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Fabrication of Nanocrystalline Ni–Co Coatings by Electrodeposition under Supergravity Field

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Ni–Co coatings on stainless steel substrates are prepared using electrodeposition assisted by a supergravity field. Transmission electron microscopy reveals the nanometer-scale grain size of the asprepared Ni–Co coatings, confined to around 15 nm, to have likely been due to crystal formation and growth under supergravity conditions. In comparison, electrodeposited coatings obtained under normal gravity without the addition of saccharin exhibit a much larger grain size. Energy dispersive spectroscopy analysis clearly shows a Co content of 40.56 wt.% in the Ni–Co coatings after having used a Co bath concentration of 40 g/l, which cannot be achieved under normal gravity. A maximum microhardness of 660 HV is obtained, also unachievable under normal gravity. Moreover, Ni–Co coatings produced under supergravity show increased resistance to wear compared with their normal-gravity counterparts. We conclude that the high quality inherent to the nanocrystalline Ni–Co coatings originates from the improved crystallinity and increased Co content arising from the use of supergravity.

Keywords: electrodeposition; Ni–Co coating; supergravity field; microhardness; wear resistance

1. INTRODUCTION

Ni–Co coatings are prime candidates for traditional Ni applications because of their high toughness, microhardness, strength, and wear resistance [1,2], and they have been used extensively in corrosion resistance, magnetic recording devices, and other applications [3,4]. It has been reported that the dimensions of coatings significantly impacts the corrosion rate and that corrosion resistance is increased with decreasing grain size [5,6]. Theoretical analysis indicates that dramatic improvements in strength can be attained when grain size is constrained to no more than 100 nm [7-10]. In addition, nanocrystalline coatings possess hugely improved strength, hardness, and wear resistance in comparison with conventional polycrystalline electrodeposits [11,12] and therefore enjoy wide

applicability in many fields.

Because of advantages such as cost-efficiency and high production efficiency, electrodeposition is a feasible and economic approach for preparing Ni–Co coatings [13-15]. To fabricate Ni–Co coatings with nanocrystals using electrodeposition involves facilitating crystal growth and increasing Co content, which have both been the focus of much research. Gluconate salt and cysteine were used to synthesize nanocrystalline Ni–Co coatings by Badawy [16]. Lokhande obtained Ni–Co alloy coatings with nanocrystals using saccharin as an additive [17]. Li researched the relationship between saccharin and Co concentration on the grain size of Ni–Co alloy when synthesizing nanocrystalline Ni–Co coatings [18]. With the addition of saccharin to the bath, Li induced nanocrystallization of Ni–Co coatings [19]. Vijayakumar employed primary dicarboxylic acids to obtain primary Ni–Co alloys with a sub-microcrystalline structure [20]. Golodnitsky achieved Ni–Co alloys deposited from sulfamate electrolyte using acetate and citrate anion as additives [3].

Although great progress has been made, it is worth noting that the excessive addition of saccharin is detrimental to Ni–Co coatings. Increasing saccharin concentration leads to a rise in sulfur and carbon impurities, resulting in poorer ductility and tensile strength [19]. Moreover, it is necessary to further refine the grain size of Ni–Co coatings. To the best of our knowledge, a supergravity field has not been applied to improve the performance of electrodeposited Ni–Co coatings. Atobe first reported the effects of supergravity on the polymerization rate of polyaniline and on the performance of polymeric aromatic compounds formed by electrodeposition [21]. Eftekhai improved the properties of soft magnetic materials by employing an external centrifugal force during the deposition process [22]. Using supergravity, Liu prepared flocky MnO₂/carbon nanotube coatings that proved extremely difficult to obtain without supergravity [23]. In this paper, a supergravity field was employed to electrodeposit nanocrystalline Ni–Co alloy coatings. Experiments were conducted to reveal the dependence of supergravity field on the grain size, Co content, surface morphology, preferred orientation and microhardness of the obtained Ni–Co alloy coatings produced.

2. EXPERIMENTAL

Figure 1 displays a principle scheme of the apparatus used, consisting of a power generator, a filter, a pump, a motor, a temperature control unit, and an electrolytic cell. The cathode (i.e., the substrate) is housed inside the cylindrical jig, where it is in close contact with the internal surface of the fixture (see Fig. 2). The right-end face of the fixture is sealed and connected to the motor that provides the supergravity field. The anode is a hollow cylinder with many small holes. To keep the inter-electrode gap constant, the anode is positioned inside the cathode concentrically. The temperature of the solution is maintained at about 45 °C by the temperature control unit. During the experiment, only the cathode rotates.

The cell can be filled with electrolyte in a very short time and is circulated continuously due to the powerful pump, guaranteeing that the cell stays filled with electrolyte for the required period; excessive electrolyte can flow out of the cell via the outlet. With the motor on, the cell and electrolyte are rotated together. Under supergravity conditions, the electrolyte is pushed towards the surface of the cylindrical electrode, resulting in unwanted bubbles emanating from buoyance and centrifugal forces, producing a force secant to the circle [24]. Due to the resultant force, the acceleration direction of the bubbles is secant instead of tangent to the circle, resulting in a trajectory of the bubbles away from the substrate. Therefore, the bubbles move away from the as-electrodeposited coating surface and can more easily be removed under the supergravity field [25].

In our experiments, the electrolyte contained 350 g/l nickel sulfamate, 15 g/l nickel chloride, 35 g/l boric acid, 0.1 g/l sodium dodecyl sulfate, and 40 g/l cobalt sulfamate. The substrate was stainless steel. Prior to the experiment, the electrolyte was circulated for 60 min to ensure an even distribution of cobalt sulfamate. During the experiment, the unilateral inter-electrode gap was 4 mm, and the current density 1 A/dm². The cathode rotation speed ranged from 300 to 1500 r/min, and all coatings maintained a thickness of approximately 40 μ m.

The surface morphologies of the as-electrodeposited Ni–Co coatings were observed using a scanning electron microscope (SEM), and an X-ray diffractometer (XRD) was used to examine the preferred orientations of the coatings. The Co contents in the coatings were determined from energy-dispersive spectra (EDS). A transmission electron microscope (TEM) was used to measure grain size of the as-prepared Ni–Co coatings. Microhardness of the Ni–Co coatings was measured using a reciprocating sliding wear tester with a loading force of 100 g and a stainless-steel ball as the counter body. For each Ni–Co coating, microhardness was averaged from five measurements taken from across the sample.



Figure 1. Schematic diagram of the apparatus used for electrodeposition under supergravity.



Figure 2. Details of the cathode.

3. RESULTS AND DISCUSSION

3.1 The effects of the supergravity coefficient on macro profiles and morphologies of coatings

The supergravity coefficient can be calculated using Equation (1). Supergravity coefficients for different speeds are calculated and listed in Table. 1.

$$G = N^2 \pi^2 r / (900g) \,, \tag{1}$$

where G is the super-gravity coefficient; N is the rotation speed (r/min); r is the radius of the fixture, 0.05 m; and g is gravitational acceleration (9.8m/s²). Under a normal gravity field, G is 0.

Table 1. G for different rotation speeds.

	Rotation speed (r/min)				
	0	300	700	1100	1500
G	0	5.04	27.42	67.70	125.89

The generation and detachment of bubbles from the electrode surface affects the over-potential of the electrode reaction, and bubble formation energy on the surface can be expressed as [24]:

$$\Delta E = 4\pi r^{2} \sigma + 4\pi r^{3} \Delta E_{v} [P_{0} + \rho(1+G)gh]/3P_{0}, \qquad (2)$$

where, r is radius of the bubble; σ is boundary tension of gas and solution; P₀ is pressure of the environment; ρ is the density of solution; g is gravitational acceleration; G is the supergravity coefficient and ΔE_V is the energy shift as hydrogen atoms become attached to the electrode, constituting one unit normal volume of hydrogen gas; and h is the solution depth in the cell.

According to Equation (2), the critical radius, r*, for generating a bubble can be calculated using $\partial \Delta E / \partial r = 0$, resulting in [24]:

$$r^{*} = -2\sigma P_{0} / \Delta E_{V} [P_{0} + \rho(1+G)gh]$$
(3)

Hence, the critical radii under normal gravity and supergravity fields can be represented by Equations (4) and (5), respectively:

$$r_1^* = -2\sigma P_0 / \Delta E_v (P_0 + \rho g h) \tag{4}$$

$$r_{2}^{*} = -2\sigma P_{0} / \Delta E_{V} [P_{0} + \rho(1+G)gh]$$
⁽⁵⁾

Thus, the ratio of r_1^* to r_2^* can be given as:

$$r_{2}^{*}/r_{1}^{*} = 1 - \rho g h G / [P_{0} + \rho (1+G)gh]$$
(6)

As can be seen from Equation (6), r_2^*/r_1^* is always less than 1 and decreases with increasing G, which can be proved mathematically; this means that supergravity is beneficial for the process of gas evolution.

Figure 3. Macro profiles of Ni–Co coatings formed using different rotation speeds: (a) 0 r/min, (b) 300 r/min, (c) 700 r/min, (d) 1100 r/min, and (e) 1500 r/min.

The macro profiles of the Ni–Co coatings obtained using the same electrolyte and parameters at various rotation speeds are shown in Fig. 3. Without rotation (rotation speed = 0 r/min), many dense pits form on the coating surface [Fig. 3(a)]. The bubbles generated during electrodeposition hinder metal ion deposition at locations where bubbles already exist; hence, when bubbles explode, pits are created. However, in the coatings formed at rotation speeds of 300 to 1500 r/min, no surface pits are



visible to the naked eye, and the surfaces appear smooth [Figs. 3(b)-3(e)]. As mentioned above, the centrifugal force provided by the supergravity field is beneficial for the timely and effective removal of bubbles from the electrodeposited coatings. Therefore, under rotation, metal ions are deposited evenly throughout the entire electrodeposition area without pit generation. The SEM images at higher resolution corresponding to Figs. 3(a)-3(e) are depicted in Fig. 4.

Figure 4 illustrates the surface morphologies of Ni-Co coatings prepared at a current density of 1 A/dm², a Co concentration of 40 g/l, and different rotation speeds. The results show that rotation speed affects surface morphology. As shown in Figs. 4(a) and 4(b), rotation speeds of 0 and 300 r/min result in the formation of spherical clusters on the surface. This indicates that the rotation speed was too low to smooth the surfaces. At a rotation speed of 700 r/min, the surface morphology changes from spherical clusters to a smooth surface [Fig. 4(c)]. Similar results were achieved by Guo for nickel deposition from aqueous solution under a supergravity field [24]. These results indicate that an appropriate supergravity field is conducive to obtaining a flat coating surface during electrodeposition. Further increasing rotation speed results in the formation of pinholes in the coatings, as shown in Fig. 4(d). It is worth noting that microcracks appear in the coating deposited at 1500 r/min, as shown in Fig. 4(e). The formation of pinholes and microcracks may be ascribed to the high rotation speed, which suppresses the escape of hydrogen bubbles. Similarly, Wang reported cracks in deposits caused by the adsorption and inclusion of hydrogen [26]. Thus, the supergravity field has a significantly positive influence on coating morphology, in accordance with Liu [27], Tong [28], and Eftekhari [29]. These results indicate that desirable coatings can be obtained through the proper selection of a supergravity field.







Figure 4. Morphologies of Ni–Co coatings formed at a current density of 1 A/dm² and Co content of 40 g/l under various rotation speeds: (a) 0 r/min, (b) 300 r/min, (c) 700 r/min, (d) 1100 r/min, and (e) 1500 r/min.

3.2 Composition and transmission electron microscopy analysis of coatings

Figure 5 illustrates the influence of rotation speed on Co content in the coatings formed at a current density of 1 A/dm² in a bath with a Co concentration of 40 g/l. The weight percent of Co in the deposit increases as rotation speed varies from 0 to 700 r/min. Co content then decreases upon further increasing the rotation speed to 1500 r/min. In traditional electrodeposition (0 r/min), a Co content of 23.57 wt.% was achieved. The minimum weight percent of Co (22.68 wt.%) was obtained at a rotation speed of 1500 r/min, while the maximum Co content (40.56 wt.%) was observed in the coating deposited at a rotation speed of 700 r/min. Without the supergravity field and using a Ni–Co electrolyte with a Co concentration of 40 g/l, Li [13], Ma [30], and Zamani [31] obtained a Co content of no more than 30 wt.%. Thus, the method presented herein is superior to traditional electrodeposition.

According to Dryden [32], during electrodeposition, Co^{2+} ions form a complex with free OH⁻ ions from hydrolysis, forming Co(OH)⁺. The Co(OH)⁺ adsorbs to the electrode surface and is simultaneously reduced to Co(s), which blocks deposition sites. Under supergravity, centrifugal forces facilitate the transport of metal ions to the cathode surface, where they are adsorbed [24,33,34]. At rotation speeds in the range of 0–700 r/min, the supergravity field increases, which increases the concentration of Co²⁺ around the cathode diffusion layer. Although the reaction of Co(OH)⁺ to Co(s) does occur, the cathode diffusion layer becomes relatively more depleted with respect to the preferentially deposited Co²⁺ ions [1], which contributes more Co²⁺ ions to the Ni–Co coating. Therefore, Co content increases with rotation speed.

In the range of 700–1500 r/min, the Co^{2+} ion concentration around the cathode diffusion layer is much higher than that at 0–700 r/min due to the larger centrifugal force. In this case, many more Co^{2+} ions are reduced to Co(s) and the predominance of Co(s) leads to a decrease in Co content in the Ni–Co coatings. However, Zamani [31] reported a lower Co content in Ni–Co coatings under the same conditions in normal gravity.



Figure 5. Effect of rotation speed on the weight percent of Co incorporated in the Ni–Co coatings

Figure 6 presents transmission electron micrographs of Ni–Co coatings prepared under different conditions. Grain size decreases as rotation speed increases from 0 to 700 r/min but then increases as rotation speed increases from 700 to 1500 r/min. The largest grain size of approximately 200 nm was obtained at a rotation speed of 1500 r/min [Fig. 6(e)]. Meanwhile, the grain size of the Ni–Co coating formed at 700 r/min was 15 nm [Fig. 6(c)]. Furthermore, the grain sizes produced at rotation speeds of 0, 300, 1100, and 1500 r/min were distributed non-uniformly, whereas those obtained at 700 r/min were relatively uniform. The bright and continuous rings in the electron diffraction pattern confirms the small and uniform grain size obtained at 700 r/min [Fig. 6(c)]; the rings in Fig. 6(c) are the brightest and smoothest among all the samples, which again confirms that the coating formed at 700 r/min had the smallest grain size. In comparison, the rings in Fig. 6(e) are dim and dashed, indicating large grains with non-uniform sizes.

As mentioned above, as the rotation speed increased from 0 to 700 r/min, the Co content increased and the grain size decreased, resulting in a refined grain size in this work. As the rotation speed increased further from 700 to 1500 r/min, the decrease in Co content in the as-deposited coatings gave rise to a larger grain size.

It is well known that limiting current density is related to diffusion layer thickness and that the crystalline nucleus formation probability is related to cathode overpotential [1]. With increasing rotation speed, diffusion layer thickness reduces. As a result, the limiting current density increases, which leads to an increase in the cathode overpotential. Accordingly, the crystalline nucleus formation probability rises; therefore, increasing rotation speed gives rise to decreasing grain size.





Figure 6. Transmission electron microscopy images of Ni–Co coatings formed at a current density of 1 A/dm² and a Co content of 40 g/l under various rotation speeds: (a) 0 r/min, (b) 300 r/min, (c) 700 r/min, (d) 1100 r/min, and (e) 1500 r/min.

3.3 XRD results

The phase constitutions of the electroplated Ni–Co alloy layers were examined using X-ray diffraction, as shown in Fig. 7. All the coatings had face-centered cubic (FCC) structures. With the introduction of the supergravity field, no transition from the FCC structure to a body-centered cubic (BCC) structure was observed. By increasing the rotation speed from 0 to 700 r/min, the intensity of

the (111) orientation increased dramatically, whereas the intensity of the (200) orientation decreased, as reported previously [24]. Upon further increasing the rotation speed to 1500 r/min, the intensity of the (200) orientation again dominated (111) orientation. Meanwhile, the intensity of the (311) orientation increased when the rotation speed increased from 0 to 700 r/min and decreased with further increasing orientation speed. The (220) orientation was only observed at rotation speeds between 300 and 700 r/min. However, the supergravity field did not seem to affect the intensity of the (400) orientation.

Under normal gravity, diffraction peaks appeared at $2\theta = 44.44^{\circ}$ and 51.96° , corresponding to the (111) and (200) crystal planes of Ni, respectively. At 700 r/min, diffraction peaks appeared at $2\theta = 45.04^{\circ}$ and 51.76° , which are closer to the diffraction angles of standard nickel crystal: 44.5° and 51.8° for the (111) and (200) crystal planes, respectively. A similar result was also reported by Guo for the deposition of nickel from aqueous solution under supergravity [24]. These results indicate that fewer defects existed in the as-prepared Ni–Co coatings. It has been reported that variation in peak width reflects changes in grain size [35,36]. As seen in Fig. 7, peak width increased with increasing rotation speed from 0 to 700 r/min, indicating a reduction in grain size, while peak width decreased as rotation speed increased further, indicating an increase in grain size. These trends in peak width confirm the changes in grain size shown in Fig. 6.





Figure 7. X-ray diffraction patterns of Ni–Co coatings formed at a current density of 1 A/dm² and a Co content of 40 g/l under various rotation speeds: (a) 0 r/min, (b) 300 r/min, (c) 700 r/min, (d) 1100 r/min, and (e) 1500 r/min.

3.4 Microhardness and wear resistance of coatings

Microhardness is a key property of Ni–Co when the alloy is employed in anti-wear coatings. Figure 8 displays the microhardness values of Ni–Co coatings produced at a current density of 1 A/dm^2 and a Co concentration of 40 g/l under different rotation speeds. The microhardness of the traditionally deposited Ni–Co coating (rotation speed = 0 r/min) is approximately 424 HV. At a rotation speed of 300 r/min, the value is slightly higher (513 HV). Microhardness maximizes (660 HV) at a rotation speed of 700 r/min and then decreases when the rotation speed increases further from 700 to 1500 r/min.

In the present investigation, the maximum Co content (40.56 wt.%) was obtained at a rotation speed of 700 r/min, which explains the maximum microhardness observed at this rotation speed. It is well known that Co content plays a key role in the microhardness of Ni–Co coatings [37], and the maximum microhardness was obtained with the maximum Co content in this work. It may be because the Co element altered the intensities of the different phase orientations and also changed the preferred coating orientation, as shown in Fig. 7.

Many researchers have attempted to enhance the microhardness of Ni–Co coatings, focusing on how to maximize Co content. Lupi created Ni–Co coatings with a maximum microhardness of <500 HV when the Co content was approximately 50 wt.% [38]. Srivastava obtained Ni–Co coatings with microhardness values of approximately 500 HV when the Co content was 50 wt.% [39]. Wang obtained a microhardness of 500 HV with a Co content of 50 wt.% [40]. Although increasing the Co content within a given range can effectively improve Ni–Co coating hardness, further increasing it beyond this range leads to a decline in microhardness, in spite of the content being as high as 80 wt.% [39,40]. Bakhit also achieved a hardness of 500 HV by increasing the Co content to 45 wt.% and adding 4 g/l saccharin [41]. By adding 2 g/l saccharin, Wasekar obtained a microhardness of 550 HV [42], and a microhardness as high as 600 HV was achieved by Li using 3 g/l saccharin [20]. However, the addition of saccharin makes it difficult to maintain the compositions of the electrolyte. Moreover, excess saccharin introduces carbon and sulfur impurities into the coatings, leading to non-compact and cracked morphologies.

Thus, although the Co content obtained in this study is lower than that previously reported [38-41], the microhardness is much higher. This suggests that the refined crystal size contributes to a vast improvement in microhardness of the Ni–Co coatings. As discussed above, the smallest grain size was obtained at a rotation speed of 700 r/min.



Figure 8. Effect of rotation speed on the microhardness of Ni–Co coatings.



Figure 9. Effect of rotation speed on the wear weight loss of Ni–Co coatings.

Figure 9 shows the wear weight loss of Ni–Co coatings prepared at a current density of 1 A/dm² and a Co concentration of 40 g/l under various rotation speeds. The Ni–Co coatings obtained under normal gravity exhibit the maximum wear weight loss, whereas those deposited under supergravity have a much lower wear weight loss. Wear weight loss decreases with increasing rotation speed from 0 to 700 r/min but subsequently increases with further increasing rotation speed from 700 to 1500 r/min. The lowest wear weight loss in the coatings was observed at a rotation speed of 700 r/min, which corresponds to the maximum microhardness.

Figure 10 shows the morphologies of the worn surfaces of the Ni–Co coatings prepared at a current density of 1 A/dm² and a Co content of 40 g/l under various rotation speeds. Under normal gravity, cracking and spalling are observed on the worn surfaces [Fig. 10(a)], and the presence of cracking and spalling lead to greater wear debris. Figure 10(b) reveals a spalling trace of narrower width and shallower depth on the worn surfaces deposited at a rotation speed of 700 r/min. Increasing the rotation speed beyond 700 r/min generates wider spalling traces, as shown in Fig. 10(c).





4. CONCLUSIONS

In this work, we demonstrated an electrodeposition technique using a supergravity field. Ni–Co coatings with an excellent property were successfully produced using this technique. Based on the experimental results, the following conclusions can be drawn.

(1) The introduction of the supergravity field altered the morphology, grain size, and preferred orientation of the Ni–Co coatings. Nanocrystallized Ni–Co coatings with an average grain size of 15 nm were obtained at a rotation speed of 700 r/min.

(2) The Co content in the Ni–Co coatings increased with increasing rotation speed from 0 to 700 r/min. Upon further increasing the rotation speed to 1500 r/min, the Co content decreased. The maximum Co content (40.56 wt.%) was obtained at a current density of 1 A/dm², Co concentration of 40 g/l, and a rotation speed of 700 r/min. In contrast, the maximum Co content obtained using traditional electrodeposition was 20–30 wt.%.

(3) Microhardness increased with increasing rotation speed from 0 to 700 r/min. A maximum microhardness of 660 HV, which cannot be achieved by traditional electrodeposition, was obtained at 700 r/min. The friction and wear behaviors of the Ni–Co coatings were closely related to the strength of the supergravity field, and the coatings produced under supergravity showed somewhat increased wear resistance compared with those produced under normal gravity.

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COMPLIANCE WITH ETHICS GUIDELINES

The authors declare no competing financial interests or financial conflicts.

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