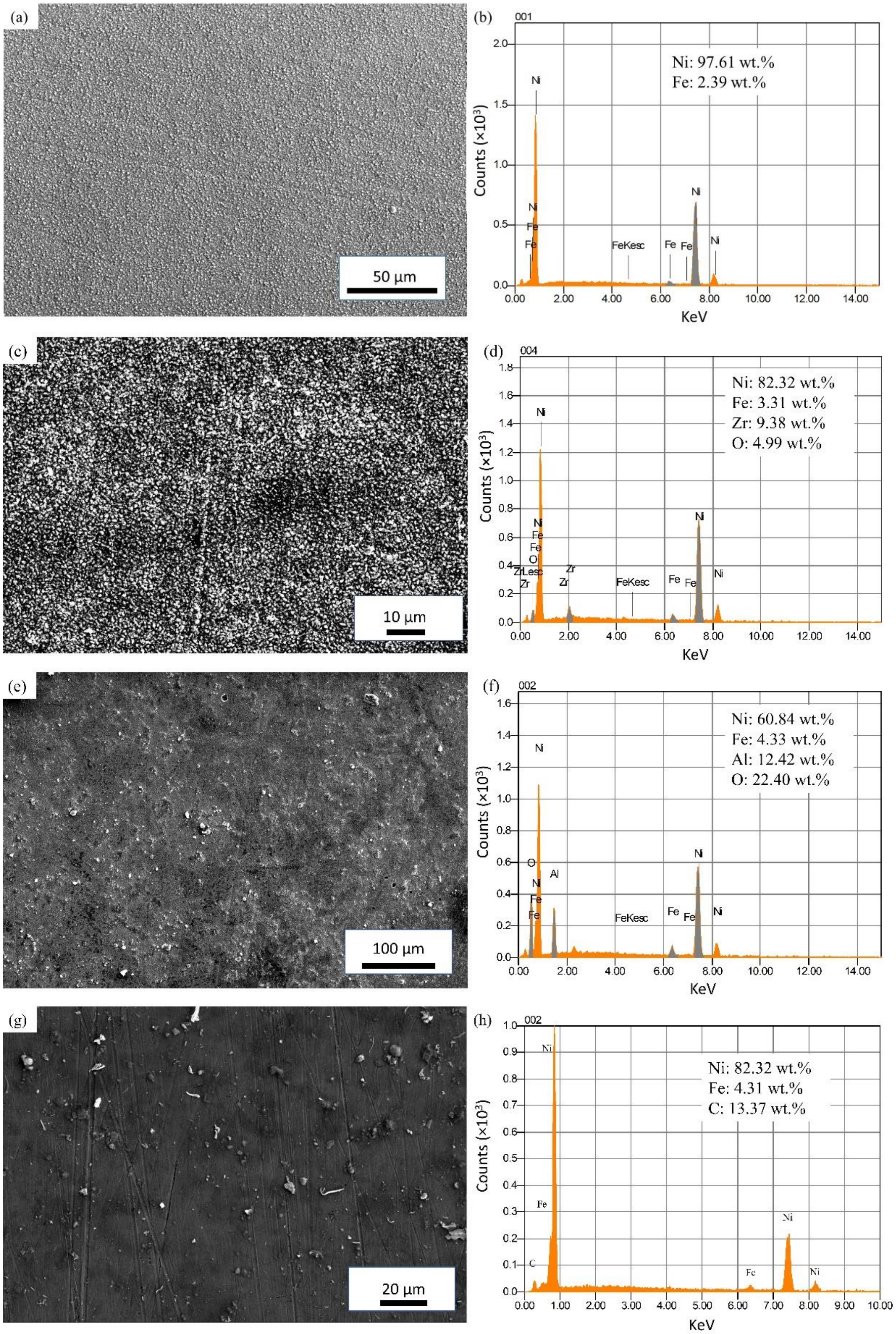

Figure 8. Pre-corrosion surface morphology of (a) Ni, (c) Ni-ZrO_2, (e) Ni-Al_2O_3 and (g) Ni-Gr with chemical composition observed by EDS.

Post-corrosion SEM micrographs for the coatings are shown in Figure 9. It can be observed that all the top surfaces of the coating start breaking into small fragments due to corrosion. Ni-ZrO_2 (Figure 9 (b)) and Ni-Al_2O_3 (Figure 9 (c)) coatings were observed to have smaller fragments compared to Ni and Ni-Gr coating. Smaller fragments have larger surface fraction of boundaries that can cause subsurface corrosion. It can also be the reason for observed ferrous corrosion in Ni-Al_2O_3 and Ni-ZrO_2.

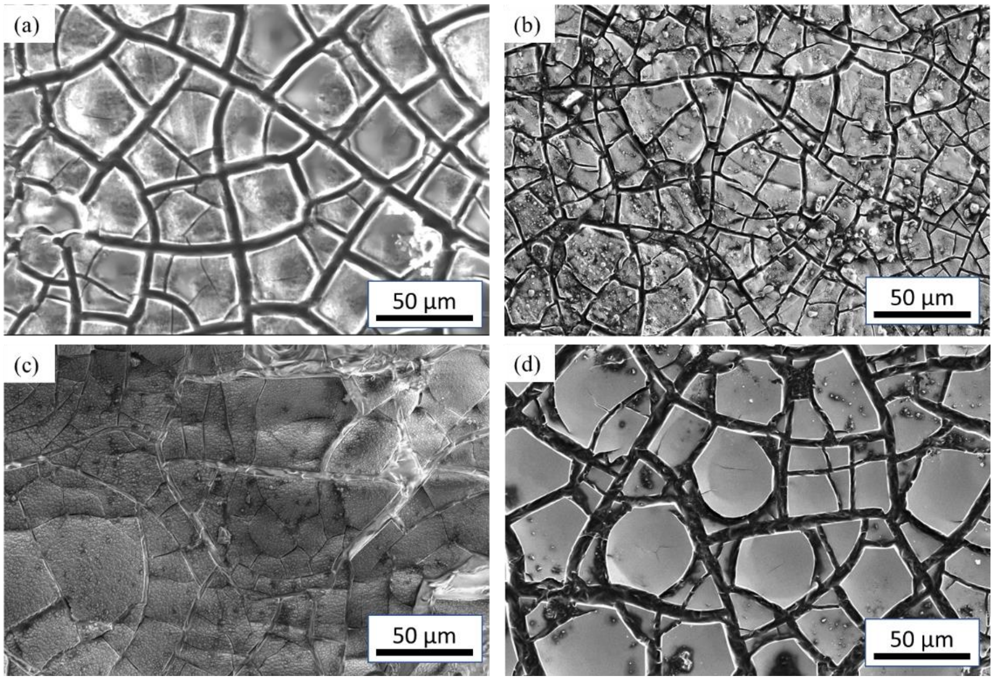

Figure 9. Post-corrosion surface morphology of (a) Ni, (b) Ni-ZrO_2, (c) Ni-Al_2O_3 and (d) Ni-Gr.

3.3 Open circuit potential

The OCP was measured in 0.5 M H_2SO_4, as shown in Figure 10. The OCP of pure Ni coating was found to be stable around -1.72 V. Whereas the OCP for Ni-ZrO_2 coating was -1.14 V, a little higher than the pure Ni coating. The OCP for Ni-Al_2O_3 and Ni-Gr coating was further increased and found to be around -0.42 V. Increase in OCP value suggests that the corrosion resistance of Ni nanocomposite coatings are higher than Ni coating. Similar behavior has been observed for Ni-CeO_2 nanocomposite coating due to the addition of nanoparticles [23].

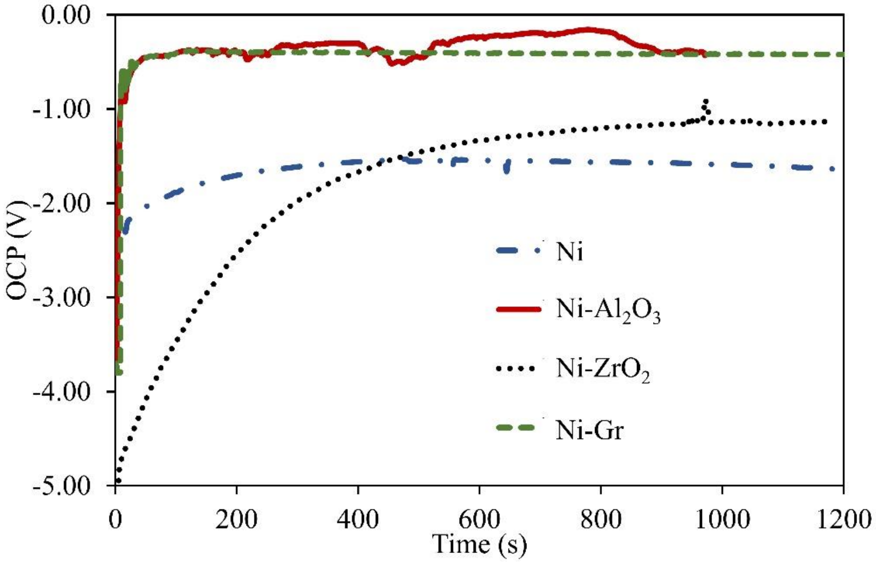

Figure 10. Open circuit potential of Ni coatings measured in 0.5M H_2SO_4

4. Cost estimation of nanocomposite coatings for large scale production

Electrodeposited Ni coatings are commercially available for different sizes of parts [24]. For nanocomposite Ni coatings the additional requirement is nano particles of required materials. These can contain nano particles in the range of 10 – 30 vol.% [25-27]. The required amount of nanoparticles for 10 μm thick coating over 1×1 m^2 with 10-30 vol.% of nanoparticles is calculated in Table 3. The calculated cost for the required amount of materials to coat an area of 1 m^2 is approximately 1.5 to 3 USD. This slight increase in cost can be easily accommodated to provide significant improvement in the mechanical and corrosion performances.

Table 3. Amount and cost of nanoparticles for 10 μm thick coating over 1×1 m^2.

Material	Density (g/cm^3)	Cost (USD/kg)	Amount of material required (g)	Cost for required weight (USD)

Al_2O_3	3.95	150 [28]	3.95-11.85	1.77
ZrO_2	5.68	200 [28]	5.68-17.04	3.04
Gr	2.26	220 [29]	2.26-6.80	1.49

Conclusions

Nickel nanocomposite coatings were prepared by electrodeposition and their mechanical and corrosion performance were evaluated. Mechanical properties evaluated by nanoindentation on the nanocomposite coatings showed that Ni-Al_2O_3, Ni-ZrO_2, Ni-Gr have higher mean hardness and elastic modulus than the pure Ni coating. The improved mechanical properties of the nanocomposite coatings can enhance the durability and applicability of the coating. Prior to corrosion testing, all coatings showed the same scratch depth of 2 μm at the end of the scratch. After the two cycles of moist SO_2 corrosion test, the nanocomposite coatings have a lower scratch depth compared to pure Ni coating. The lower scratch depth suggests that the nanocomposite coatings have higher wear resistance compared to pure Ni coating. After two cycles of moist SO_2 exposure, lower surface corrosion was observed for Ni-Gr followed by Ni-ZrO_2, Ni-Al_2O_3, and pure Ni. The OCP of Ni-Gr, Ni-Al_2O_3 is more positive than that of pure Ni, it suggests improved corrosion resistance.

Acknowledgment

Authors would like to acknowledge financial and in-kind support provided by Bournemouth University, UK through their QR funding and startup funding from Department of Mechanical Engineering, University of Nevada, Reno to conduct joint research between Bournemouth University and University of Nevada, Reno, USA as part of international collaboration initiative.

References

1. Qu N, Zhu D, Chan K, Lei W (2003) Pulse electrodeposition of nanocrystalline nickel using ultra narrow pulse width and high peak current density. Surface and Coatings Technology 168 (2-3):123-128

2. Aperador Chaparro WA, Lopez EV (2007) Electrodeposition of nickel plates on copper substrates using PC y PRC. Matéria (Rio de Janeiro) 12 (4):583-588

3. Balasubramanian A, Srikumar D, Raja G, Saravanan G, Mohan S (2009) Effect of pulse parameter on pulsed electrodeposition of copper on stainless steel. Surface Engineering 25 (5):389-392

4. Nazir MH, Khan ZA, Saeed A, Siddaiah A, Menezes PL (2018) Synergistic wear-corrosion analysis and modelling of nanocomposite coatings. Tribology International 121:30-44. doi:https://doi.org/10.1016/j.triboint.2018.01.027

5. Nazir MH, Khan Z (2015) Maximising the interfacial toughness of thin coatings and substrate through optimisation of defined parameters. International Journal of Computational Methods and Experimental Measurements 3 (4):316-328

6. Bajwa RS, Khan Z, Bakolas V, Braun W (2016) Effect of bath ionic strength on adhesion and tribological properties of pure nickel and Ni-based nanocomposite coatings. Journal of adhesion science and Technology 30 (6):653-665

7. Kim SK, Yoo HJ (1998) Formation of bilayer Ni–SiC composite coatings by electrodeposition. Surface and coatings Technology 108:564-569

8. Benea L, Bonora PL, Borello A, Martelli S (2001) Wear corrosion properties of nano-structured SiC–nickel composite coatings obtained by electroplating. Wear 249 (10-11):995-1003

9. Vaezi M, Sadrnezhaad S, Nikzad L (2008) Electrodeposition of Ni–SiC nano-composite coatings and evaluation of wear and corrosion resistance and electroplating characteristics. Colloids and Surfaces A: Physicochemical and Engineering Aspects 315 (1-3):176-182

10. Chen L, Wang L, Zeng Z, Xu T (2006) Influence of pulse frequency on the microstructure and wear resistance of electrodeposited Ni–Al2O3 composite coatings. Surface and Coatings Technology 201 (3-4):599-605

11. Borkar T, Harimkar S (2011) Microstructure and wear behaviour of pulse electrodeposited Ni–CNT composite coatings. Surface Engineering 27 (7):524-530

12. Chen X, Chen C, Xiao H, Cheng F, Zhang G, Yi G (2005) Corrosion behavior of carbon nanotubes–Ni composite coating. Surface and Coatings Technology 191 (2-3):351-356

13. Benea L (2009) Electrodeposition and tribocorrosion behaviour of ZrO 2–Ni composite coatings. Journal of applied electrochemistry 39 (10):1671

14. Kumar CP, Venkatesha T, Shabadi R (2013) Preparation and corrosion behavior of Ni and Ni–graphene composite coatings. Materials Research Bulletin 48 (4):1477-1483

15. Bajwa RS, Khan Z, Bakolas V, Braun W (2016) Water-lubricated Ni-based composite (Ni–Al 2 O 3, Ni–SiC and Ni–ZrO 2) thin film coatings for industrial applications. Acta Metallurgica Sinica (English Letters) 29 (1):8-16

16. Nazir M, Khan ZA, Saeed A, Stokes K (2015) Modeling the effect of residual and diffusion-induced stresses on corrosion at the interface of coating and substrate. Corrosion 72 (4):500-517

17. Nazir M, Khan ZA (2017) A review of theoretical analysis techniques for cracking and corrosive degradation of film-substrate systems. Engineering Failure Analysis 72:80-113

18. Nazir M, Khan Z, Stokes K (2015) Modelling of metal-coating delamination incorporating variable environmental parameters. Journal of Adhesion Science and Technology 29 (5):392-423

19. Nazir MH, Khan ZA, Saeed A, Bakolas V, Braun W, Bajwa R, Rafique S (2017) Analyzing and modelling the corrosion behavior of Ni/Al2O3, Ni/SiC, Ni/ZrO2 and Ni/Graphene nanocomposite coatings. Materials 10 (11):1225

20. Nazir MH, Saeed A, Khan Z (2017) A comprehensive predictive corrosion model incorporating varying environmental gas pollutants applied to wider steel applications. Materials Chemistry and Physics 193:19-34
21. Lopez J, Stremsdoerfer G, Trejo G, Ortega R, Perez J, Meas Y (2012) Corrosion Resistance of Nickel Coatings Obtained by Electrodeposition in a Sulfamate Bath in the Presence of Samarium (III). Int J Electrochem Sci 7:12244-12253
22. ASTM G87-02 Standard Practice for Conducting Moist SO2 Tests (2002). ASTM International, West Conshohocken, PA. doi:https://doi.org/10.1520/G0087-02
23. Aruna S, Bindu C, Selvi VE, Grips VW, Rajam K (2006) Synthesis and properties of electrodeposited Ni/ceria nanocomposite coatings. Surface and Coatings Technology 200 (24):6871-6880
24. Donohue B (2020) How It Works-The Ins and Outs of Electroplating. Today's Machining World. https://todaysmachiningworld.com/magazine/how-it-works-the-ins-and-outs-of-electroplating/. Accessed 03 January 2020
25. Kuo S-L, Chen Y-C, Ger M-D, Hwu W-H (2004) Nano-particles dispersion effect on Ni/Al2O3 composite coatings. Materials Chemistry and Physics 86 (1):5-10. doi:https://doi.org/10.1016/j.matchemphys.2003.11.040
26. Ciubotariu AC, Benea L, Lakatos–Varsanyi M, Dragan V (2008) Electrochemical impedance spectroscopy and corrosion behaviour of Al2O3–Ni nano composite coatings. Electrochimica Acta 53 (13):4557-4563. doi:https://doi.org/10.1016/j.electacta.2008.01.020
27. Electroless Nickel Plating Services. (2020) Surface treatment experts. https://www.sharrettsplating.com/coatings/electroless-nickel. Accessed 03 January 2020
28. US Research Nanomaterials, Inc. (2019). https://www.us-nano.com/. Accessed 25 December 2019
29. GRAPHENE PRICE. (2020) Graphene Lab. http://www.i-graphenelab.com/price/. Accessed 03 January 2020