

ELECTRODEPOSITION OF NANOCRYSTALLINE NICKEL

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Pulse electrodeposition method was used to produce nanocrystalline nickel particles of size ranging from 25 nm from saccharin containing Watts type baths. The advantages of using electrodeposition over other methods for synthesis of these particles are discussed, laying special emphasis on the difference between pulse and d.c. plating techniques. The effect of saccharin concentration on the grain size and orientation is described briefly. The superior properties of the nano nickel particles produced by electrodeposition, like negligible porosity, enhanced electrical conductivity etc., are brought to light in comparison with the properties of conventional microcrystalline particles. The preferred orientation of the deposits progressively changed from a strong (2 0 0)-fiber texture for a saccharin free bath to a (1 1 1) (2 0 0) double fiber texture for a bath containing 10 g/l saccharin. These are proved by the XRD micrographs obtained.

Keywords: Nanocrystals, nickel, electrodeposition, pulse plating

INTRODUCTION

Electroplated Nickel has been extensively used in many engineering applications ranging from the production of thin water resistant films to bulk electroformed products like rotary printing cylinders [1] for over a century now. It plays a major role in the finishing parts of most automobile and bicycle industries. But in the recent past, efforts have been dedicated to the development of stiffer, stronger and lighter particles. The mechanical, electrical and magnetic properties of these materials are affected by their grain size and particle orientation to a great extent. It has been found that reduction of particle size, is the novel way to attain the above mentioned characteristics [2-8]. This has led to the development of a new class of materials of small grain size namely nanocrystalline materials.

These particles have been found to exhibit excellent properties often superior to the conventional micro sized grains and are characterised improved hardness, enhanced diffusivity, high electrical resistivity and better magnetic properties. Their porosity is visibly low. So, in the contemporary world of material science, nanocrystalline materials are the cynosure of all eyes. The understanding of grain boundaries and their effects on properties of materials has led to considerable amount of research pouring in these

days, into the field of nanostructured materials where the particle size ranges from 10-100 nm [9]. So a great deal of time and work has been devoted to synthesize, characterize and analyze these materials. These efforts were mainly concentrated on improving the properties by subjecting to various experimental conditions and thereby studying the resulting crystallites formed which could be used for specific significant purposes.

Electrodeposition - An edge over others

Starting from the very earliest of works done on nano materials [9], a number of techniques have been developed to synthesize these nanoparticles. Sol-gel technique, gas condensation, metal alloying, chemical vapor deposition, ball milling, spark erosion etc., [27] are a few of them. All these methods are not suitable for the production of large quantities of pure metals or alloys as processes like ball milling yield impure products. The pulsed electrodeposition technique stands out as a versatile technique for the production of pure metals and alloys. So special emphasis in this paper is laid on this electrodeposition technique. This method definitely has a marked edge over its competent techniques but there has been very little work reported on these lines [10], to substantiate its superiority. These are some of the relative merits of this method over other techniques:

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- i) The primary advantage is the low initial costs [9] and substantially high production rates [10]
- ii) There is a greater possibility of producing a potentially large number of metals, alloys and other composite systems by this method with great ease.
- iii) It poses a minimum number of limitations as to the shape and size of nanoparticles formed [11].
- iv) There is no need to use any post processing techniques, even in the production of bulk nano crystals.
- v) Nickel particles produced by this method stand evidence to the superiority of this method with its high density and least porosity.
- vi) Finally there is minimum technological barrier in transferring the technique from the laboratories to the industries [12].

EXPERIMENTAL

Watts type bath containing Saccharin (Table I) was used to produce upto 300 μm thick nanocrystalline nickel electrodeposits. Analytical grade reagents and distilled water were used to prepare the solutions. The plating cell was immersed in a thermostatted water bath with temperature maintained at 333 K. The saccharin concentration was varied in the sequence 0, 2.5, 5, 10 g/l. Saccharin in the form of powder was added to the plating bath and stirred until complete dissolution was achieved. A pure electrolytic nickel sheet placed in a titanium mesh basket was used as the soluble anode.

The surface area of this anode is normally ten times greater than the area of the cathode to avoid problems arising from anode polarization, especially at high current densities [13]. Titanium is the cathode with an area of 1 cm^2 . After electrodeposition nickel was mechanically removed off the titanium cathode. Pulsed electrodeposition was carried out galvanostatically using cathode square wave pulse with complete current cut off during the interval between the pulses. The parameters corresponding to the pulse plating experiment carried out is given in Table I [14,15]. These parameters have been pre-optimized and yield acceptable nickel deposits.

RESULTS AND DISCUSSION

From Figs. 1(a-b), a clear picture of the texture of the nickel deposit can be visualized. In the absence of saccharin, the deposit shows a uniform $\langle 200 \rangle$ surface texture. However, on the introduction of saccharin, a mixed texture comprising of $\langle 111 \rangle$ and $\langle 200 \rangle$ phases is noticed as is evident from the peaks in the XRD spectra. Fig. 2 shows the X-ray diffraction patterns obtained for various concentrations of saccharin using CuK_α radiation ($\lambda = 1540 \text{ nm}$) in a standard θ - 2θ diffractometer. A peak search followed by subsequent analysis using standard formulae [32] revealed the particle sizes as reported in Table II. A uniform distribution of particles in the range of 25 to 50 nm was noticed in the saccharin-modified bath. Saccharin concentration in the Watts type bath is an obvious telling factor with respect to the size of the nickel particles produced in electrodeposition [17]. A few important factors other than the saccharin concentration also affect the grain size. Mass transfer on the solution side of the bath is an important factor. The Ni^{2+} content on the cathode- electrolyte interface and the amount of adsorbed hydrogen have an influence on the crystal growth [18]. The bath parameters are adjusted in order to promote nucleation ahead of crystal growth. High negative over-potential and high adion concentration along with low adion surface mobility are the prerequisites for the grain size reduction. However, in the case of all Watts type baths the amount of organic additives added is the most important factor [17]. Surface morphology of nickel deposits produced with varying saccharin concentration put up various results of interest

TABLE I: Composition of the Watts type nickel plating bath

Parameter	Range
Nickel sulphate	300 g/l
Nickel chloride	45 g/l
Boric acid	45 g/l
Saccharin	0-10 g/l
pH	2
Temperature	333-343 K
On-time (ms)	2.5
Off-time (ms)	45
Peak current density (mA/cm^2)	1900

thus showing its effect on the size [17] and appearance of the nano particles formed.

Effect of Saccharin concentration

- i) Absence of saccharin leads to particles of relatively large crystals in the micrometer range. These deposits are also characterized by greater surface roughness and dull appearance.
- ii) A saccharin concentration of 0.5 g/l results in a transition to a colony like morphology [17] with smoother surface brighter appearance and smaller grains.
- iii) On further increasing the concentration of saccharin step by step up to 5 g/l, grain size was found to decrease rapidly with further increase in brightness of appearance of the crystals. Some authors have come to the conclusion that incorporation of organic additives in the plating bath results in an inhibited pyramidal growth and a concomitant reduction in surface roughness and increase in surface brightness [31]. Addition of other organic additives like coumarin or thiourea in place of saccharin has also been reported to contribute to the reduction of grain size [16,19].

Grain refinement with respect to crystal size is evident in most leveling and brightening cases of electrodeposits. The dimensions of the grains depend on:

- a) the number of grain producing locations
- b) number of nuclei which appear during electrodeposition of metal

There is a possibility of grain size reduction accompanying grain refinement in all cases of leveling and brightening. The grain dimensions depend on the number of nuclei appearing during the process of electrodeposition as well as on the number of grain-producing dislocations. There is no possibility of two different grains merging into a single one, except in the case of coupled screw dislocation, which is also very remote. Lines of coalescence therefore form grain boundaries. Consequently, the electrodeposits are found to have finer grain structures with increasing density of the grain precursors. So, all the factors leading to the formation of dislocations or nucleation contribute to the grain size reduction and refinement [20]. Of all the factors known, addition of organic additives to the bath is the best.

The grain refinement is caused by the following combined effects of saccharin: (i) increasing nucleation frequency caused by blockage of crystal growth [21], (ii) retaining diffusion of nickel adatoms on the cathode surface [22] and (iii) lowering of the over potential for the reduction of Ni^{2+} ions [17]. The reduction of the Ni^{2+} ions is enhanced with an increase in adsorbability of the additives used.

Increasing the saccharin concentration from 5 g/l to any higher value say up to 10 g/l shows very little effect on the grain size reduction. There is almost no reduction in grain size. This is supported by the fact that the over potential curves of saccharin yield a plateau, with increasing saccharin concentrations after a

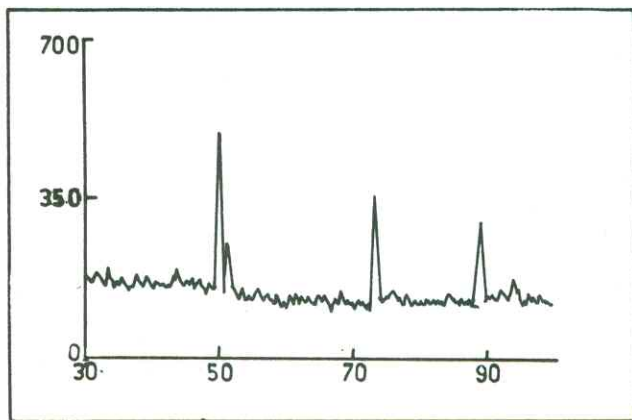


Fig. 1a: X-ray diffraction pattern of nickel in the absence of Saccharin

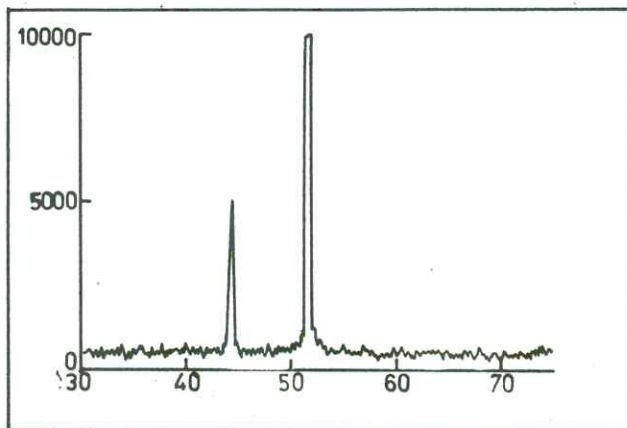


Fig. 1b: X-ray diffraction pattern of nickel in the presence of Saccharin

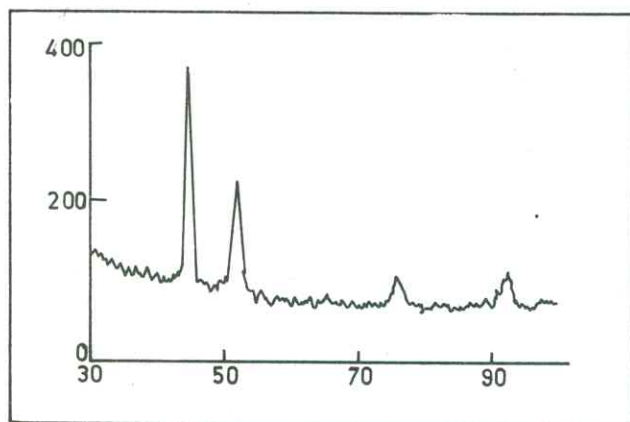


Fig. 2a: XRD spectrum of nano nickel in the presence of 2.5 g/l of Saccharin

particular point [23]. This is explained to be due to the:

- Levelling off of the overpotential at that limit
- Saturation of the adsorption sites on the cathode surface by saccharin molecules over a particular concentration [24]

Merits of pulse plating

The most significant and practically important difference between d.c and pulsed current deposition is that in d.c plating either current or voltage alone can be varied, whereas, in pulsed plating the on-time, off-time, peak current can be chosen at our will to get the desired composition. Some of its relatively significant points scored over the d.c plating method are

- Pulse plating provides superior parameters like fine grain structure [22], and hence reduced porosity, improved hardness and internal stress. The ductility of the material also increases while employing this method
- Density and electrical conductivity are enhanced.
- The deposition current density in the case of pulse plating is more than that for d.c plating, which implies faster plating rate. This is attributed to the fact that the method is carried out at values close to the instantaneous limiting current density
- Adhesion properties improve with reduction of the oxide film
- Plating distribution is uniform and therefore there is uniformity of the thickness [25] of the film formed.

In the case of d.c plating we have a limitation in the form of current density which is not the case with pulsed plating.

Effects of pulse parameters

The on-time which represents the length of the pulse, off-time representing the time between two pulses, peak height and current density are some of the important pulse parameters. These parameters are found to affect the formation of nanocrystalline nickel. The temperature of the experiment is always maintained at about 333 K. The on-time and off-time values of the experiment also have a pronounced effect on the grain size of the particles [26]. As per the observed trend:

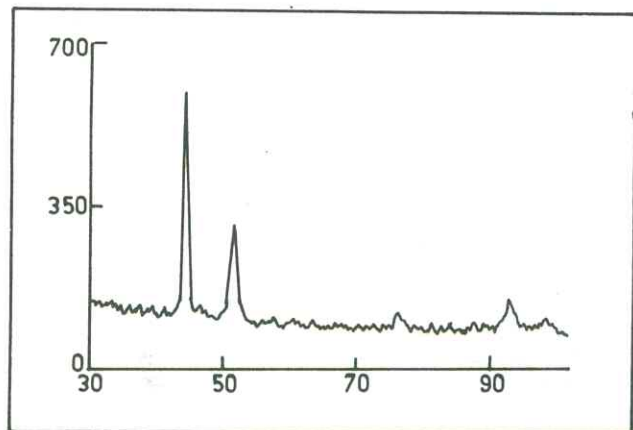


Fig. 2b: XRD spectrum of nano nickel in the presence of 5 g/l of Saccharin

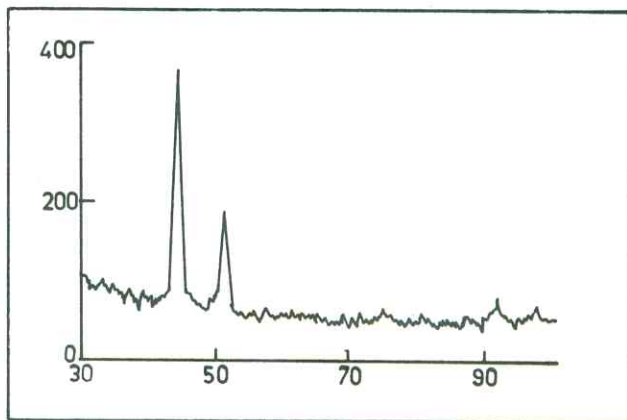


Fig. 2c: XRD spectrum of nano nickel in the presence of 10 g/l of Saccharin

- i) The grain size of the deposits increases with decrease in off-time (t_{off}). This is attributed to the fact that, at short t_{off} value, the metal ions migrate faster than the big organic molecules. The metal ions are deposited first, and then the inhibitor molecules occupy the active sites. In a short t_{off} time a decreased number of inhibitor molecules reach the active steps, before the growth continues at the next pulse.
- ii) The grain size decreases with decrease in on time. A short on time (t_{on}) means higher current density. In the case of high current density we get small crystallites. But the grain size decreases only slightly when the on-time is very long.

Properties of the deposit

The significance of reducing the particle size and its impact on the material properties has already been mentioned. Higher electrical resistivity, increased specific heat, higher thermal expansion coefficient are a few notable points. They are also reported to have superior soft magnetic properties, better adhesion properties and enhanced corrosion control. In the case of these nano nickel electrodeposits the d.c electrical resistivity shows a three-fold increase. Reduced porosity and the resultant high density are specific properties of the electrodeposited Ni. Thermal studies show that the nano nickel samples are stable up to a temperature of 573 K, when these particles show rapid grain coarsening by two or three times with subsequent stabilization. Some of the properties like microhardness, corrosion resistance and adhesion properties of the nano nickel particles are discussed briefly here.

Microhardness

Hardness analyses show that the hardness increases from 150 kg/mm² at micrometer level to 650 kg/mm² at nanoscale dimensions. Vicker's

test on nano nickel shows a three-fold increase in microhardness. These properties are attributed to the grain refinement. The hardness is found to increase with the particle size. But after a particular grain size the hardness is seen to decrease. The particular grain size at which this occurs is characteristic of each substance. This is called as Inverse Hall-Petch relation [27]. Annealing of the sample also increases the hardness of particles.

Adhesion properties

Adhesion of the particles onto the substrate was studied by performing bend tests. The samples showed good adhesion according to ASTM standards [28]. The samples were able to withstand burnishing and peel tests as well. A minor amount of titanium is always found to accompany the deposit because of the adhesion of the deposit to the Titanium electrode.

Corrosion resistance

The corrosion study [29] involved the specimen preparation by grinding the substance to 800 grit, using SiC emery, washing with soap and cleaning with a jet of distilled water. Before plating, the specimen was degreased with acetone; then it was plated to a thickness of about 12 μm , again cleaning with acetone and distilled water. This specimen was placed in a salt spray cabinet, exposing a pre-determined area, and visually inspecting the specimen hour by hour (for 8 hours), with a daily record.

The results of this experiment reveal the fact that the corrosion rate of the uncoated macrosized specimen was higher, which was apparent from a plot made between percentage red rust covered area versus the time of observation. The amount of corroded area read from the graph indicated that this value decreases from 80%- 90% for the macro sized specimen to 30% for the case of nanonickel produced by electrodeposition. So this indicates that the nanonickel is a good anti-corrosive reagent.

Applications

Nano materials have become the area of research in the present day with excellent technological advancement. Electrodeposition has become the most viable method of synthesis of these materials both in bulk as well as in the form of coatings of varying thickness. The industrial applications of

TABLE II: Particle size at different Saccharin concentrations

Saccharin concentration (g/l)	Particle size (nm)
0.0	152
2.5	48
5.0	26
10.0	25

these materials range from the production of water resistant coatings to heat exchanger repair technology, involving electronic connectors, electrodes for the catalysis of hydrogen oxidation and evolution reactions. Owing to their increased anti corrosive property, nano nickel has been used in anti corrosive coatings. The production of capacitors using base metal technology proves a cost effective alternative to the traditional manufacture of metal Multi Layer Ceramic Capacitors (MLCC).

Recent studies [30] have also revealed that nano nickel plays an important role in yielding diamonds. The nickel atom is in a 3d absent state, and can attract the electrons in the carbon fullerenes, leading to the transformation of sp² fullerene to diamond like sp³ fullerene structures. High reactivity can be mentioned as a secondary reason as it helps in effective promotion of the transformation process in short duration, during the shock wave load.

CONCLUSION

The demand for nanomaterials is increasing and their unique properties finding them applications in many latest developments in the metal finishing industries. Production of nanoparticles of size ranging from 25-60 nm by means of pulse electrodeposition from saccharin containing Watts type bath was explained here. Pulse plating, using Watts type bath is found to exhibit the best results. The nickel particles produced by this method are found to be smooth exhibiting higher brightness. The scope for the advancement in this field is vast with new innovations being added to the old production techniques and greater sophistications attained in the characterization techniques. The recent trend in the electroplating industry drives it towards more and more functional applications and as explained earlier, the nano materials prepared by the above mentioned method are found to exhibit many superior properties that make it suitable for a variety of industrial applications.

REFERENCES

1. S Kaja, H W Pickering and W R Bitler, *Plat Surf Fin*, **72** (1986) 58
2. A M El Sherik, U Erb, G Palumbo and K Aust, *Scripta Metall Mater*, **27** (1992) 1185
3. A M El Sherik, K Boylan, U Erb, G Palumbo and K Aust, *MRS Symp Proc*, **238** (1992) 727
4. R Rofagha, R Langer, A M El Sherik, U Erb, G Palumbo and K Aust, *Scripta Metall Mater*, **25** (1991) 2867
5. M J Aus, B Szpunar, A M El Sherik, U Erb, G Palumbo and K Aust, *ibid*, **27** (1992) 1639
6. M J Aus, B Szpunar, A M El Sherik, U Erb, G Palumbo and K Aust, *J Appl Phys*, **75** (1994) 3632
7. G Palumbo, D M Doyle, A M El Sherik, U Erb and K Aust, *Scripta Metall Mater*, **25** (1991) 679
8. D M Doyle, G Palumbo, A M El Sherik, U Erb and K Aust, *Acta Metall Mater*, **43** (1995) 3027
9. H Gleiter, *Progr Mater Sci*, **33** (1989) 223
10. U Erb, A M El Sherik, G Palumbo and K Aust, *Nanostr Mater*, **2** (1993) 383
11. A Brenner, "Electrodeposition of Alloys- Principles and Practice" Academic Press, New York (1963)
12. G McMohan and U Erb, *Microstr Sci*, **17** (1989) 865
13. N V Parthasarathy, "Practical Electroplating Handbook", Prentice Hall, Englewood Cliffs, New Jersey (1989)
14. A M Sherik, *Ph D thesis*, Queen's University, Kingston, Ontario (1993)
15. U Erb and A M El Sherik, "Nanocrystalline materials and process of producing the same" *US Pat 5,352,266*, (1994)
16. R Weil and W N Jacobus Jr, *Plating*, **53** (1966) 102
17. Y Nakamura, N Kaneko, M Watanabe and H Nezu, *J Appl Electrochem*, **24** (1994) 227
18. Wang *et al*, *Acta Mater*, **45** (1995) 1655
19. R Weil and H C Cook, *J Electrochem Soc*, **109** (1962) 295
20. A R Despic, *Deposition and Dissolution of metals and alloys, Part-B*, "Comprehensive Treatise of electrochemistry", Vol. 7, Plenum, New York (1983)
21. J P Bonino, P Poudroux, C Rossignol and A Rousset, *Plat Surf Fin*, **78** (1992)
22. R T C Choo, J Toguri, A M El Sherik and U Erb, *J Appl Electrochem*, **25** (1995) 384
23. C C Roth and H Leidheiser Jr, *J Electrochem Soc*, **100** (1953) 553
24. J Edwards, *Trans Inst Metal Fin*, **41** (1964) 169
25. N Ibl, *Surface Tech*, **10** (1981) 81
26. H Natter and R Hempelmann, *J Phys Chem*, **100** (1996) 19525
27. C Suryanarayana, *Bull Mater Sci*, **17**(4) August (1994) 62
28. *Annual book of ASTM standards*, **02-05** (1995) B-571
29. *Annual book of ASTM standards*, **02-03** (1995) B-117
30. Hongliang *et al*, *J Mater Sci Lett*, **14** (1994) 913
31. J K Dennis and J Fuggle, *Electroplat Metal Fin*, **20** (1967) 370
32. B D Cullity, *Elements of X-ray diffraction*, Second Edition, Addison - Wesley Publishing Company, Inc