Effects of Rotating Magnetic Fields on Nickel Electro-Deposition

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Nickel was electrodeposited in alternative magnetic field generated by rotating magnets. The variations of coatings’ surface morphology and texture were investigated and characterized by SEM, AFM, XRD and chronopotentiometry curves. The interpretation of the experimental results involves the effect of induced electric field. At the rotating frequency of 1500 rpm and 3000 rpm, some unexpected results were observed. A new engineering approach of fabricating nickel coating of high surface finish and tunable crystal texture under spinning magnets has been developed.

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Numerous studies concerning the electro-deposition in the presence of a magnetic field have been published in the past years.¹⁻⁸ All these investigations are involved in the application of static magnetic field. So far, less emphasis has been focused on the employment of alternative magnetic field as an electrochemical method,⁹⁻¹⁰ rather than an engineering approach.

In this paper, the effects of alternative magnetic field on the properties of nickel electro-deposition were examined. The alternative magnetic field was generated by spinning permanent magnets. Special attention was paid to the relationship between the magnets’ rotating speed and the nickel deposit’s surface morphology and preferred orientation. The characterization of the deposited nickel was conducted by electrochemical tests, SEM, AFM, and XRD techniques.

Experimental

Electrolysis system.— Nickel was electrodeposited galvanostatically with a 3-electrode system. A 4 × 8 mm nickel foil was employed as the counter electrode. The reference electrode was a standard calomel electrode (SCE). The working electrode was a 3 × 3 × 0.7 mm square copper sheet.

In experiments, the bath temperature was maintained at 22 ± 2°C. No agitation was provided. The electrolyte consists of 0.05 M NiSO₄·6H₂O, 0.1 M boric acid and 0.1 M sodium sulfate anhydrate. The solution pH was maintained at 4.00 during electrodeposition tests, which were performed at 6.7 mA/cm² for 40 minutes.

Electro-deposition in the presence of rotating magnets.— A specially designed nylon cup was used in the experiment. The sample was placed inside a bore of the nylon cup. A pair of permanent magnet groups was mounted onto a frame outside and around the bore. Each magnet group consisted of four cylindrical magnets which were magnetized parallel to their axes. With such an arrangement, the magnetic field inside the bore was measured to be 0.18 T.

To generate alternative magnetic fields, a drill press was used to drive the magnets to spin around the sample at speeds of 1000, 1500, 2000, 2500 and 3000 rpm, respectively.

Characterization of the nickel deposition.— Surface morphologies were characterized by a JEOL (JSM-6301FXV) field emission SEM. The atomic force microscope (AFM) (MFP-3D, Asylum Research) was employed to measure the roughness and reveal detailed features of the coating surfaces. X-ray diffraction measurements were carried out in a Rigaku-Ultima IV X-ray diffractometer using Cu Kα radiation with a wavelength of 1.54 Å. The electrochemical characterization was conducted with a Gamry Reference 600 electrochemical workstation.

Results and Discussion

Magnetic and electric fields in spinning magnets.— The magnets spinning around the sample not only exert a magnetic field, which varies periodically, but also induce an eddy electric field. According to Maxwell equation,¹⁰

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \tag{1}$$

Where $\vec{B}$ is the magnetic flux density on the sample surface; $\vec{E}$ denotes the induced electric field generated by spinning magnets. From Equation 1, $\vec{E}$ rotates periodically along with $\vec{B}$. Accordingly, $\vec{E}$ around the sample varies periodically with the spinning magnets. Suppose that the component of the eddy electric field along the sample surface is $E_s$, the distribution of $E_s$ on the sample surface can be decided from Equation 1, and depicted in Fig. 1.

Electrochemical characterization.— Fig. 2 demonstrates the chronopotentiometry curves during depositions. For magnets’ spinning rate $f = 1000, 2000$ and 2500 rpm, the chronopotentiometry curves shifted to more positive potentials as $f$ increased. This can be

![Figure 1. Schematic presentation of the changing process of $E_s$: B is (a) parallel; (b) oblique and (c) vertical to the electrode.](image-url)

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attributed to the additional MHD convection produced by the induced electric field, $\vec{E}$, because from Equation 1, a higher $f$ results in a stronger $\vec{E}$. However, for $f = 1500$ and $3000$ rpm, the chronopotentiometry curve shifted to more negative potential levels than the other three curves, indicating the diminishing of MHD convection. These are unusual results which later also occurred in other characterization experiments.

Moreover, the more negative potentials at the initial stage in Fig. 2 for $f = 1500$ and $3000$ rpm, can be explained in terms of the weak MHD convection that made the electrode potential decrease drastically to attract more nickel ions.

**Morphological examination by SEM and AFM.**—Fig. 3 features the SEM and AFM images of the nickel coatings developed under various magnetic field conditions. The corresponding surface roughness was determined by AFM and listed in Table I.

At $f = 1000$, $2000$, and $2500$ rpm, the coating surface turned smoother with higher spinning rate, shown in Figs. 3a, 3c, 3d and Table I. The sample fabricated at $f = 2500$ rpm was the smoothest and had a shiny finish. At $f = 1500$ rpm, the rough spherical nodules appeared (Fig. 3b), which resembles that when the magnetic field was absent (Fig. 3f), and implies the loss of the leveling effects from $\vec{B}$ and $\vec{E}$.

The nodule-like morphology observed at $1500$ rpm implies the mass transfer control of the nickel ions, which might be caused by the lowest potential level in Fig. 2 resulted from the diminishing of MHD convection; and the disappearance of the leveling effect of $\vec{B}$ and $\vec{E}$ was also responsible for the nodules’ formation.

In addition, the coating became rougher when $f$ increased from $2500$ rpm to $3000$ rpm (Fig. 3e). The occurrence of the outstanding results that the coating surface turned rougher at $f = 1500$ and $3000$ rpm is consistent with the electrochemical characterization result in Fig. 2, the reason is unclear at present. On the other hand, when $f = 1000$, $2000$, and $2500$ rpm, the deposit turned increasingly smoother, showing the leveling effect of $\vec{E}$. To rationalize this effect, $\vec{E}$ is resolved into two components: $E_n$ and $E_s$, which are normal and parallel to the electrode surface, respectively. Because $E_n$ drives the nickel ions into and from the electrode surface periodically, its influence can be neglected. The effect of $E_s$ is illustrated in Fig. 4. Suppose a semi-spherical nodule exists on the coating surface that is exposed to $E_s$ (Fig. 4a). The nickel ions are

| Experimental Conditions | B = 0.18 T, f = 1000 rpm | B = 0.18 T, f = 1500 rpm | B = 0.18 T, f = 2000 rpm | B = 0.18 T, f = 2500 rpm | B = 0.18 T, f = 3000 rpm | B = 0 |
|------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Surface Roughness RMS (nm) | 32.9 | 222.6 | 27.7 | 21.3 | 43.8 | 222.4 |

*Each value of RMS in the table is the average of three tests randomly chosen on the sample surface except for B = 0.18 T, f = 1500 rpm and B = 0, which have two measurements to average due to the coarse surface conditions that broke the cantilever tip several times.
Figure 4. Illustration of the mechanism of the induced electric field leveling a grain: (a) different influences on various parts of the grain; and (b) the resultant growth.

Driven by $E_s$ to move toward the side of the nodule facing $E_s$ (the front surface). The top and the other side of the nodule (the rear surface), however, are surrounded by electrolyte with lower nickel ion concentration because the nickel ions are propelled by the $E_s$ to pass by the top surface or to migrate away from the rear surface. As a result, the deposition on the front surface is facilitated, while on the top and rear surface it is suppressed (Fig. 4b). As the magnet spins around equally in all directions, the circumference of the nodule is leveled.

In addition to the levelling effect discussed above, another effect of the spinning magnets on the coating morphology was observed. In Fig. 3g, the AFM image reveals that at $f = 3000$ rpm, some elongated grains appeared on the sample surface, which are similar to those reported in Fe or its alloys deposition in parallel magnetic field. 11-13 This kind of morphological feature was found only in AFM image obtained at a scanning range of $10 \times 10 \mu m$ and under $f = 3000$ rpm.

One explanation to the elongated grains is that in Fig. 1, around the middle line (drown as dashed lines), $E_s$ is always parallel to one direction (the direction of the axis of the magnets rotation). Consequently, on the coating surface close to this middle line, $E_s$ facilitated the grains' growth in one direction and elongated them.

Another explanation for these elongated grains is going to be proposed in our next paper which studies the mechanisms of the static magnetic field effects on Ni deposition.

As seen in Fig. 3 and Table I, at 3000 rpm, the coating's surface roughness increased to be higher than that for $f = 1000$, 2000 and 2500 rpm, indicating the leveling ability of $\vec{B}$ and $\vec{E}$ declined for some unknown reason, which made the occurrence of the elongated grains possible.

The alternative magnetic field may find potential applications to produce smooth coatings by employing strong magnets and spin at high speed; or to tailor the deposit's morphology by adjusting its position and orientation in the field, e.g., to form special patterns with elongated grains as in Fig. 1a to 1c.

**Structural investigation by XRD.**—Fig. 5 shows the X-ray diffraction results. The diffraction intensity values have been re-scaled such that the (111) plane intensity in each diagram is normalized to 100. The texture coefficient, $T_c$, in Fig. 5b is calculated using the formula in Ref. 14:

$$T_c = \frac{I(hkl)}{\sum I(hkl)} \times 100$$

Fig. 5b clearly demonstrates that (200) is the preferred orientation for $f = 2000$ and 2500 rpm. At $f = 1500$ rpm, the preferred orientation is (111). When $f = 1000$ and 3000 rpm, the $T_c$ for (200) and (311) are almost equal.

It is also noticeable that Fig. 5 exhibits the similar tendency as Fig. 2 and 3, that for $f = 1000$, 2000 and 2500 rpm, (200) $T_c$ turned higher when $f$ increased; and at $f = 1500$ and 3000 rpm, (200) $T_c$ decreased, especially, $f = 1500$ rpm corresponds to the lowest $T_c$ value.

Furthermore, the (311) $T_c$ in Fig. 5b fluctuated with the spinning rate increase; the (220) $T_c$ showed a weak dependence on the spinning rate.

In addition, from Fig. 3g, it is obvious that the elongated grains obtained at $f = 3000$ rpm exhibit the two-folded pyramid morphology which resembles that displayed in Ref. 15, in which the two facets of

![Figure 5](image-url)
the elongated pyramid were identified to be nickel (111). Therefore, it can be inferred that when the leveling effect of \( \vec{B} \) and \( \vec{E} \) decreased at 3000 rpm, the two-folded pyramids were exposed which promoted (111) growth. This might be the reason for the reduced (200) \( T_c \) at \( f = 3000 \) rpm in Fig. 5b.

About the outstanding results at \( f = 1500 \) and 3000 rpm.— By comparing the results of this investigation, unusual results occurred in the electrochemical, morphological and structural characteristics when \( f = 1500 \) and 3000 rpm, especially for \( f = 1500 \) rpm, under which the levelling effect of both the magnetic and electric field disappeared as through no field existed, according to Fig. 3b and 3f. Because of the unusualness, two repeated experiments were conducted at \( f = 1500 \) rpm, the obtained results were consistent.

The origin of these coincidences is unclear at present. In our opinion, these abnormalities could be the result of the combined actions of the superimposed magnetic field, the induced electric field, the properties of the electrolyte, and the plating cell geometry as a boundary condition. Some theoretical calculations might be needed to clarify the interactions and influences of these factors on the migration and reduction of nickel ions in the electroplating process. This will be a subject of future investigations.

Conclusions

1. Nickel was electrodeposited under various magnets’ spinning rates. The characterization results suggest that the spinning magnets produced more positive electrode potential, smoother coating surface and higher (200) texture coefficient at certain spinning rates.
2. The electric field induced by the alternative magnetic field has been identified to modify the coating morphology in two ways. One is to accelerate the lateral growth of the bumps on the coating and reduce the surface roughness; the other is to yield elongated grains at certain spinning rate.
3. Employing spinning magnets during electrodeposition provides a new engineering approach to tailor the morphological and crystallographic properties of the deposits.
4. Abnormal results were recorded when the magnets were rotated at 1500 and 3000 rpm. Further research is required to rationalize these abnormal observations.

Acknowledgment

The authors acknowledge the financial support by Natural Science and Engineering Research Council of Canada (NSERC) and Royal Canadian Mint.

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