

Effect of deposition parameters on microstructure of electrodeposited nickel thin films

Amaresh Chandra Mishra · Awalendra K. Thakur · V. Srinivas

Received: 31 October 2008 / Accepted: 7 April 2009 / Published online: 28 April 2009
© Springer Science+Business Media, LLC 2009

Abstract Nickel thin films were prepared using electro-deposition process on a copper substrate. The effect of deposition parameters on film microstructure has been investigated with and without an organic additive (saccharin). Electrodeposition has been carried out using direct current electrodeposition (DCED) method and pulsed electrodeposition (PED) method. Significant reduction in crystallite size has been observed with the increase in saccharin concentration (~ 10 g/L) irrespective of the electrodeposition method. In PED, it has been observed that an increase in pulse width causes a drastic reduction in crystallite dimension (~ 15 nm) of the deposited Ni-film. Further PED process yielded needle-shaped Ni grains under controlled process conditions unlike in DCED, where spherical grain structure was observed in the micrographs. However, these needle-shaped grains change their microstructure on addition of saccharin to the bath. A phenomenological model is presented to explain the observed microstructural changes.

Introduction

Nanostructured materials are considered to be of great importance for industrial application in view of their enhanced physical property and chemical stability. Nanostructured nickel is one such example which is used as a coating material on metal and metal alloys to enhance their corrosion resistance which have substantial importance in

engineering application [1, 2]. Technological developments in recent years such as MEMS and actuators require soft magnetic films that can exhibit optimal performance under external applied magnetic field [3–6]. Again nickel and nickel-based alloys are obvious choices for such application. Further, in nanostructured (both in powder and thin film) form, the performance of nickel and nickel-based alloys may be expected to enhance. A variety of methods for preparation of nanostructured materials have been developed, and preparation conditions have been optimized ever since the introduction of nanostructured materials by Gleiter [7] Granqvist and Buhrman [8], and these methods are either physical [ball milling (BM), thermal evaporation, inert gas condensation] or by chemical routes (chemical reduction, sol–gel method). BM technique produces nanostructured material with large size and shape variations in the particles that depend on a number of factors of which the ratio between the weight of ball and material plays a crucial role. This also results in large impurity content. On the other hand, particles produced with inert gas condensation method have a uniform distribution in shape and size that in turn depend on deposition parameters, which is very difficult to control. Practical applications require a methodology which is simple, cost effective with a better control on the quality and thickness of the film under deposition. Electrodeposition method of thin film preparation is one such versatile technique for producing nanostructured films where a meticulous control on the film quality and properties can be implemented with ease by means of an external control over input deposition current and time [9]. However, there is an essential prerequisite that the substrate for electrodeposition must be a conductive one [10].

Recently, Natter et.al. have reported nanostructured metallic thin films of palladium, i.e., n-Pd [11] and copper,

A. C. Mishra · A. K. Thakur (✉) · V. Srinivas
Department of Physics & Meteorology, Indian Institute of Technology, Kharagpur 721302, India
e-mail: akt@phy.iitkgp.ernet.in

i.e., n-Cu [12] prepared by electrodeposition. Electrodeposition of Ni has been reported both through direct d.c. [13–17] and pulse [18] methods of deposition and studied extensively. Literature reveals that in direct current electrodeposition (DCED), an increase in current density leads to a corresponding increase in grain size, the cause being attributed to the evolution of more hydrogen at the cathode interface. A modification of the growth interface by hydrogen changes the surface energy and growth mechanisms which in turn facilitate the formation of larger grain size [15, 19]. Effect of external parameters such as the magnetic field on electrodeposited nickel film indicates that the deposition rate of Ni gets enhanced due to magnetic field-induced convection which in turn assists fine grain growth [20]. On the other hand, in the case of pulsed electrodeposition (PED) process, it has been observed that increment of peak current density of the pulse results in a finer grain size of the film with an improved homogeneity in microstructure [21]. The added advantage in PED is that it enables us to achieve a better control on microstructure by the tunability of ‘off time’ keeping ‘on time’ fixed, whereas a variation of ‘on time’ keeping ‘off time’ fixed has no significant effect [22].

However, the effect of simultaneous variation of ‘on’ and ‘off’ times on microstructure of PED nickel film is yet to be studied and reported. In addition, the microstructure of electrodeposited nickel films (metal films in general) can also be controlled at a desirable level by the use of an appropriate organic additives such as aromatic compounds comprising of unsaturated groups (i.e. $>C=O$, $>C=S$, $-C=N$, etc.), known commonly as brighteners [23–31]. These organic compounds used in small concentration in metal plating baths reduce the grain size and relieve the strains present in the film [32]. Strain dependence of creep rate of electrodeposited nanocrystalline nickel thin films has already been studied [33]. Although, a change in microstructure of the metallic films depending on the concentration of the organic additives has been observed experimentally, its influence on the mechanism of electrodeposition is not yet clearly understood. Further, there has been no systematic investigation on the effect of deposition parameters on the quality of deposited thin film to arrive at a correlation of the parameters with the film microstructure.

In this report, we have made a systematic study on the effect of deposition parameters on the microstructure of electrodeposited nickel thin films on copper substrates prepared through both the DCED and PED. The effects of the concentration variation of an organic additive (saccharin) on the correlation of the deposition parameters and the film microstructure of the sample developed both the DCED and PED methods have been analyzed. Our results indicate significant changes in microstructure when the process parameters are tuned. A mechanism on the role of

the organic additive on changes in the film microstructure has been proposed.

Experimental details

Thin nickel films were electrodeposited on foil-type copper electrode (cathode) (area $1.5\text{ cm} \times 1.5\text{ cm}$ and thickness $80\text{ }\mu\text{m}$). It was pretreated with dilute nitric acid (acid to water ratio 1:5) followed by a wash under a jet of distilled water. A Ni plate of 99.9% purity (Aldrich) was used as the counter electrode. All the applied potential was measured with respect to an Ag/AgCl reference electrode provided by CH instruments, USA. The solution used for electrodeposition was a standard Watt’s bath [34] comprising of nickel sulfate, nickel chloride, and boric acid in the volumetric ratio of 300, 45, 45 g/L, respectively. The solution mixture was stirred for 10 min and kept for 2 h prior to the start of electrodeposition process. The pH value of the homogeneous precursor solution was adjusted to be 3.0 using sulfuric acid. Two different sets of samples with and without saccharin additive into the Watt’s bath were electrodeposited under ambient conditions through the processes of (1) DCED and (2) PED.

Direct current electrodeposition

In this method, deposition of Ni film on Cu substrate was carried out by applying a constant potential (-1.5 V) throughout the deposition process. Corresponding current was approximately 6 mA. One set of Ni samples was prepared with varying deposition times of 20, 30, 40, and 60 min, in order to study the effect of deposition on the microstructure. Another set of samples were prepared with a fixed deposition time of 20 min but by varying the sodium saccharin additive concentration (0, 0.3, 3, 6, 10 g/L) to electrolytic bath solution.

Pulsed electrodeposition

In PED, applied potential was rectangular pulses with equal on and off time. During the on time a constant potential of -2 V is applied to cathode and during off time no potential is applied. Sum of on and off time is referred as time period of pulse. The corresponding peak current during on time was ($\sim 400\text{ mA}$). The time period ($t_{\text{on}} + t_{\text{off}}$) of the pulse in PED was varied from 10 to 200 ms with total number of steps for each deposition, so adjusted that total on time (i.e., deposition time) remains the same (60 s) for all cases irrespective of the pulse width (10–200 ms). This ensures that total mass of the deposited nickel on substrate remains constant. In PED mode, different concentrations of sodium saccharin (same as in the DCED mode) were added for

depositing the samples with a time period (of pulse) of 200 ms only.

The X-ray diffraction (XRD) patterns of the films were obtained using Philips X'pert X-ray diffractometer (Model No.1710) at a scan rate of 1°/min with CuK α radiation. The full-width at half-maxima (FWHM) of the diffraction peaks were estimated by pseudo-Voigt profile fitting using Peakfit software provided by Jandel Scientific. Grain size of the deposits was calculated from the (111) diffraction peak broadening after subtracting the instrumental line broadening (estimated using Si single crystal data as the standard), using the Scherrer equation [35],

$$D = \frac{0.9\lambda}{\beta \cos \theta},$$

where λ is wavelength of X-ray used for diffraction, β is the FWHM of the XRD (111) peak, and θ is the Bragg's angle.

The microstructure of the electrodeposited thin film samples prepared under varying conditions was studied with scanning electron microscope (SEM) model-CAM-SCAN-2 (JEOL) with an operating voltage of 20 kV. High-resolution images were recorded with field electron SEM (FESEM) instrument provided by Carl Zeiss SMT Ltd., Germany, which is operated at 5 kV.

The grain size distribution can be determined by transmission electron microscopy (TEM) as the use of XRD, may lead to an underestimation of the average grain size [36]. But a disadvantage of TEM is the difficult sample preparation (sample thickness ≤ 100 nm), because the different preparation methods can modify the microstructure of the samples; textures can be initiated by cutting, and thinning by Ar ions can initiate crystal defects and grain growth. TEM measures the bulk grain size distribution, whereas SEM is a surface sensitive technique without any complicated sample preparation. The main problem of microscopic techniques is the resolution of single grain because the crystallites are often overlapped [12]. So we have used XRD for the crystallite size determination and SEM for the surface particle size (grain size) determination [37].

Results

As discussed earlier, electrodeposition has been carried out by two different methods, namely DCED and PED. The effect of these methods on microstructure of nickel films has been discussed separately in this section.

Direct current electrodeposition

The electrodeposition of nickel films has been carried out by varying the deposition time duration and additive

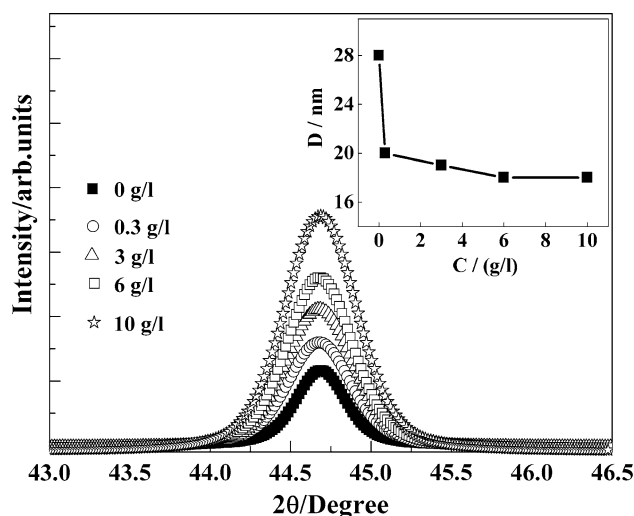
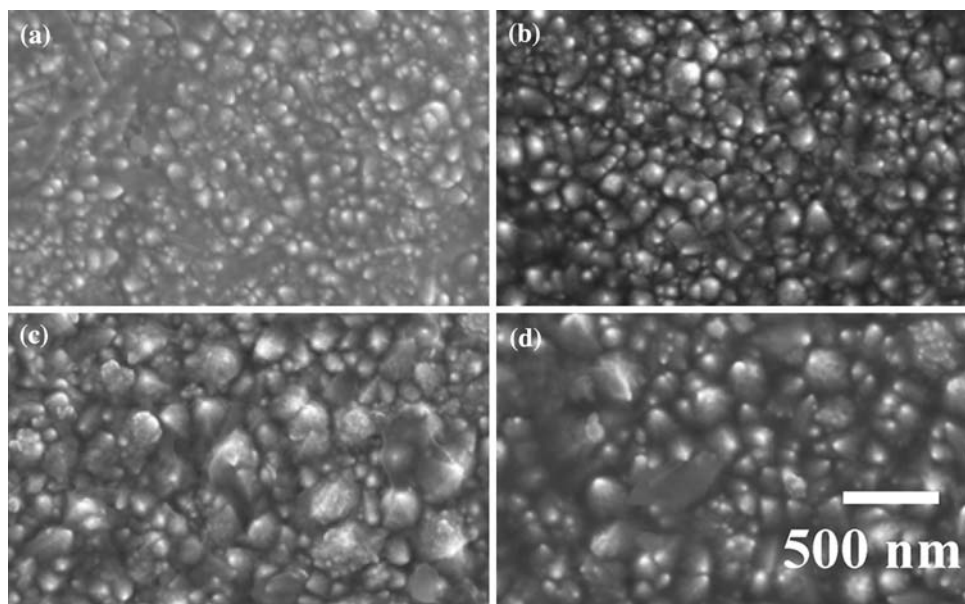


Fig. 1 XRD Ni [111] peaks of DC electrodeposited films for different saccharin concentrations. Variation of crystallite size D as a function of saccharin concentration C is presented in the inset

concentration. The gross features, such as surface microstructure and crystallite size, obtained from the XRD peaks are observed to be same even if the deposition was carried out for prolonged periods of 60 min. As shown in Fig. 1, appreciable Ni (111) XRD peak broadening has been observed with increase in saccharin concentration (C) in the bath. This change in the peak width manifests its impact on a corresponding change in the crystallite dimension (D) of the deposited Ni films as plotted in inset of Fig. 1 for DC electrodeposited films with and without sodium saccharin. The experimental values suggest that crystallite size remains fairly constant irrespective of the deposition time in direct current deposition (~ 25 nm). However, addition of saccharin to the bath causes substantial decrease in the crystallite size of Ni to the tune of 35% at a saccharin concentration of 10 g/L. The crystallite size reduction was observed to be significant (25%) even at low concentration (0.3 g/L) of saccharin. This is not surprising since typical Ni Watt's bath contain nominally 1 g/L of saccharin [38].

In Fig. 2, the microstructure of DCED nickel film is shown in FESEM micrographs for the deposition time of 20 and 60 min without any saccharin in the deposition bath. The grains seem to increase with deposition time which can be attributed to the agglomeration of crystallites as more deposition takes place. However, addition of sodium saccharin under similar condition of electrodeposition (deposition time = 20 min) has resulted in substantial modification of microstructure of the films as revealed in SEM micrographs (Fig. 3). The micrographs show spherical and more ordered grains on addition of various concentration of saccharin when compared to micrograph obtained for the case without saccharin additive in deposition bath.

Fig. 2 FESEM images of DC electrodeposited samples for **a** 20, **b** 30, **c** 40, and **d** 60 min from 0 g/L saccharin solution



The striking microstructural changes on addition of saccharin (10 g/L) clearly resolved in FESEM images as shown in Fig. 4. From the micrographs of sample prepared without saccharin additive, it is observed that there is a grain size distribution, whose average size is about 100 nm, while the samples obtained after saccharin addition shows a significant increase in the grain size (800 nm).

Pulsed electrodeposition

Current versus time graph is shown in Fig. 5 for the pulsed deposited samples for different time periods. The films were not allowed to relax between pulses completely. Clarity of this aspect can be noticed from Fig. 5. XRD pattern of Ni (111) peak broadening is given with variation of time period (on time + off time) maintaining on and off time equal in PED without any additive in the bath in Fig. 6. The peak broadening is increasing with increasing time period. As we increase time period from 10 to 200 ms, the crystallite size (D) is decreasing up to 44% (from 27 to 15 nm), which is quite appreciable and plotted in the inset of Fig. 6. This is in agreement with the results reported in the literature [22].

As shown in Fig. 7, on addition of saccharin to the bath the peak width of Ni (111) increases, effecting a further reduction of crystallite size by 20% at saccharin concentration (C) of 10 g/L. A similar observation is made in DCED discussed earlier. These observations suggest that the additive (saccharin) helps in significant reduction of crystallite size (D) and useful for the synthesis of nanostructured nickel thin films.

From Fig. 8, it is observed that when the voltage pulse duration of PED is maintained at 10 or 20 ms the surface of

film exhibits cracks. When the pulse duration increased to 50 ms the grain structure starts developing and grows further on increasing pulse width. The grains formed at a higher pulse period of 200 ms are observed to be needle-shaped with average size of 200 nm, which is interesting and useful for various applications. We further investigated the microstructural variations of this particular sample with saccharin addition. The FESEM micrographs of these samples are shown in Fig. 9. The variation of surface morphology with increase in saccharin concentration in the bath can be seen clearly, i.e., the sample deposited at a time period of 200 ms, saccharin was added gradually and seen that as soon as saccharin is added the needle-shaped grains disappear. With addition of saccharin concentration in deposition bath, nanometer-sized spherical grains are developed.

Discussion

The present experimental observations show that the crystallite size evaluated from the XRD patterns shows systematic decrease in the crystallite size in both DCED and PED methods upon increasing the concentration of additive saccharin. The crystallite size is observed to reach a minimum value of 18 nm in the case of DCED, whereas in the case of PED this value further reduces to 12 nm if an optimum pulse width of 200 ms is used during the deposition. The effect of saccharin in the electrodeposition bath can be explained using the resonance structure of saccharin. The negative charge in saccharide ion affects its interaction with the cathode. However, delocalization of the electron lone pair of the nitrogen atom in the N–C bond

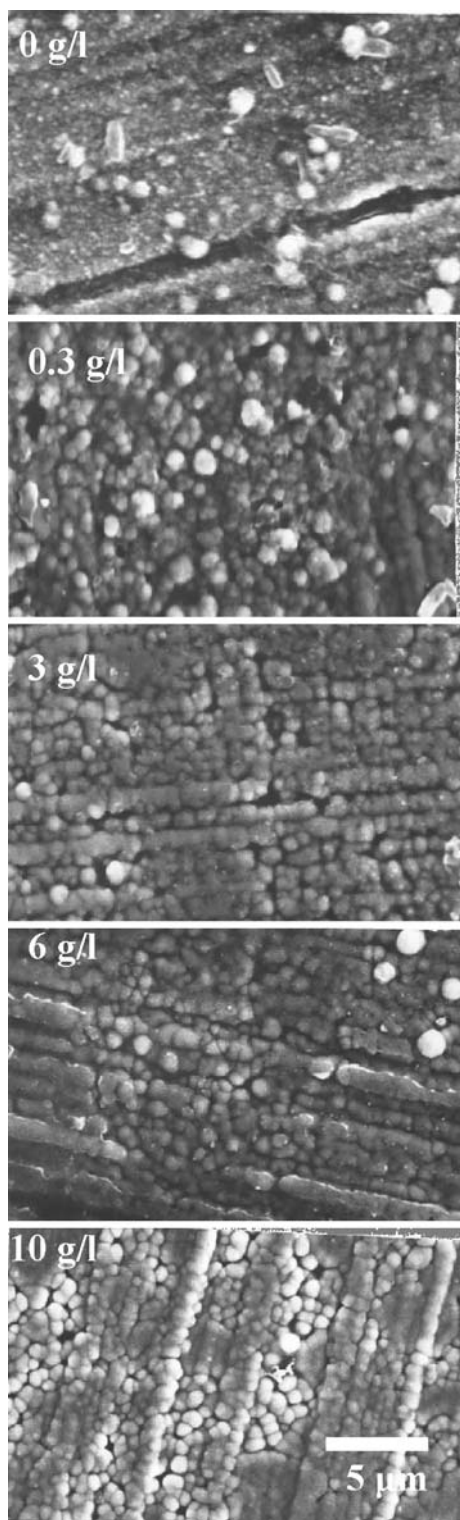


Fig. 3 SEM images of DC electrodeposited samples with various saccharin concentrations: 0, 0.3, 3, 6, 10 g/L

makes N atom fractionally positive (δ^+) and O atom fractionally negative (δ^-) (see Fig. 10). Due to this transient ionic character, saccharide ion may start competing

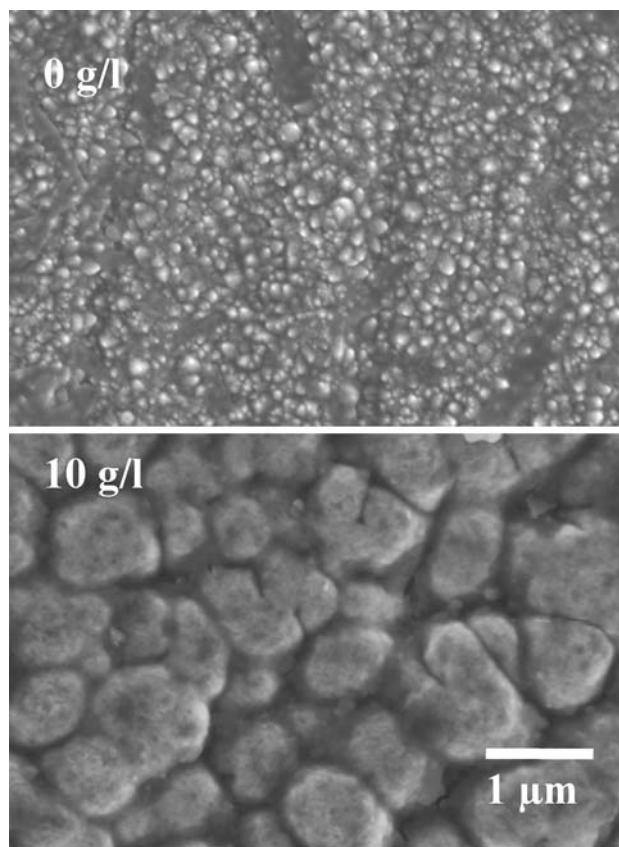


Fig. 4 FESEM images of DC electrodeposited films without saccharin and with 10 g/L saccharin

with Ni^+ cations in the rush toward cathode. The Ni^+ ions being smaller in size than saccharides may move faster and deposited at a faster rate. Consequently saccharide ion may be arriving at the substrate after a few batches of nickel ions been deposited. Saccharide ions so adsorbed on the substrate block the active sites and prevent the growth in a preferential direction (determined by position of N and O atoms) thereby reducing the crystallite size. Furthermore, the surface diffusion of the adions is impeded by adsorbed saccharide ions [22]. Therefore less metal adions reach the growth sites and formation of new nuclei is preferred. Due to the presence of fractionally negative charge on O atom makes a preferable position on the substrate for Ni^+ ions to deposit. This makes many small crystallites at one place constructing a larger grain.

In PED during the on time a large numbers of nickel ions are created and the current is high. Immediately after the strong current pulse the electrolyte in the vicinity of cathode is depleted of cations but during the off time the material supply continues. So creation of large number of ions at the cathode followed by a strong impede of growth of the nuclei by the off time probably helps in formation of anisotropic growth that results in the needle-shaped grains formation. However, saccharin addition can act like a

Fig. 5 *I* versus *t* graphs for PED Ni films for different time periods of pulses

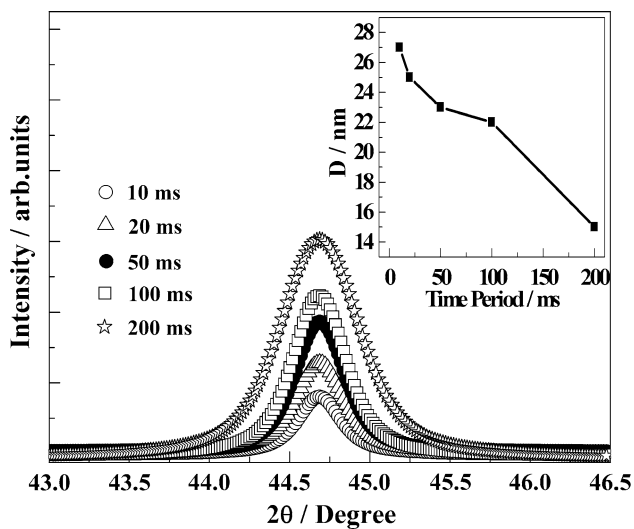
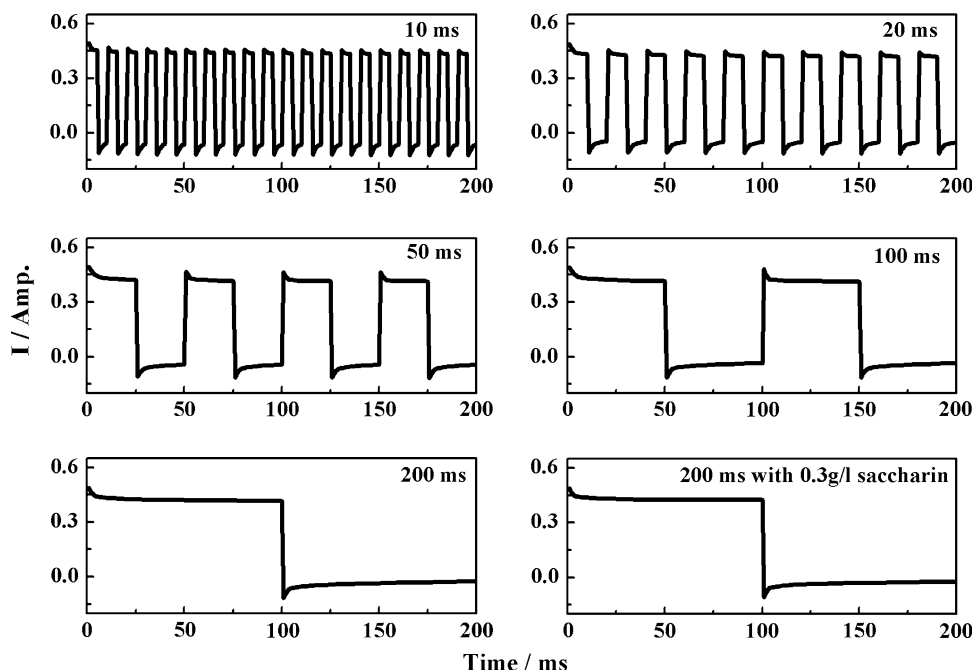


Fig. 6 XRD Ni [111] peaks of pulse electrodeposited films without saccharin as a function of pulse period. The variation of the crystallite size *D* as a function of the pulse period is presented in the inset

catalyst for the isotropic growth of the particles due to the mechanism explained earlier. However, a further study in this direction is in progress to throw more light on the growth mechanism of the Ni.

Conclusions

The electrodeposition of nickel films has been carried out by DCED and PED methods by varying time duration and

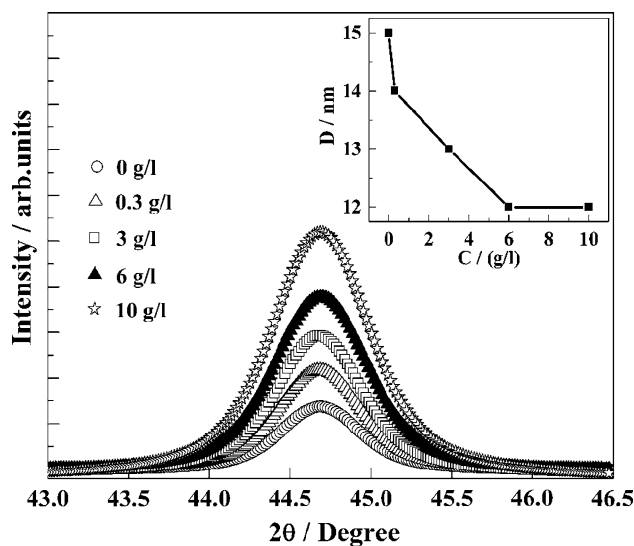


Fig. 7 XRD Ni [111] peaks of pulse electrodeposited films for different saccharin concentrations. The variation of the crystallite size *D* as a function of the saccharin concentration *C* is presented in the inset

also additive (saccharin) concentration. It is observed that the crystallite size decreases upon the addition of saccharin to an electrodeposition bath, in both these methods. Further both the methods provide nano-granular surface structure with spherical grains (DCED) and needle-shaped grains (PED) morphology with additives. Saccharin addition enhances the isotropy in surface morphology of film in PED and develops nanometer size grains; in contrast in DC

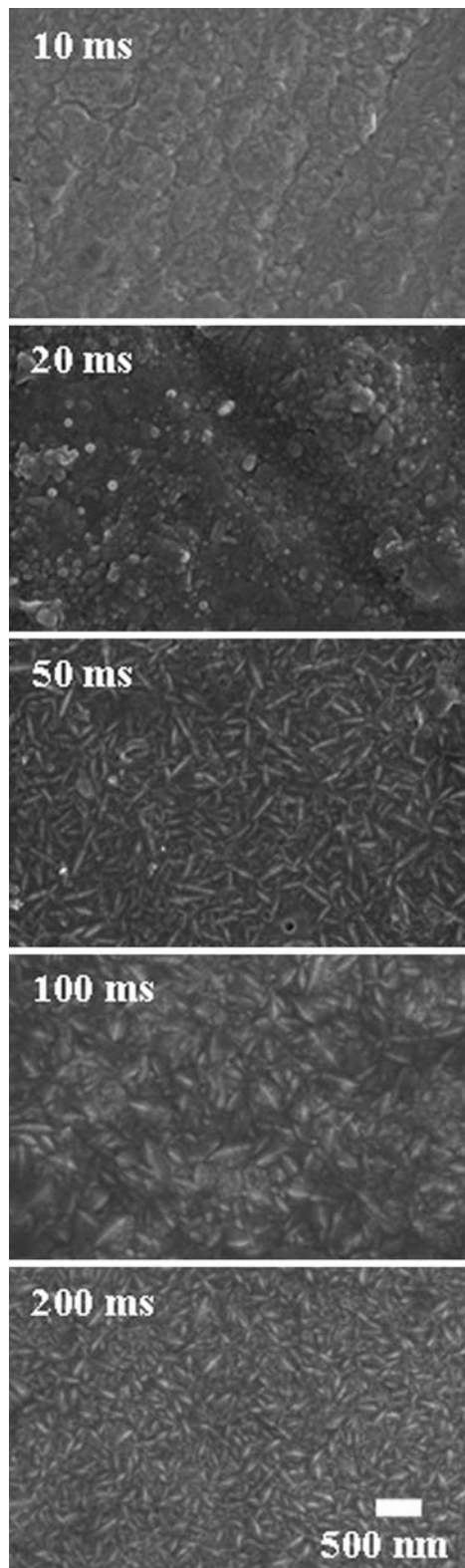


Fig. 8 FESEM images of pulse electrodeposited films without saccharin for pulse period of 10, 20, 50, 100, and 200 ms

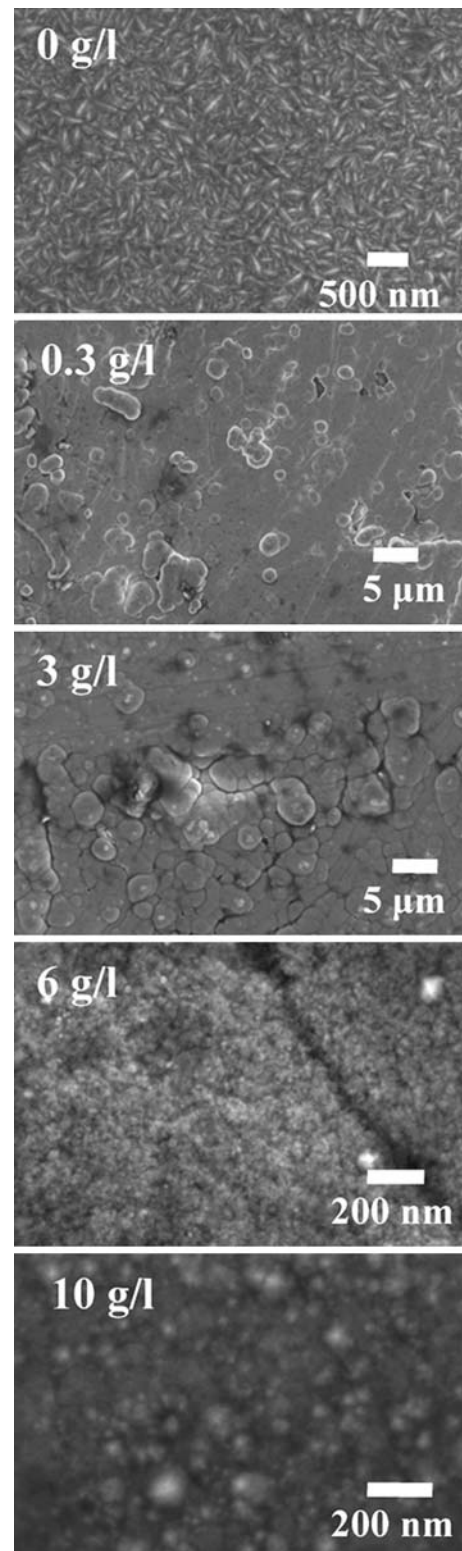


Fig. 9 FESEM images of pulse electrodeposited films with pulse period of 200 ms and saccharin concentration of 0, 0.3, 3, 6, and 10 g/L

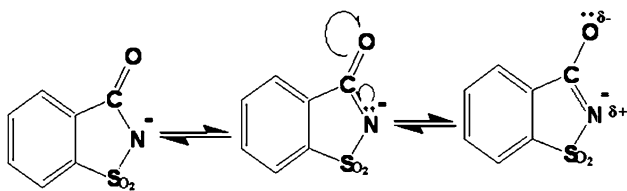


Fig. 10 Schematic representation of the delocalization of electron pair in nitrogen atom of saccharide ion over C–N bond

electrodeposition it increases the grain size. The reduction in crystallite size and increase in grain size have been explained using resonance structure of saccharin.

Acknowledgements Amaresh Chandra Mishra would like to thank Council of scientific and Industrial Research (CSIR) for providing financial assistance for carrying out this study. This study was partially supported by the Defence Research Development Organization (DRDO), New Delhi, India.

References

- Roy I, Yang HW, Dinh L, Lund I, Earthman JC, Mohamed FA (2008) *Scr Mater* 59:305
- Palumbo G, Gonzalez F, Brennenstuhl AM, Erb U, Shmayda W, Lichtenberger PC (1997) *Nanostruct Mater* 9:737
- Osaka T (1997) *Electrochim Acta* 42:3015
- Osaka T, Sawaguchi T, Mizutani F, Yokoshima T, Takai M, Okinaka Y (1999) *J Electrochem Soc* 146:3295
- Tabakovic I, Inturi V, Riemer S (2002) *J Electrochem Soc* 149: C18
- Lallemand F, Comte D, Ricq L, Renaux P, Pagetti J, Dieppedale C, Gaud P (2004) *Appl Surf Sci* 225:59
- Gleiter H (1989) *Prog Mater Sci* 33:223
- Granqvist CG, Buhman RA (1976) *J Appl Phys* 47:2200
- Erb U (1995) *Nanostruct Mater* 6:533
- Glasstone S (1964) *An introduction to electrochemistry*. Van Nostrand Inc., Princeton, NJ
- Natter H, Krajewski T, Hempelmann R (1996) *Ber Bunsen Phys Chem* 100:55
- Natter H, Hempelmann R (1996) *J Phys Chem* 100:19525
- O'Reilly C, Sanvito S, Rhen FMF, Stamenov P, Coey JMD (2006) *J Appl Phys* 99:08J301
- Karayianni HS, Patermarakis GS, Papaioannou JC (2002) *Mater Lett* 53:91
- Zhao H, Liu L, Zhu J, Tang Y, Hu W (2007) *Mater Lett* 61:1605
- Tang Y, Zhao D, Shen D, Zhang J, Li B, Lu Y, Fan X (2008) *Thin Solid Films* 516:2094
- Motoyama M, Fukunaka Y, Sakka T, Ogatab YH (2006) *J Electrochem Soc* 153:C502
- Li Y, Jiang H, Pang L, Wang B, Liang X (2007) *Surf Coat Technol* 201:5925
- Ebrahimi F, Ahmed Z (2003) *J Appl Electrochem* 33:733
- Ganesh V, Vijayaraghavan D, Lakshminarayanan V (2005) *Appl Surf Sci* 240:286
- Qu NS, Zhu D, Chan KC, Lei WN (2003) *Surf Coat Technol* 168:123
- Natter H, Schmelzer M, Hempelmann R (1998) *J Mater Res* 13:1186
- Gamburg YD, Grosheva MY, Bialozor S, Hass M (2002) *Surf Coat Technol* 150:95
- Oniciu L, Muresan L (1991) *J Appl Electrochem* 21:565
- Galvani F, Carlos IA (1997) *Metal Finish* 95:70
- Carlos IA, Malaquias MA, Oizumi MM, Matsuo TT (2001) *J Power Sources* 92:56
- Almeida MRH, Carlos IA, Barbosa LL, Carlos RM, Lima-Neto BS, Pallone EMJA (2002) *J Appl Electrochem* 32:763
- Carlos IA, Siqueira JL, Finazzi GA, Almeida MRH (2003) *J Power Sources* 117:179
- Carlos IA, Almeida MRH (2004) *J Electroanal Chem* 562:153
- Finazzi GA, Oliveira EM, Carlos IA (2004) *Surf Coat Technol* 187:377
- Barbosa LL, Almeida MRH, Carlos RM, Yonashiro M, Oliveira GM, Carlos IA (2005) *Surf Coat Technol* 192:145
- Darrort V, Troyon M, Ebotht J, Bissieux C, Nicollin C (1995) *Thin Solid Films* 265:52
- Mohamed FA, Chauhan M (2006) *Metall Mater Trans A* 37A:3555
- El-Sherik AM, Shirokoff J, Erb U (2005) *J Alloys Compd* 389:140
- Cullity BD (1978) *Elements of X-ray diffraction*, 2nd edn. Addison-Wesley, Reading, MA
- Chauhan M, Mohamed FA (2007) *J Mater Sci* 42:1606. doi: [10.1007/s10853-006-0823-z](https://doi.org/10.1007/s10853-006-0823-z)
- Ares JR, Pascual A, Ferrer IJ, Sanchez C (2005) *Thin Solid Films* 480–481:477
- Dini JW (1996) *Electrodeposition, the materials science of coatings and substrates*. Noyes Publications, Norwich