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ELECTROWINNING OF NICKEL FROM AMMONICAL SULPHATE BATH AND EFFECT OF ACETONE ON MORPHOLOGY OF NICKEL DEPOSIT AND ITS CORRELATION WITH KINETIC PARAMETERS

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The electrodeposition of nickel from nickel sulphate bath was studied in ammonia medium. The electrolytic conditions for nickel deposition was optimized at room temperature. The effect of acetone on current efficiency, morphology, stability and particle size of deposited nickel powder was studied. The effect of organic additive Tribenzyl ammonium chloride (TBAC) on the morphology of nickel powder was also studied. The kinetics of electrodeposition was studied and the results were utilized in developing mathematical model. During electrodeposition the current efficiency was found to increase with increase in acetone concentration up to 15% V/V in bath solution. On further increase of acetone concentration in bath solution current efficiency decreases. The stability of the electrowon deposited nickel powder was found to be in the range of 85 to 89 %. Powder morphology was found to be dendritic, porous and irregular. The morphology was also found to be underdeveloped dendritic to rounded aggregate as the concentration of organic additive TBAC increases. The average particle size of the deposited powder was found to be decreasing as the concentration of the acetone increases. The average size of the particle is in the range of 13-16 μm .

Key words: powder metallurgy, electrowinning, nickel powder

Elektrolitička proizvodnja nikla iz amonijačno sulfatne kupke i utjecaj acetona na morfologiju taloga nikla i njihov odnos s kinetičkim čimbenicima. Istraživano je elektrolitičko taloženje nikla iz kupke niklovog sulfata. Elektrolitički uvjeti za taloženje nikla su optimizirani za sobnu temperaturu. Istraživan je utjecaj acetona na učinkovitost struje, morfologiju, stabilnost i veličinu čestica istaloženog nikla. Također je istraživana utjecaj organskog dodatka tribenzil amonij klorida (TBAC) na morfologiju niklovog praha. Istraživana je kinetika elektrodepozicije i rezultati su korišteni za razvijanje matematičkog modela. Tijekom elektrolitičkog taloženja učinkovitost struje rasla je s porastom koncentracije acetona u kupci do 15 %. Pri daljnjem povećanju koncentracije acetona u kupci učinkovitost struje opada. Stabilnost taloga niklovog praha pripremljenog elektrolitičkim taloženjem je između 85 - 89 %. Morfologija praha je dendritična, porozna i nepravilna. S porastom koncentracije organskog aditiva TBAC morfologija poprima oblik od nepotpuno razvijenih dendrita do zaobljenih nakupina. Prosječna veličina čestica istaloženog praha opada s porastom koncentracije acetona i kreće se u rasponu 13-16 μm .

Cljučne riječi: praškasta metalurgija, elektrolitička priprava, prah nikla

INTRODUCTION

Powder metallurgy has the distinction of being at the same time one of the oldest and one of the most modern methods known for the fabrication of metal articles. A number of patents have been taken on the powder fabrication since early decades of twentieth century. Iron, copper, nickel and zinc

are the most studied metals. Nickel powder has important applications in industry. It is employed in the manufacture of alkaline batteries. In the chemical industries as catalyst, as pigment in corrosion paints, etc. Copson et al. [1] and Kuroda et al. [2] got patent for their work on electrolytic nickel powder preparation. Cathodic preparation of finely dispersed nickel was presented by Loshkarev [3]. Kerfoot et al. [4] produced nickel powder by reduction of oxides of nickel with hydrogen gas. Rambla et al. [5] performed nickel electrowinning using platinum catalyzed hydrogen diffusion anode and stainless steel cathode. Jana et al. [6] studied the direct electrowinning of valuable metals from sea nodules

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using aqueous chloride bath and the effect of addition of sodium sulphide to the ground nodules on the dissolution behaviour of various metals. Holm and O'Keefe [7] studied the effect of electrolytic parameters on the electrowinning of nickel. Brillas et al. [8] studied the nickel electrowinning using platinum catalysed hydrogen diffusion anode and the effect of chloride and sulphate ions. Lupi and Pasquali [9] studied the electrolytic nickel recovery from lithium ion batteries. In our previous work [10, 11] the electrolytic conditions for copper powder preparation and the effect of acetone on the process was studied.

In the present work, an attempt has been made to optimize the electrolytic conditions for preparation of nickel powder from sulphate bath at room temperature. The influence of concentration of acetone on current efficiency (C. E.), particle size, shape and stability of the deposited nickel powder is studied. The effect of organic additive tribenzyl ammonium chloride (TBAC) on the morphology of nickel powder is also studied.

EXPERIMENTAL

All the chemicals used for the experiments were of AR grade and the bath solution was prepared using double distilled water. The bath solution ($\text{NiSO}_4 + \text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$) was taken in a single compartment three electrode cell. The electrowinning experiments were performed using steel plate ($1,5 \text{ cm} \times 9 \text{ cm} \times 0,15 \text{ cm}$) as working electrode, graphite electrode ($2,5 \text{ cm} \times 2,5 \text{ cm} \times 9 \text{ cm}$) as counter electrode and saturated calomel electrode as reference electrode. The steel electrode was cleaned with emery paper and washed with distilled water and acetone before the experiments. Constant potential was supplied by using Potentiostatic model 1399 fabricated by Central Electrochemical Research Institute (CECRI), Karaikudi, (CSIR Lab), India.

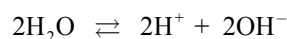
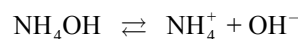
In order to optimize the electrodeposition conditions for nickel powder, a series of laboratory scale experiments were performed by varying the electrolytic conditions i.e. bath solution concentration (concentrations of NiSO_4 and NH_4OH) and electrolytic potential. Under the optimum conditions, the effect of acetone on the deposition of nickel powder was studied by varying the concentration of acetone from 5 to 35 % V/V. The kinetics of electrodeposition of nickel powder was studied by withdrawing 1 ml of bath solution (reaction mixture) at the interval of 10 minutes and titrated against standard EDTA using ammonium perpurate as indicator. The volume of EDTA used was a measure of the concentration of Ni^{2+} in the bath solution. The electrolytic depositions were continued for two hours. The nickel powder was removed from electrode, washed with methanol and dried under vacuum. The prepared nickel powder was characterized for its particle size, morphology and stability. The particle size analysis and Scanning electronic microscopy (SEM) studies were performed on Fritsch particle sizer - ANALYSETTE

22 and JEOL, JXA 240A microscope operated at 15 kV respectively at JNARDDC, Wadi, Nagpur.

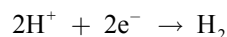
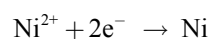
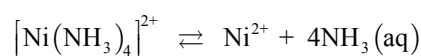
RESULTS AND DISCUSSION

Deposition of nickel

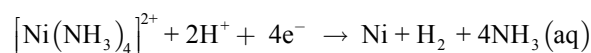
During electrowinning process significant cathodic and anodic reactions occur as follows:



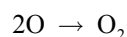
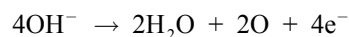
Reactions at cathode are:



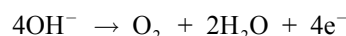
Overall reaction at cathode is:



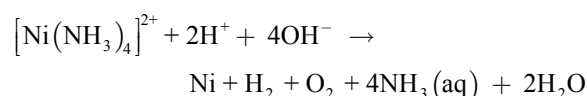
Reactions at anode is:



The overall reaction at anode is:



The overall reaction is:



The evolution of hydrogen at cathode makes nickel deposition loose which can be easily scraped out by water blowing. The oxygen evolution at anode oxidises acetone to acetic acid and formic acid due to which basicity of bath solution decreases as the electrowinning progresses.



The optimized electrolytic conditions for electrowinning are as follows:

- bath solution: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (5,25 g/l) + NH_4Cl (12,5 g/l) in 0,1 M NH_4OH ,

- potential: 4,0 V,
- temperature: 30 °C.

Stability of nickel powder

Stability of prepared nickel powder was determined by dissolving 0,5 g of nickel powder in 100 ml 0,1 M Nitric acid and dissolved nickel was estimated by titrating the solution against 0,01M EDTA using Ammonium perpurate as indicator. From the difference in weight due to oxide formation (NiO, Ni₂O₃), the percent oxidative stability was calculated as

$$\text{Oxidative Stability} = \frac{\text{Wt. of nickel taken} - \text{Loss in wt. of nickel}}{\text{Wt. of nickel taken}} \times 100$$

On increasing the concentration of acetone in the bath solution the oxidative stability of electrowon deposited nickel powder decreased. This may be due to the formation of nickel powder of smaller size which possessed larger surface area. Larger the surface area susceptibility towards oxidation is more and the oxidative stability of deposited nickel powder decreases. The oxidative stability lies in the range of 85 - 89 % (Figure 1.).

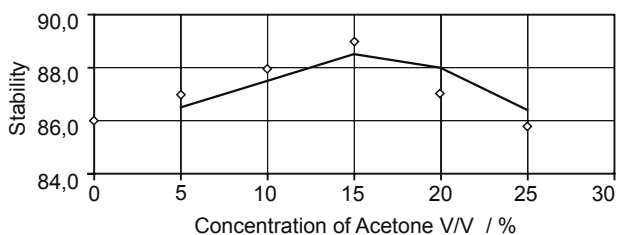


Figure 1. Effect of bath acetone concentration on stability of the deposited nickel powder
Slika 1. Utjecaj koncentracije acetona u kupci na stabilnost istaloženog praha nikla

Cathodic current efficiency

The CE increases as the acetone concentration in the bath solution increases from 0 to 15%. On further increase in acetone concentration CE decreases (Figure 2.). Above

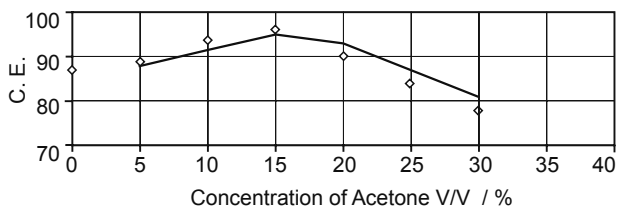


Figure 2. Effect of bath acetone concentration on current efficiency
Slika 2. Utjecaj koncentracije acetona u kupci na učinkovitost struje

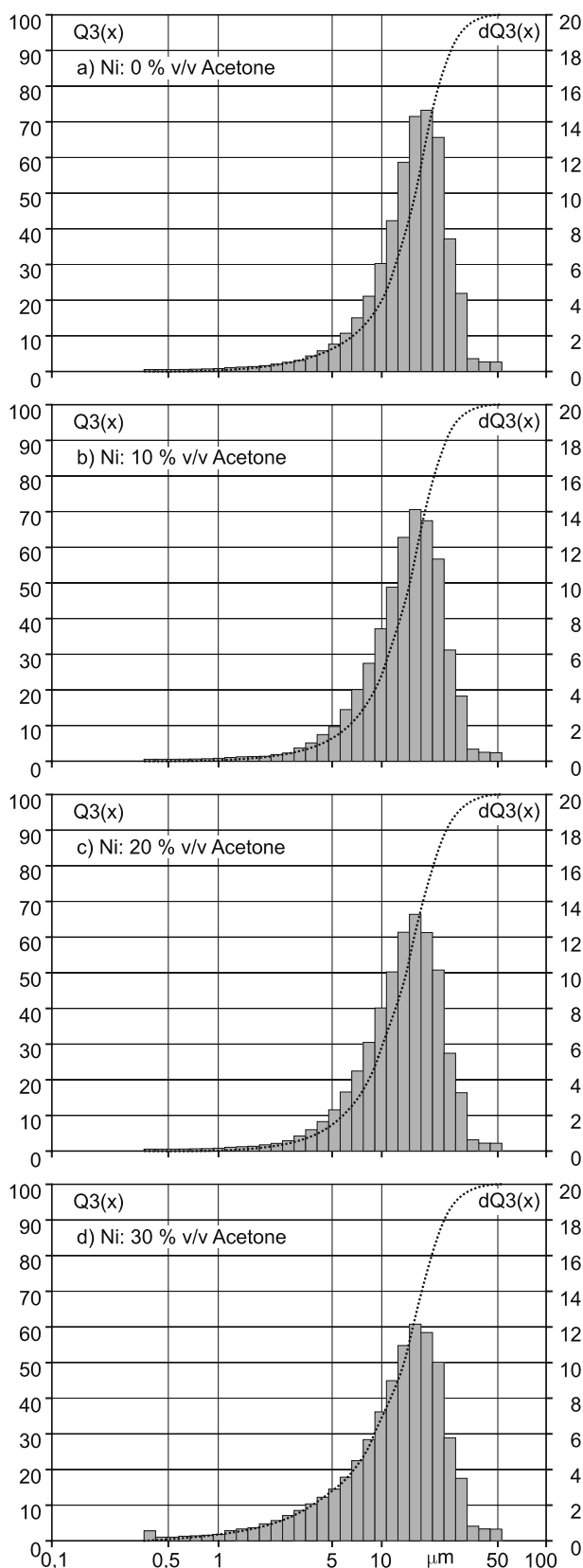


Figure 3. Distribution of particle size of nickel powder
Slika 3. Raspodjela veličina čestica praha nikla

15 % acetone concentration in the bath, the passivation at cathode takes place due to deposition of $\text{Ni}(\text{OH})_2$ at cathode and hence CE decreases [12].

Particle size analysis

The distribution of prepared nickel particle size is shown in Figure 3. and the data of distribution is tabulated in Table 1. As the concentration of the acetone increases in the bath solution, the average size of the nickel powder

Table 1. Particle size distribution
Tablica 1. Raspodjela veličine čestica

Acetone %	Particle size					% decrease in average particle size
	Fixed percent value (undersize) / μm					
	10 %	20 %	50 %	70 %	90 %	
0	6,63	9,75	15,73	19,55	25,75	-
10	6,40	9,06	14,68	18,54	24,58	6,67
20	5,91	8,39	13,99	17,89	23,94	11,06
30	4,01	6,89	13,47	17,72	24,08	14,36

decreases (Figure 4.). For 30 % V/V increase in acetone the average size of the metal powder decreases by 14,36 %. It is also observed that the decrease in the average particle size has the linear relation with the acetone concentration in the bath solution.

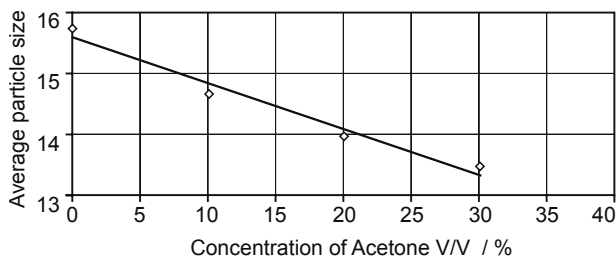


Figure 4. Average particle size and bath acetone concentration
Slika 4. Prosječna veličina čestica i koncentracija acetona u kupci

Morphological studies

SEM micrographs (Figure 5a, a', b, b', c, c') of nickel powder obtained from bath solutions having varying concentration of acetone were investigated. From Figure 5. one can observe that morphology of the nickel powder prepared in the same conditions changes, upon varying concentration of acetone and TBAC. Nickel powder obtained from the bath without any additive (Figure 5a, a') consists of rounded agglomerated patterns which changes to rounded and irregular for 10% V/V acetone concentration. The morphology shows small spherulites of diameter of about 4 μm . The size and shape of nickel powder can change with electrolytic condition but spherulites are usually present. Addition of acetone and TBAC

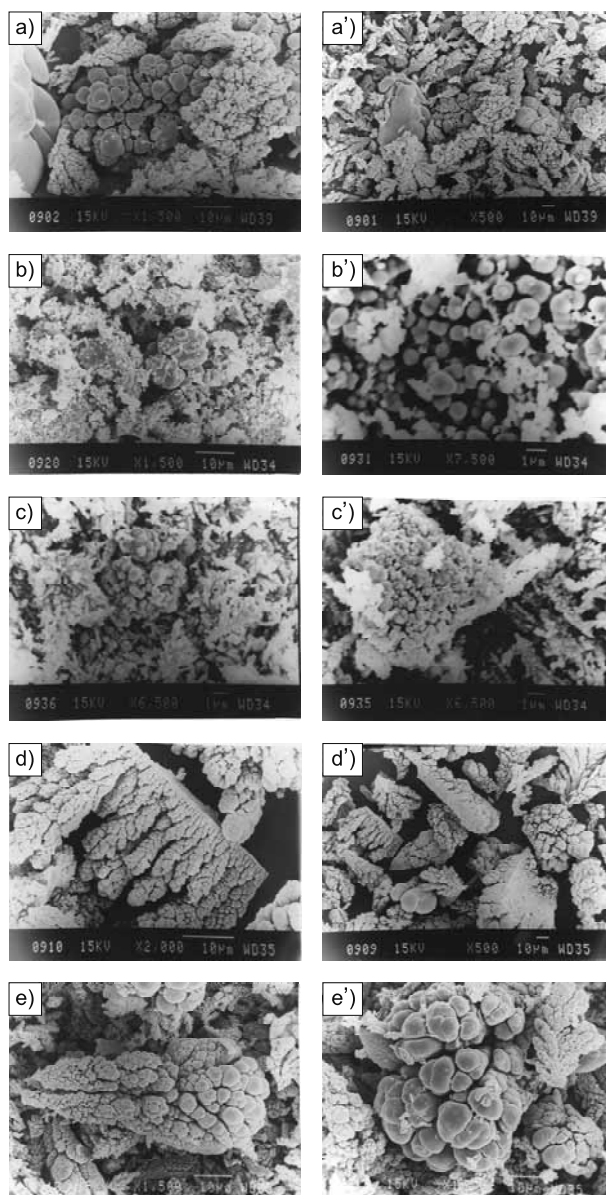


Figure 5. SEM micrographs of nickel powder obtained from bath solution with different additive concentrations: a), a') Bath without additive; b), b') Bath with 10 % V/V Acetone; c), c') Bath with 20 % V/V Acetone; d), d') Bath with 2,5g/l TBAC; e), e') Bath with 5 g/l TBAC

Slika 5. SEM mikrofografije praha nikla dobivenog iz kupke pri različitim koncentracijama dodatka: a), a') kupka bez dodatka; b), b') kupka s 10 % acetone; c), c') kupka s 20 % acetone; d), d') kupka s 2,5 g/l TBAC; e), e') kupka s 5 g/l TBAC

in bath solution has influence on spherulitic morphology observed for nickel powder. With 10 % acetone content the morphology presented the growth of dendrites. On increasing the acetone concentration to 20 % (Figure 5c, c') which spread over the surface. Surface becomes porous aggregated in structure. The spherulite diameter changes to minimum 2 μm . The morphology changes to sponge

or porous on 20 % V/V increase in the concentration of acetone. The morphological changes were also observed in the presence of Tribenzyl ammonium chloride (TBAC). With the addition of 2,5 g/l TBAC in the bath solution the morphology changes from dendritic and rounded to semi developed dendritic (Figure 5d, d'). But on increasing the concentration of TBAC to 5 g/l, the morphology of nickel changed to spherical aggregate (Figure 5e, e').

General chemical kinetics

During the electrowinning the kinetics of the electro-deposition of nickel was studied in presence of acetone. The plot of 'α' against time 't' (Figure 6a) shows linear relationship passing through origin which may be expressed as

$$\alpha = \frac{C_i - C_t}{C_i} = kt \tag{1}$$

where, C_i and C_t are initial concentration of Ni^{2+} and concentration of Ni^{2+} at time t respectively, m is the slope. The linear relationship indicates the electrodeposition

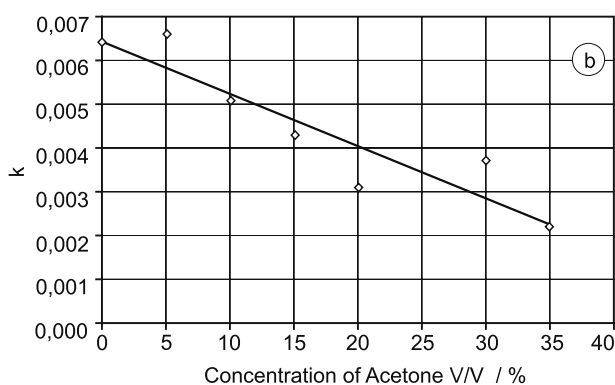
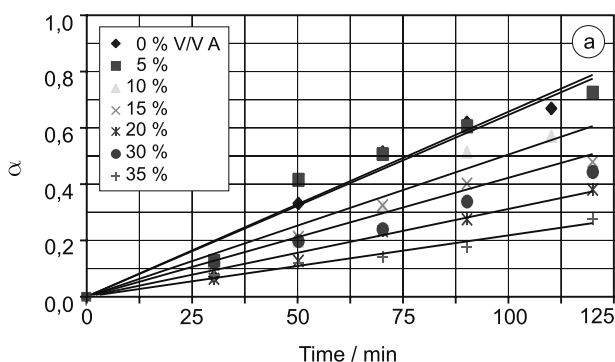


Figure 6. General chemical kinetics of powdered deposition of nickel

Slika 6. Opća kemijska kinetika praškastog taloga nikla

follows the zero order kinetics. The value of rate constant although decreasing with the increase in the concentration of acetone, the reaction follows the zero order reaction.

Plot of rate constant against concentration of acetone 'a' (Figure 6b) suggests that the rate constant is linearly related with concentration of acetone (equation (2)). Evidently the rate of electrodeposition depends on the concentration of acetone in the bath solution:

$$k = ma + c \tag{2}$$

Combination of equations (1) and (2) gives equation (3) as

$$\frac{C_i - C_t}{C_i} = (ma + c)t \tag{3}$$

where, 'c' is the intercept.

Thus equation (3) shows that kinetics of deposition depends not only on concentration of electrolyte but also on the concentration of acetone in the bath at fixed potential.

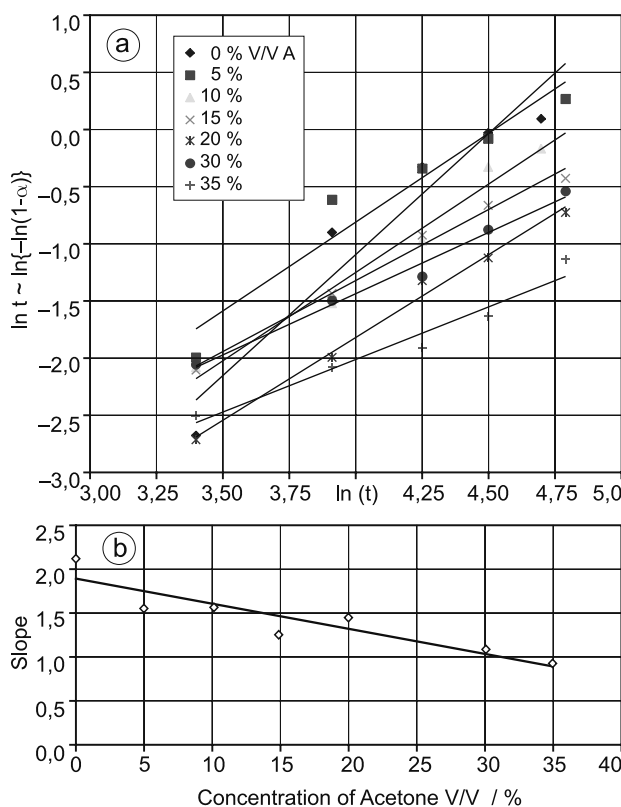


Figure 7. Avrami Erofeyev kinetics (n ~ concentration of acetone)

Slika 7. Avrami Erofejevova kinetika (n ~ koncentracija acetona)

Avrami - Erofeyev kinetics

The electrowinning kinetics of electrodeposition of nickel was also compared using Avrami - Erofeyev (AE) equation. The equation describing the kinetics is as follows:

$$1 - \alpha = e^{-kt^n}$$

$$\ln(1 - \alpha) = -kt^n$$

$$-\ln(1 - \alpha) = kt^n$$

$$\ln[-\ln(1 - \alpha)] = n \ln t + \ln k$$

where, $\alpha = \frac{C_i - C_t}{C_i}$, C_i is initial concentration of Ni^{2+} and C_t is concentration of Ni^{2+} at time t respectively. $\ln[-\ln(1 - \alpha)]$ was plotted against $\ln t$ (Figure 7.a) for various systems having varying concentrations of acetone up to 35 % V/V in the bath solution. The values of slope, n are given in the Table 2. Values of n decrease from 2,1242 for the system

Table 2. Relation of n value of Avrami - Erofejev graphs with morphology of Nickel powder

Tablica 2. Odnos vrijednosti n iz Avrami - Erofejev grafova i morfologije praha nikla

Acetone concentration in bath solution (% v/v)	n (from Avrami-Erofejev kinetics)	Morphology of electrodeposited nickel powder
without acetone	2,1242	dendritic, rounded agglomerated, sponge
5	1,5595	-
10	1,5466	rounded, irregular
15	1,2417	-
20	1,4538	sponge or porous, flaky
30	1,0751	-
35	0,9255	-

without acetone to 0,9255 for the system with 35 % V/V acetone indicating a prominent change in morphology of nickel powder. The morphology of nickel powder changes from rounded to porous and aggregate as the value of ' n ' decreases which is due to increase in acetone concentration in the bath solution. The decrease in the values of n has linear relation with increase in concentration of acetone.

Table 3. Effect of TBAC on morphology of nickel powder

Tablica 3. Utjecaj TBAC na morfologiju praha nikla

Amount of TBAC in Bath solution	Morphology of electrodeposited nickel powder
Without TBAC	dendritic, rounded aggregate, sponge
2,5 g/L TBAC	semi developed dendritic
5,0 g/L TBAC	rounded aggregate

CONCLUSION

The powdered deposition of nickel is favored by lower concentrations of Ni^{2+} and ammonium hydroxide.

With higher concentration of acetone current efficiency and particle size decrease. The decrease in stability with increase in concentration of acetone is due to decrease in average particle size of nickel.

From the morphological studies, it is observed that acetone free system produce powder of dendritic shape. The dendritic shape changes with increase in acetone to rounded and irregular shapes and at higher concentration of acetone it becomes porous or sponge. Addition of organic compound TBAC changes the morphology of nickel powder from dendritic to semi-dendritic at lower concentration of TBAC and at higher concentration it becomes rounded aggregate. From the slope versus acetone concentration plot in general chemical kinetics, we infer that increase in slope increases the dendritic shape to sponge or porous shape. Avrami - Erofejev kinetics indicates that n value ranges from 2,1242 to 0,9255 with increase in acetone concentration and the shape of nickel powder changes from dendritic to sponge or porous. As the slope of the graph of α against time increases with increase in acetone percent, average particle size decreases. The decrease in particle size has linear relation with percent of acetone added. The average particle size decrease is 14,36 % for 30 %V/V increase of acetone concentration.

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