Influence of lower current densities on the residual stress and structure of thick nickel electrodeposits

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Abstract

Thick Ni electrodeposits, with thicknesses ranging from 18 to 90 μm, have been produced from sulfamate baths using very low current densities (1.5–5 mA cm⁻²). Increasing grain sizes, with a corresponding decrease in the hardness values, and more columnar grain morphologies were observed with increasing current densities in the deposits. The anisotropy in the mechanical properties of the deposits were found to correlate strongly with the deposit texture, where the change from a <101> dominated orientation at 1.5 mA cm⁻² to a <001> orientation at the higher (5 mA cm⁻²) current density led to a corresponding decrease in the indentation modulus values for the respective Ni films. The residual stress values measured in the deposits (75–136 MPa) were found to be comparable to literature values of deposits plated at higher current densities, which rules out any potential advantage from the use of such low current densities for producing lower residual stresses.

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1. Introduction

Electrodeposited nickel, particularly using sulfamate electrolytes, are widely popular in the electroplating and microfabrication industry due to their high deposition rates, greater film thickness, good mechanical and corrosion resistant properties, and low residual stress [1–5]. Recent reports have also suggested the use of thick (~tens or hundreds of microns) nickel films as matrix for the production of nickel–diamond composite coatings for high precision wear-resistant complex shaped grinding or cutting tools [6–8]. However, like most electrodeposited metals, nickel suffers from some common problems, such as anisotropic material properties, poor repeatability, and high sensitivity to electroplating conditions [3,4]. For example, an increase in current density is often used to reduce the yield time and increase the output of these electrodeposits for greater film thickness [1,2,9], and thus most of the reported investigations on Ni electrodeposits have been performed on films made using high current densities in the range of 5–40 mA cm⁻² [2,3,9] or higher [1]. However a higher current density can be detrimental for the mechanical properties of the thick deposits due to structural changes occurring in the film, deformation of the tools [6], as well as residual stresses developed during the processing operations [5,10]. On the other hand, lower deposition rates (current density) are expected to produce deposits with improved mechanical properties along with lower tensile stresses for films thicker than 1 μm [3,11]. As such lower current densities are often used in the electroplating industry in order to produce stress-free deposits, although such a practice is detrimental to the production speed. The focus of the current paper is to verify the relationship between residual stress and current density using Ni electrodeposits over a range of thicknesses (18–90 μm) made using unusually low current densities (1.5–5 mA cm⁻²).

Both grain geometry and grain size, as well as the crystallographic texture of electrodeposited Ni microstructures, are known to depend strongly on the plating conditions [2]. Thick Ni electrodeposits plated at lower current densities (3–15 mA cm⁻²) have been reported to have a characteristic columnar microstructure where the grains often extend through the thickness of the deposit, with the grain size increasing with increasing current densities [9,12]. The surface morphologies of the deposits have also been shown to change from a ‘cauliflower’ to a ‘truncated pyramidal’ structure with increase (>10 mA cm⁻²) in current densities [13,14]. The crystallographic texture for thick (~microns) Ni electrodeposits is known to be independent of the substrate material; instead it is found to depend strongly on the current density, pH, and presence of organic additives.
in the electroplating solution. Two general textures have been reported for electrodeposited Ni: a strong <100> texture caused by a regime of free growth at higher current densities (≥ 10 mA cm⁻²), and a <110> texture at lower current densities (≤ 5 mA cm⁻²) where Ni growth is inhibited due to impurities and/or hydrogen adsorption on the plating surface [3,9]. Indentation hardness values for electrodeposited Ni are also generally found to decrease with increasing current densities [2,3].

The highly textured-oriented grain morphology in electrodeposited Ni suggests a significant anisotropy in the mechanical response of this material, which needs to be considered in detail [15–17]. Indeed, a significant range of mechanical properties have been reported in literature for electrodeposited Ni [2,3,12,16], which could have been caused in part by simply averaging the response from different locations of the polycrystalline sample without accounting for their underlying orientations. It is now possible to measure the local lattice orientation in polycrystalline samples using a technique called Orientation Imaging Microscopy (OIM) [18,19], which is based on automated indexing of back-scattered electron diffraction (EBSD) patterns (obtained using a scanning electron microscope) and has a spatial resolution of less than a micron. Therefore, a judicious coupling the structure information obtained from OIM with the mechanical data obtained at the same length scale (using nanoindentation) could provide interesting insights about the anisotropic mechanical response of the local Ni film structure.

The present work is an experimental study on the residual stresses, and the resulting structural and mechanical changes, occurring in nickel electrodeposits produced using very low current densities. We utilize the combined capabilities of profilometry, nanoindentation and EBSD to study the anisotropic microstructure–property relationships in electrodeposited nickel in light of the above observations.

2. Experimental techniques

2.1. Materials and processing

Microcrystalline nickel electrodeposits were produced by direct current (DC) plating in a nickel sulfate electrolyte with 1.5 g/L of nickel chloride, 1.5 mL/L of wetting agent and 35 g/L of boric acid. Three current densities were chosen in order to study their effect on residual stresses developed in electrodeposited Ni: 1.5, 2.5 and 5.0 mA cm⁻². Note that these current densities are lower than the typical range (5–40 mA cm⁻²) generally studied in literature [2,3,9]. The electrodeposition was conducted at 30 ± 1 °C without stirring and at a pH of 3.5. Nickel balls in a plastic basket were used as anode.

The substrate was an aluminium alloy 2017 (1 mm thick plates with a typical range (5–10 mA cm⁻²) generally studied in literature [2,3,9]. The electrodeposition was conducted at 30 ± 1 °C without stirring and at a pH of 3.5. Nickel balls in a plastic basket were used as anode.

A detailed study of the microstructure–property correlations in the Ni deposits was carried out on the largest nominal thicknesses of the deposits (90 μm), chosen for the ease of their surface preparation. For these tests, the samples were cut into ten pieces of 1.8 cm² with a circular saw, and the center pieces were chosen for further analysis. After the cutting, the samples were cleaned ultrasonically by a three-step cleaning process using acetone, ethanol and water. They were polished to a high surface finish (0.25 μm diamond suspension) and subsequently subjected to lapping for 5 minutes using an alkaline colloidal silica suspension. Finally the samples were polished with Ar ions at 4 kV and 2.5 mA for 1 hour (angle of incidence 5°) using a Baltec RES 010 device.

The EBSD patterns were obtained using 20 kV acceleration voltage at 15 mm working distance and 69 μA beam current with a 70° sample tilt. Orientation maps were collected using a hexagonal grid of points with a step size of 150 nm and typical collection speed of 18.5 patterns per second. The patterns were collected, indexed and analyzed with the commercial EDAX/TSL software OIM™ 5.2. Since this technique of automatic pattern indexing probes only the very top layer of the sample, orientation maps were collected on the deposits' top surfaces, as well as along their cross-sections, in order to evaluate their structure both normal and parallel to the growth direction, respectively. Grain sizes along both these directions were calculated using the orientation maps [21].

2.2. Mechanical measurements

Nanoindentation studies were carried out on the top surface of the deposits in order to correlate the structure information obtained from OIM-EBSD with the mechanical properties of the deposits. All tests were performed using a nanoindenter (MTS XP® System) with a Berkovich diamond indenter tip under load control to peak displacements of 2000 nm at 50 nm/s loading/unloading rate with a 10 s hold before unloading in all samples. At least 10 tests were carried out for each sample. Since this indentation depth is significantly lower than the thickness of the deposits, the mechanical data obtained from nanoindentation can be taken to be representative of the properties of the deposits without any substrate influence. The modulus and hardness of the deposits were obtained from the nanoindentation load–displacement curves by analyzing the initial (50%) unloading segment using the Oliver and Pharr method [22]. The projected contact area for indentation was obtained by calibration on fused silica, in order to account for deviations from non-ideal indenter geometry.

Note that the Oliver and Pharr method is largely based on Hertz's theory [23,24], and as such addresses only the elastic indentation of an isotropic sample [25]. However, in practice, the elastic response of the sample at the typical length scale of nanoindentation is often inherently anisotropic [26], especially in polycrystalline metals such as Ni where the indents are comparable to or smaller than the typical grain size. In order to analyze the elastic indentation of anisotropic samples, the treatment suggested by Vlassak and Nix [27–30] was used in this work. These authors suggest that a modified Hertz theory can be used for elastic indentation of cubic crystals, provided an anisotropy parameter, β, is appropriately introduced into the definition of the effective indentation modulus as given below:

$$E_{eff} = \frac{1}{\beta} \left( \frac{1 - \nu_{sample}^2}{E_{sample}} + \frac{1 - \nu_{indenter}^2}{E_{indenter}} \right)$$

where $E_{eff}$ denotes the effective Young's modulus of the indenter and the specimen system, $E_{sample}$ and $\nu_{sample} = 0.31$ [31–33]) denote the effective values of Young's modulus and Poisson’s ratio, respectively, for a randomly textured polycrystalline aggregate of crystals with the same elastic properties as the single-crystal being studied [28,29], and $\nu_{indenter} = 0.07$ and $E_{indenter} = 1411$ GPa denote the Poisson's ratio and the Young's modulus for the indenter material (diamond). For cubic crystals, the value of β depends strongly on the crystal lattice orientation and the degree of cubic elastic anisotropy. The elastic anisotropy (A) of a cubic crystal is usually defined as $A = 2C_{44}/(C_{11} - C_{12})$, where $C_{11}$, $C_{12}$, and $C_{44}$ denote the cubic elastic constants used to define the crystal elastic stiffness in its own reference frame. Based on the values reported
by Vlassak and Nix [28,29], \( \beta \) should range from 0.9 to 1.05 (a range of \(-15\%\)) for Ni crystals (for which \( A = 2.45 \) [31,32]) of different orientations. Note that this range is around 10% if the orientations vary only from \( (100) \) to \( (101) \). In this work, the modulus values for our electro-deposit samples \( (E_{\text{sample}}) \) were corrected for anisotropy using the values of \( \beta \) as reported in [28,29].

During electrodeposition metal thin films typically grow under non-equilibrium conditions, which often result in internal (or residual) stresses even in the absence of any external force or temperature gradient [34]. The Stoney equation [35], or one of its variants, is typically used to experimentally determine such stresses present in a thin film. However, the inherent assumptions of the Stoney formula – such as a negligible thickness of the film as compared to the substrate and the lateral dimensions – are not applicable for the thick films developed in this work. Here we have used a modified version of the Stoney equation, shown by Clyne [36,37], to relate the measured curvature to the stress in our thick films, as shown below:

\[
\sigma^R = M_{lf} \frac{E_f^2 t_f^4 + 4E_f E_s t_f^2 t_s + 6E_f E_s t_f^2 t_s^2 + 4E_f E_s t_f t_s^3 + E_s^2 t_s^4}{6E_f E_s (t_s + t_f) t_f t_s} \quad (2)
\]

Here, \( M_f = E_f/(1 - \nu_f) \) is the effective biaxial modulus of the film, \( \kappa = 1/R - 1/R_0 \) is the curvature, \( R_0 \) and \( R \) are respectively the sample curvatures before and after electrodeposition, \( \nu \), \( E \) and \( t \) are the Poisson’s ratio, Young’s modulus and thickness, and the subscripts \( s \) and \( f \) refer to the substrate (aluminium alloy 2017) and the film, respectively. The Young’s moduli of the Ni films and the Al alloy substrate were measured by indentation \( (E_{\text{sample}}) \) using Eq. (1) as described above. The indentation modulus for the Al alloy substrate was measured to be 79 GPa, which is close to the reported modulus value for this alloy (73.2 GPa [38]). A value of 0.31 was used for the Poisson’s ratio \( (\nu_s) \) of the film [31–33]. The sample curvatures were determined using a white light surface profilometer ALTISURF 500 with a 3 cm distance between sample and light spot, both before and after electrodeposition. The substrate thickness was 1000 ± 1 \( \mu \)m in all cases.

3. Results

3.1. Grain morphology

SEM images of the 69 \( \mu \)m thick deposit surfaces (Fig. 1) show that an increase in the current density from 1.5 to 5 mA cm\(^{-2}\) induces a change in the grain morphology of the Ni electrodeposits. Ni deposited at the lowest current density of 1.5 mA cm\(^{-2}\) (Fig. 1a) appears to have a “cauliflower” [14] or “colony” [13] structure, with deep crevices outlining groups of smaller substructures. Increasing the current density causes the morphology to slowly change to a “truncated pyramidal type” structure [13,14] (Fig. 1b and c). The sizes of the surface structures are also seen to increase with increasing current density.

A change in the current density is also seen to greatly influence the cross-sectional grain morphology, as seen from Fig. 2 for the 90 \( \mu \)m thick deposits. The EBSD maps of the specimen and the cross-section in this figure show that the structure of the deposits evolves into a more columnar structure at higher current densities. At the highest current density of 5 mA cm\(^{-2}\), some grains can be seen to extend almost through the thickness of the deposit. There is also an increase in the grain size as the current density increases from 1.5 to 5 mA cm\(^{-2}\). Both these effects are summarized by the grain size measurements normal and parallel to the plating/growth direction in Table 1.

The structure-property correlations from the OIM-EBSD and nanoindentation studies are summarized in Fig. 2 and Table 1 for the 90 \( \mu \)m thick deposits. In Fig. 2, the grain orientations are color-coded to reflect their positions in the inverse pole figure map. Thus, the grains that have a \( (001) \) crystallographic plane parallel to the sample surface are colored red. Note that since Ni is cubic, this also means that the grains colored red have a \( <001> \) crystallographic
direction parallel to the sample normal direction (ND; also the indentation direction). Similarly, grains with {101} and {111} planes parallel to the surface are colored green and blue respectively. The crystallographic textures within the cross sections of the deposits are shown in inverse pole figure (IPF) density distributions, obtained by a Gaussian convolution with a half width of 5° within the harmonic calculus (bin size 5°) [19]. In the IPF density distribution maps, the IPF for a random standard sample is designated as ‘×1’ of all points. Thus, all points marked ‘×4’ indicate an IPF density of four times random.

It can be seen from Fig. 2 that the current density has a marked effect on both the grain orientation as well as the grain morphology. At the lowest current density (1.5 mA cm\(^{-2}\)) the texture is dominated by the {101} orientation along the plating direction, which slowly changes to favor the {100} planes at the higher (5 mA cm\(^{-2}\)) current density. The {101} texture is still dominant at the intermediate current density level (2.5 mA cm\(^{-2}\)), but small regions with {100} grains can also be seen here.

### 3.3. Nanoindentation modulus and hardness

Current density also has a significant influence on the hardness and modulus values of the deposits, as measured by nanoindentation using the Oliver and Pharr method [22]. As seen from Table 1 for the 90 μm thick deposits, the hardness of the deposits slowly decreases from 3.46 to 2.49 GPa with increasing current density. A similar trend is seen for the modulus measurements, where the average effective modulus

<table>
<thead>
<tr>
<th>Current Density</th>
<th>1.5 mA cm(^{-2})</th>
<th>2.5 mA cm(^{-2})</th>
<th>5.0 mA cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual stress</td>
<td>74.5 MPa</td>
<td>83.2 MPa</td>
<td>94.1 MPa</td>
</tr>
<tr>
<td>Hardness</td>
<td>3.46 GPa</td>
<td>2.74 GPa</td>
<td>2.49 GPa</td>
</tr>
<tr>
<td>Grain size (surface)</td>
<td>0.8 ± 0.4 μm</td>
<td>1.1 ± 0.8 μm</td>
<td>1.8 ± 1.5 μm</td>
</tr>
<tr>
<td>Grain size (parallel to growth direction)</td>
<td>1.5 ± 1.4 μm</td>
<td>2.0 ± 2.3 μm</td>
<td>3.9 ± 6.1 μm</td>
</tr>
<tr>
<td>Effective modulus ((E_{\text{eff}}))</td>
<td>186.3 ± 15 GPa</td>
<td>179.5 ± 9 GPa</td>
<td>176.2 ± 14 GPa</td>
</tr>
<tr>
<td>Sample modulus ((E_{\text{sample}}))</td>
<td>214.5 ± 14 GPa</td>
<td>213.9 ± 9 GPa</td>
<td>213.9 ± 14 GPa</td>
</tr>
</tbody>
</table>

Fig. 2. (Color online) Texture and grain morphology of the (a) sample surface and (b) sample cross-section for the 90 μm thick Ni deposits at three different current densities. The grain orientations in the OIM-EBSD maps have been color-coded to reflect their positions in the inverse pole figure (IPF) map. The orientation density IPF contour maps in the bottom represent the densities of various orientations as compared to a standard sample of random orientation (the orientation density for a random orientation is equal to 1).

Table 1

Summary of the microstructure–property correlations for the 90 μm thick Ni deposits at three different current densities. The residual stresses were calculated using Eq. (2), while the grain sizes were calculated from the OIM-EBSD maps (Fig 2). Since the grain size distributions are skewed towards the smaller grains in all of the samples, the standard deviations in grain size measurements are relatively large. The hardness and effective modulus values (\(E_{\text{eff}}\)) were calculated from nanoindentation [22]. The values for sample modulus (\(E_{\text{sample}}\)) were corrected for the anisotropy parameter \(\beta\) using Eq. (1).
modulus ($E_{\text{eff}}$) is seen to decrease from 186.3 to 176.2 GPa, with increasing current density. However, this difference disappears when the sample modulus ($E_{\text{sample}}$) is corrected for the anisotropy parameter $\beta$ using Eq. (1). After this correction the sample modulus values were measured to be consistently around 214 GPa, which is comparable to the modulus value of 219.6 GPa for randomly textured polycrystalline Ni [33]. For calculating the values of $E_{\text{sample}}$ using Eq. (1), the following values for $\beta$ were used [28,29], $\beta = 0.95, 0.91$ and 0.89 for $E_{\text{eff}} = 186.3, 179.5$ and 176.2 GPa, corresponding to the three current densities of 1.5, 2.5 and 5.0 mA cm$^{-2}$ respectively.

### 3.4. Residual stress vs. current density

Table 2 shows the evolution of residual stress, calculated using Eq. (2) as a function of the current density. All residual stress values were in the range of 74.5 to 135.7 MPa. The thicker deposits (90 μm thickness) were seen to have lower values of residual stress, while the values were the highest at 5 mA cm$^{-2}$ for the 18 μm thick deposit. Two trends are evident from this table. Firstly, the residual stresses are seen to decrease with increasing film thickness – except for the lowest current density of 1.5 mA cm$^{-2}$, where all three thicknesses have similar stress values. And secondly, an increase in current density is seen to induce a steady increase in internal stress of the deposit.

Note that the modulus values for the deposits ($E_i$) and substrate ($E_s$) used in the calculation of residual stresses in Eq. (2) were obtained using the indentation results ($E_{\text{sample}}$) described in Eq. (1). As described in Section 3.3, these values of $E_{\text{sample}}$ have been corrected for anisotropy, and as such are comparable to the modulus for randomly textured polycrystalline Ni.

A more accurate calculation of the residual stresses is also possible if one uses the effective biaxial modulus ($M_f$) of the deposit for a given texture. For example, for the (100) texture (such as the one shown in Fig. 2 for the 5.0 mA cm$^{-2}$ current density), $M_f = 209.6$ GPa [39] using literature values for elastic constants of Ni [33], while for the (110) surface the effective biaxial modulus is very close to the random polycrystalline average [28,29]. However since the texture measurements (which require significant experimental resources and machine time) were carried out for only the largest nominal deposit thicknesses (90 μm), it was not possible to calculate the effective biaxial modulus for all of the textures developed in this work. Instead the $E_{\text{sample}}$ values obtained from indentation experiments were used in Eq. (2) for residual stress calculations. This approximation is not expected to change the main findings of this paper.

### 4. Discussion

#### 4.1. Crystallographic texture and morphology of electrodeposited Ni

Although deposited at much lower current densities, the morphology and texture of the electrodeposited Ni films shown in this work share similar features to the Ni films described in literature produced using higher current densities. The change in the surface morphologies of Ni deposits, from a ‘cauliflower’ (or ‘colony’) to a ‘truncated pyramidal’ structure, with increase in current density is well documented in literature [13,14]. Foreign ions, incorporated during the deposition process, is thought to block the emerging screw dislocations (which are associated with pyramidal growth), resulting in the truncated structures on the surface. Thus, a higher incorporation of foreign ions into the deposit leads to a decrease in size and eventual disappearance of the pyramids at lower current densities [13]. It is interesting to note here that the transition from the ‘cauliflower’ to a ‘truncated pyramidal’ structure is happening at a much lower current density of 5 mA cm$^{-2}$ for the 69 μm thick deposits shown in Fig. 1, as compared to 10 mA cm$^{-2}$ [13] and 30 mA cm$^{-2}$ [14] for –100 μm thick deposits reported in literature – a likely consequence of the difference in purity of the sulphamate bath solutions used in these studies.

The crystallographic texture of thick Ni deposits, such as the ones studied in this work, is also known to be related to the grain growth in these films, which in turn is controlled by the electric field defined by the plating process [40–42]. Thus at lower current densities the appearance of a fine grained (101) texture is typically associated with ‘inhibited’ growth and deposition processes at these conditions, with the growth mode transitioning to ‘uninhibited’ or ‘free’ growth characterized by coarser (100) grains at higher deposition rates (current densities) [3,4,9]. This transition is clearly visible in Fig. 2. Thus, once grains with the favored (100) orientation have occluded majority of the other grains, columnar grain structures with almost parallel boundaries [40] are produced, such as the ones seen in the OIM cross-section map in Fig. 2 at the highest current density of 5 mA cm$^{-2}$. These results agree well with those of Marquis et al. [9], where a similar transition from (101) to (100) texture, along with a more columnar grain morphology, were observed at 10 mA cm$^{-2}$ current density for 10 μm thick Ni electrodeposits.

#### 4.2. Microstructure–property relationships

The grain morphology and texture of the Ni electrodeposits strongly influences their mechanical response during indentation, as shown in Fig. 2 and Table 1. Thus an increase in the grain size observed with increasing current density directly corresponds to a decreasing trend in hardnes values, which is a predictable result given the well known grain boundary strengthening considerations (such as the Hall-Petch effect [13,43,44]). Similarly, since the (100) grains have the lowest modulus values for Ni [28,32], the decrease in the effective modulus ($E_{\text{eff}}$) with increasing current density is also a direct consequence of the change in the grain orientation from (101) to (100). This underlines the importance of correcting the sample modulus $E_{\text{sample}}$ values for the anisotropy parameter $\beta$, as defined in Eq. (1); otherwise the range of the modulus values can be misinterpreted as a larger standard deviation or porosity-related changes in the results. As seen from Table 1, once this correction is introduced, the modulus values correspond well to those of polycrystalline Ni.

Interestingly enough, the spread (standard deviation) in the $E_{\text{eff}}$ modulus measurements for each current density is also around 10% of the average (Table 1), which is close to the standard deviation expected from Vlassak and Nix’s model (~10% based on the difference in indentation modulus between the (100) and (101) orientations). This may imply that the Berkovich indenter is probing regions of varying texture each time, such that spread is close to the spread expected if the indents were evenly distributed between the (100) and (101) orientations. However one needs to carefully correlate each indent to its underlying microstructure before arriving at any concrete conclusions regarding these correlations. Here we merely point out the similarity between our experiment and the model developed by Vlassak and Nix – a more careful study is currently underway to better

### Table 2

<table>
<thead>
<tr>
<th>Deposit thickness (μm)</th>
<th>Current density (mA cm$^{-2}$)</th>
<th>Residual stress (MPa)</th>
<th>Curvature (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>1.5</td>
<td>76.5</td>
<td>0.058 ± 0.014</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>131.1</td>
<td>0.192 ± 0.004</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>135.7</td>
<td>0.187 ± 0.024</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>89.7</td>
<td>0.103 ± 0.005</td>
</tr>
<tr>
<td>69</td>
<td>2.5</td>
<td>90.3</td>
<td>0.192 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>129.6</td>
<td>0.199 ± 0.037</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>74.5</td>
<td>0.114 ± 0.018</td>
</tr>
<tr>
<td>90</td>
<td>2.5</td>
<td>63.2</td>
<td>0.263 ± 0.022</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>94.1</td>
<td>0.221 ± 0.044</td>
</tr>
</tbody>
</table>
understand the influence of the nanoindentation modulus and β to the exact grain orientation under the indenter.

The indentation modulus values shown in Table 1 compare well to the values reported in literature using other test methods on Ni deposits. For example, a macroscopic sample modulus of 169–179 GPa using axial loading for films deposited at 26.8 μm cm\(^{-2}\) has been reported in [45]. As discussed earlier, at these high current densities the Ni film is expected to have a predominantly (100) orientation, and as such these values correspond well to the effective orientation, and as such these values correspond well to the effective modulus value of \(E_{\text{eff}} = 176.2 \pm 14\) GPa (Table 1) for the (100) oriented 90 μm thick Ni film deposited at 5 μm cm\(^{-2}\). On the other hand, the hardness (~3.46 GPa) of the 90 μm Ni films deposited at the lowest current density of 1.5 μm cm\(^{-2}\), is consistently higher than the values reported in literature for Ni electrodeposits prepared in similar sulfamate electrolytes but at higher current densities (for example, a Vickers hardness, HV, of 2.3 GPa for 70 μm thick Ni deposits produced at 20 mA cm\(^{-2}\) [46], HV = 1.8–2.7 GPa for 30–35 μm thick deposits produced at 18 mA cm\(^{-2}\) [47], HV = 2 GPa for 100 μm thick deposits produced at 10–200 mA cm\(^{-2}\) [14], HV = 2.25 GPa for >100 μm thick deposits produced at 20 μm cm\(^{-2}\) [3]). This is thought to be a direct consequence of the low grain sizes (~0.8 μm) occurring in the Ni films produced at the unusually low current densities used in this work (as compared to larger grain sizes of ~1.8 μm reported in [46] for Ni deposits produced at 20 μm cm\(^{-2}\)), and the resultant grain boundary strengthening considerations. As such, our results agree well with the Hall-Petch type relationship shown by Banovic et al. [13], where a similar high value (~3 GPa) of Knoop hardness was noted for the transition of thick Ni films to that of the (100) orientation. Thus, the following main trends can be summarized from Table 2 – for a constant film thickness lower residual stress values are obtained for deposits produced at the lower current density (1.5 mA cm\(^{-2}\)), while at a particular current density the thickest film (90 μm) has the lowest stress.

4.3. Use of low current densities during electrodeposition of Ni

For the electroplating industry, change in current density is generally regarded as the most relevant control parameter for electrodeposition, since it determines the process time and the consumed energy. Since the internal stresses in thick (~microns) deposits are known to decrease with decreasing current densities [11], use of very low current densities can be of potential advantage for producing negligible stress values. However, the current work demonstrates that the range in the values of residual stresses (74.5 to 135.7 MPa, Table 2) produced here using unusually low current densities (1.5–5 mA cm\(^{-2}\)) are well within the range of reported literature values of internal stresses for Ni electrodeposits produced from similar sulfamate bath compositions (20–90 MPa at 5–25 mA cm\(^{-2}\) for 1 μm thick Ni deposits [48], ~100 MPa at 50 mA cm\(^{-2}\) for 63–76 μm thick Ni deposits [5], 200–250 MPa at 20 mA cm\(^{-2}\) for 3 μm thick Ni deposits [52], 150 to 200 MPa at 180 mA cm\(^{-2}\) for 20 μm thick Ni deposits [53,54]). As such, the use of very low current densities for electrodeposition of thick Ni films is not expected to be of any significant advantage in producing low stress deposits – in fact they may prove detrimental to the productivity/output speed for the industry.

5. Conclusions

In summary, this work demonstrates the feasibility of producing thick Ni electrodeposits from Ni sulfamate baths using a lower range of current densities than typically used in literature. Even at the unusually low current densities used in this work the mechanical properties of the electrodeposits are seen to correlate strongly with the grain morphology and texture of the Ni films. In particular, accounting for the film texture allowed a more accurate calculation of the Young’s modulus and the residual stresses developed in the films. The higher hardness of the Ni films plated at the lower current densities, along with low residual stress values for the larger film thicknesses makes them an attractive option for the electroforming of nickel–diamond composites used in high-precision grinding or cutting tools where thicker deposits are desired. However, the residual stress values obtained using such low current densities were found to be comparable to literature values of deposits plated at higher current densities; thus effectively ruling out the attractiveness of employing very low current densities for producing thick stress-free precise parts using electrodeposition.

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