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ELECTROWINNING OF ZINC FROM AMMONIA AND GLYCEROL BATH AND STUDY OF THE MORPHOLOGY OF ZINC DEPOSIT

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Abstract

Electrowinning of zinc from ammonia and glycerol with glycerol varying from 0 to 20% and ammonia from 0.5 to 1.5 N was studied. The zinc powder thus produced was studied for its morphology and particle size. The particles were spherical in shape with size varying from 2.63 to 79 μm, depending on the concentration of glycerol and the ammonia. The apparent density of zinc powder can be correlated to the particle size. Stability of the powder and current efficiency were also studied. A mathematical relation between apparent density, current efficiency, stability and kinetics of rate constant as a function of glycerol percent and ammonia concentration were presented.
Key words: electrowinning, zinc powder, stability, SEM, particle size, Avrami-Erofeyev kinetics

Introduction

Zinc is an important member of the nonferrous metal and mainly produced from sulfide, oxide and siliceous ores by pyro-metallurgical, hydro-metallurgical and electro-metallurgical techniques. About 80% of the world's zinc production is carried out by this technique. Guiirmen and Emre [1] studied the advantage of the alkaline electrowinng over the acidic electrowinning process as it reduces the energy cost. Brown et al. [2] studied alcaline leach and electrolysis process for zinc production which is found to be better than the conventional acid sulphate process in terms of energy saving and technical advantage. Tripathy et al. [3] investigated the effect of perfluro carboxylic acids on the electrowinning of zinc from sulphate solutions. Hewaidy et al. [4] reviewed the technology of electrodeposition of zinc produced from zinc dross. Beigler and Swift [5] studied the influence of oxygen reduction in the electrowinning of zinc, whereas Stephenson et al. [6] recovered zinc from waste water

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treatment sludge. Pande et al. [7] carried out a single cell extraction from zinc sulphide concentrate. Stefanov and Ivanov [8,9]studied the influence of nickel ions and triethylebenzyleammonium chloride on the electrowinning of zinc and electroextraction of zinc from sulfate electrolytes.

Viswanath et al**.** [10] studied the effect of acetone on the electrowinning process for preparing zinc powders. Recently, Viswanath and George reported preparation of cadmium [11] and copper [12] powders in sulphuric acid and glycerol medium and nickel [13] in ammonia and glycerol medium.

In the present work an attempt has been made to study the influence of glycerol and ammonium concentration on the electrowon zinc powder morphology and particle size. The density of the powder may be correlated with the particle size. An attempt was made to study Avrami-Erofeyev kinetics in order to relate the value of Avrami kinetics to the shape of the particles.

Experimental

Instruments

The bath solution contained ZnSO4 (0.05M), NH_4OH(0.5-1.5M), NH4Cl(0.05M) and glycerol (0-20 vol.%). The solution was transferred to a single compartment of two-electrode cell. 0.05M of NH4Cl is added to get a stable zinc-ammonia complex as well as to maintain common ion effect, Electrowinning experiments were performed using the zinc plate (6cm×1.5cm×1mm) as cathode and the gold plate of the same dimension as anode. Current was supplied by digital DC Power Supplier Model L3202 (Aplab). 0.5A of current was applied to the bath. The current variation was ± 0.01A. All experiments were carried out at the room temperature. The temperature of the bath remained almost constant during experiment.

The particle size analysis and scanning electron microscopy (SEM) studies were performed on Fritsch Particle Sizer-ANALYSETTE-22 and JEOL JAX, respectively. SEM operating at 15 kv was located at JNRDDC, Wadi, Nagpur.

Procedure

2 ml of bath solution was taken at 10 min intervals and analyzed for zinc. The kinetics of zinc deposition was studied by titration of the solution against 0.0M ethylenediaminetetraacetic acid (EDTA) using Eriochrome Black T (EBT) indicator. The deposition was continued for about 2-3 h to get sufficient quantity of powder for different types of analysis. The zinc concentration initially taken was 0.05M for all experiments. The percentage of glycerol and ammonium hydroxide concentration varied.

Determination of apparent density of zinc powder

The apparent density, d_a is given by the formula as

$$d_a = d_w(W_3 - W_1)/(W_2 - W_1 + W_4 - W_3) \quad (1)$$

where: W_1 – the mass of dry empty dry density bottle**;** W_2 – mass of density bottle with distilled water**;** W_3 – mass dry empty density bottle and nickel powder

(about 1 to 1.5g)**;** W_4 – mass of density bottle with nickel powder and distilled water**;** d_w – the density of water at that temperature.

Apparent density of nickel powder, obtained at different concentrations of ammonium hydroxide, and percent of glycerol are presented in Table 1. The apparent density, d_a**,** can be expressed as a function of concentration of ammonium hydroxide, c_a**,** and percent of glycerol, c_g**,** as**:**

$$d_a = 2.1c_a - 0.0602c_g + 8.071 \quad (2)$$

*Table 1. Apparent density of zinc at various concentration of **a**mmonium hydroxide and glycerol medium*

NH_4 OH Concentration (M)	Percent of glycerol (%)				
	0	5	10	15	20
	Apparent density of zinc (g/ml)				
0.5	7	6.8	6.4	6.1	6
1.0	6	5.8	5.4	5.1	5
1.5	4.9	4.7	4.3	4	3.9

Cathodic current efficiency (CE)

Study of C.E. was performed by measuring the zinc content in the bath solution. The deposited metallic zinc was estimated by titrating the bath solution against standard EDTA using EBT indicator. Based on the current applied for the particular period of time, the theoretically expected weight of zinc deposition is calculated using Faraday's Law:

$$W = Z\,It. \quad (3)$$

where**:** W, Z, I and are theoretically expected weight of zinc deposition, electrochemical equivalent of zinc, current in amperes and, time in seconds**,** respectively. The C.E. was calculated using the relation**:**

$$C.E = (w/W) \times 100 \quad (4)$$

where: w – the weight of the zinc deposited in the actual practice.

The CE data are presented in Table 2. The CE can be expressed as a function of concentration of ammonium hydroxide, c_a and percent of glycerol, c_g**,** as:

$$CE = -(0.51c_g + 5.8)c_a + 77 \quad (5)$$

Table 2. Cathodic current efficiency of zinc winning process at different concentrations of ammonium hydroxide and glycerol medium

NH_4 OH Concentration (M)	Percent of glycerol (%)				
	0	5	10	15	20
	Cathodic current efficiency (%)				
0.5	74	72.5	71.8	70.3	69
1	71	68.9	66.5	64.7	60.4
1.5	68	64	61	57.3	52.5

Determination of oxidative stability of zinc powder

Zinc powder was kept for forty-five days in an air tight sealed bottle. About one gram of zinc powder was taken in 100 ml 0.1M nitric acid. The solution was stirred with a magnetic stirrer for 1 h. The solution was filtered and the dissolved zinc in the filtrate was estimated by titration of the solution against 0.0M ethylenediaminetetraacetic acid (EDTA) using Eriochrome Black T (EBT) indicator. The zinc powder is susceptible to oxidation and forms zinc oxide (ZnO). The stability of zinc was estimated using the formula:

$$Stability = \frac{\text{Weight of metallic powder undissolved}}{\text{Weight of metal powder taken}} \times 100 \quad (6)$$

The data are presented in the Table 3. The stability of the powder can be expressed as a function of concentration of ammonium hydroxide, c_a and percent of glycerol, c_g, as:

$$OS = + 59.784c_a^{-0.193} - (0.048ca^2 + 0.1c_a + 0.48)c_g \quad (7)$$

$$OS = -0.669c_g + 59.987 - (0.184c_g + 11.89)\ln(c_a) \quad (8)$$

Table 3. Stability of zinc powder obtained at various concentrations of ammonium hydroxide and glycerol medium

NH_4OH Concentration (M)	Percent of glycerol (%)				
	0	5	10	15	20
	Stability of the powder (%)				
0.5	68.3	65.5	63	60,2	57.4
1	60	56.2	53.1	49.7	46.3
1.5	55.2	51.4	48.3	44.1	40.4

Results

Mechanism of reactions during electro deposition of zinc

The important reactions and electrode reactions during the electrowinning process are given below.

$$4H_2O \rightarrow 4H^+ + 4OH^- \quad (9)$$

$$ZnSO_4 \rightarrow Zn^{2+} + SO_4^{2-} \quad (10)$$

$$2H^+ + SO_4^{2} \rightarrow H_2SO_4$$

Zinc ion reacts with ammonia and gives complex ion

$$Zn^2 + 4NH_4OH \rightarrow [Zn(NH_3)_4]^{2+} + 4H_2O \quad (11)$$

The reactions at cathode may be described as follows:

$$[Zn(NH_3)_4]^{2+} + 4H_2O + 2e \rightarrow Zn + 4NH_4OH \quad (12)$$

$$2H^+ + 2e^- \rightarrow H_2$$

The net reaction at cathode is:

$[Zn(NH_3)_4]^{2+} + 2H^+ + 4e + 4H_2O \rightarrow Zn + H_2 + 4NH_4OH$ *(14)*

The reaction at anode is**:**

$4OH^- \rightarrow 2H_2O + 2O + 4e^-$ *(15)*

$2O \rightarrow O_2$ *(16)*

The net reaction at anode was

$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$ *(17)*

The overall reaction is:

$[Zn(NH_3)_4]^{2+} + 2H^+ + 4HO^- + 2H_2O \rightarrow Zn + H_2 + O_2 + 4NH_4OH$ *(18)*

$H_2SO_4 + 2NH_4OH \rightarrow (NH_4)_2SO_4 + 2H_2O$

The reaction follows zero order kinetics and hence the rate law is independent of zinc ion concentration. This is shown in the kinetic studies. While liberated oxygen at anode reacts with glycerol and forms several products, the two primary alcoholic groups in glycerol are capable of being oxidized to aldehyde and then to the carboxyl group**:**

$CH_2OH\text{-}CHOH\text{-}CH_2OH \rightarrow CHO.CHOH\text{-}CH_2OH \rightarrow COOH.CHOH\text{-}CH_2OH \rightarrow$

(glycerol) (glyceraldehydes) (glyceric acid)

$COOH.CHOH\text{-}COOH \rightarrow COOH.CO - COOH$ *(19)*

(tartonic acid) (mesoxalic acid)

The secondary alcoholic group is oxidized to carbonyl group following the reaction:

$CH_2OH\text{-}CHOH\text{-}CH_2OH \rightarrow CH_2OH\text{-}CO\text{-}CH_2OH \rightarrow COOH.CO - COOH$ *(20)*

(glycerol) (dihydroxy acetone) (mesoxalic acid)

Particle size analysis

The distribution of zinc particle size is shown in Fig. 1, whereas the data of distribution are shown in Table 4. With 15% glycerol in the bath solution, the cumulative frequency of particle size decreases by about 5.42 %. It is also observed that the concentration of ammonia in the range from 0 to 1.0 N and glycerol in 5 to 10% range yields nano-sized particles. This is evident from the SEM studies.

Table 4.Particle size of zinc in different concentrations of NH_4OH and glycerol medium

Concentration NH_4OH(M) + glycerol (%)	Particle size of Zn (μm) with cumulative frequency (%)				
	0.89-10.13	10.13-22.59	22.59-69.43	69.43-95.7	95.7-131.9
0.5+ 0	23.82	24.09	46.01	4.06	2.02
0.5 + 5	19.38	15.99	50.28	8.47	5.88
1.0 + 10	35.53	27.8	33.79	1.61	1.27
1.0+ 20	25.31	24.66	48.82	1.00	0.21

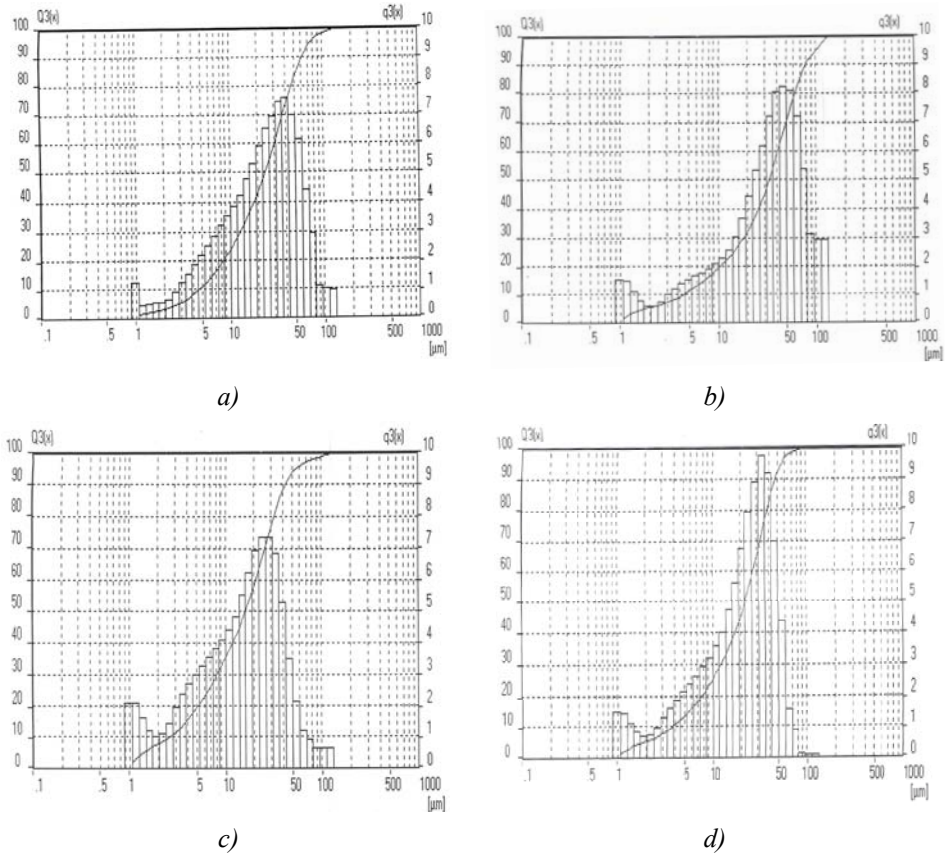


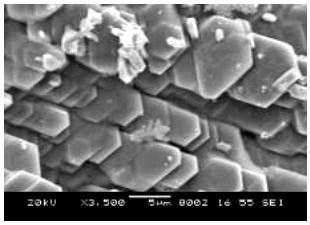
Fig.1 Distribution of particle size of zinc powder obtained from different media (a) 0.5M NH_4OH +0 % glycerol; (b) 0.5M NH_4OH + 5 % glycerol; (c) 1M NH_4OH +10% glycerol; (d) 1M NH_4OH + 20% glycerol

Morphological Studies

SEM micrographs of zinc powder are investigated and micrographs are presented in Fig. 2. The morphology of the powder and relevant physical data of respective powders are presented in Table 5. These data show some sort of relationship between these properties and morphology of electrodeposited powders.

Table 5.Morphology of zinc powders and related data.

NH_4OH concentration and % glycerol	Apparent density (g/ml)	Stability	Morphology of electrodeposited powder
0.5M + 0%	7.3	70.2	Hexagonal, dendrites
0.5 M +5%	6	65.5	Hexagonal spherical
1 M + 10%	4.2	56.2	Spherical, dendrites
1M + 20%	2.5	46.3	Spherical



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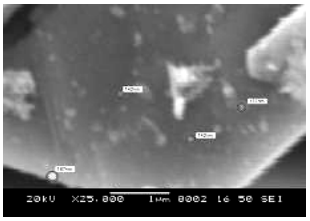

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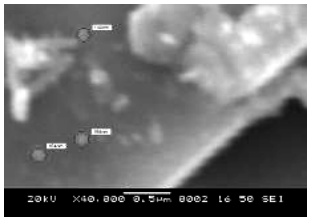

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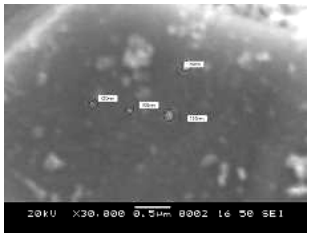

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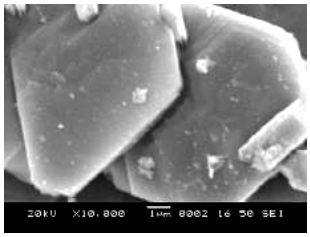
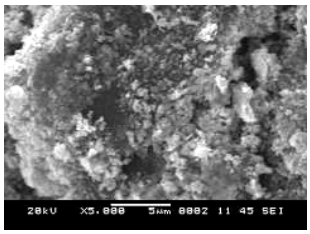


a6)

0.5M NH_4OH + 0% glycerol



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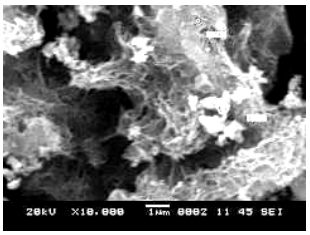

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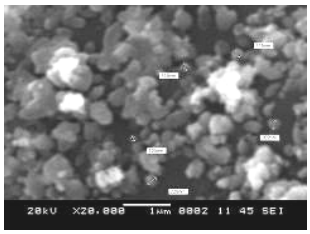

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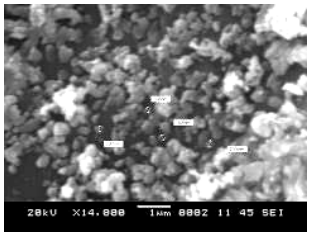

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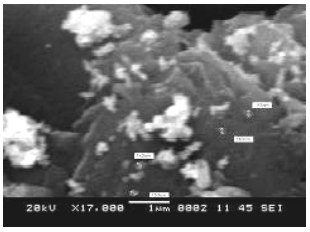

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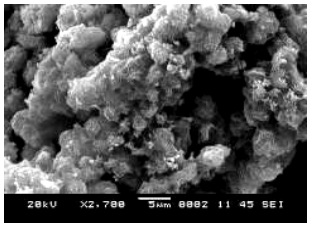
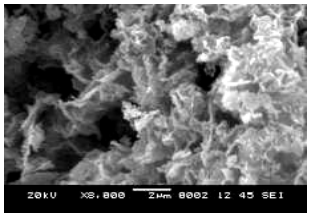
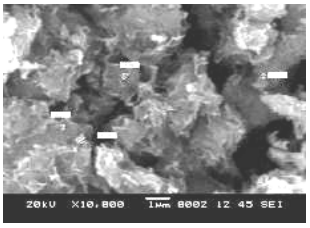


b6)

0.5 M NH_4OH + 5 % glycerol



c1)



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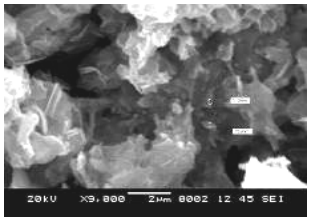

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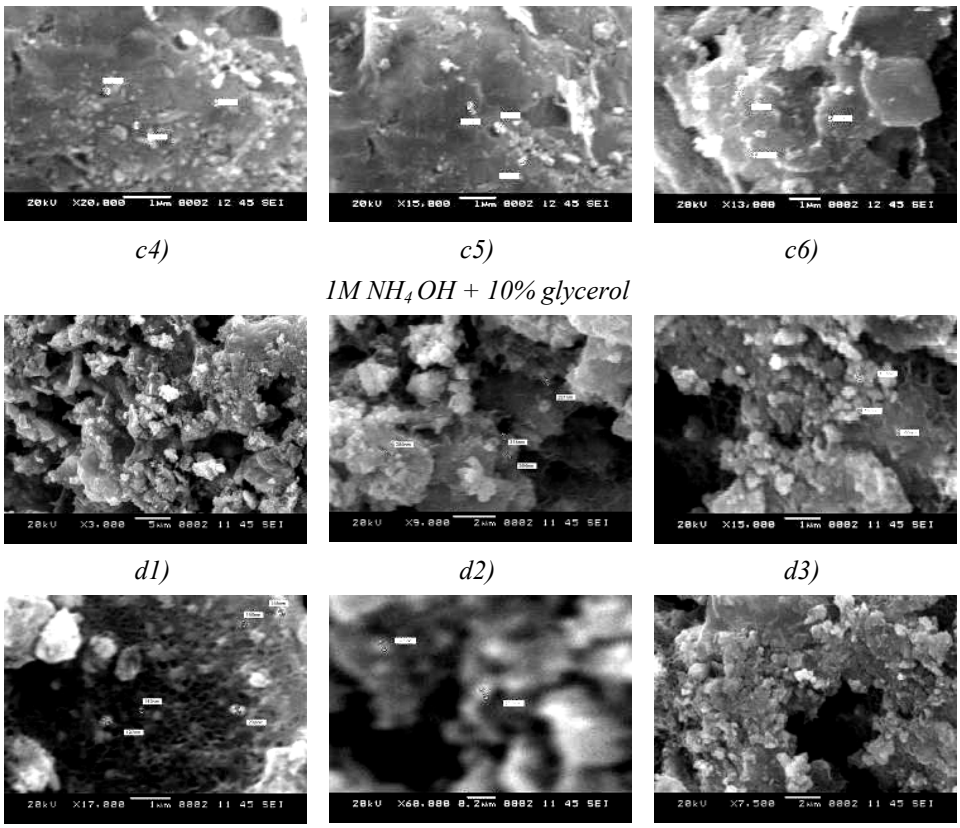

c4) *c5)* *c6)*

1M NH_4OH + 10% glycerol

d1) *d2)* *d3)*

d4) *d5)* *d6)*

1 M NH_4OH + 20 % glycerol

Fig.2 SEM micrographs of zinc powder obtained from different media (a) 0.5N NH_4OH +0% glycerol; (b) 0.5N NH_4OH + 5% glycerol; (c) 1M NH_4OH + 10% glycerol and (d) 1M NH_4OH + 20% glycerol

Kinetics of electrodepositon of zinc

Chemical kinetics

α, the fraction deposited is defined as:

$$\alpha = C_t / C_i \qquad (21)$$

where: C_i and C_t are initial concentration and concentration of Zn^{2+} at any time t**,** respectively. (1-α) is the fraction of zinc metal deposited. The rate of change of concentration with respective time is written as:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \qquad (22)$$

where: n and k are order of reaction and reaction rate constant**,** respectively. For zero order reaction, n=1, and the integrated form of the above equation may be written as

$$\alpha = kt. \qquad (22)$$

Plot of α against time, t, gives a linear plot passing through the origin with the slope equals to k. Fig. 3(a-c) are the zero order plots for the electrodeposition of zinc in different concentration of ammonium hydroxide and volume percent of glycerol.

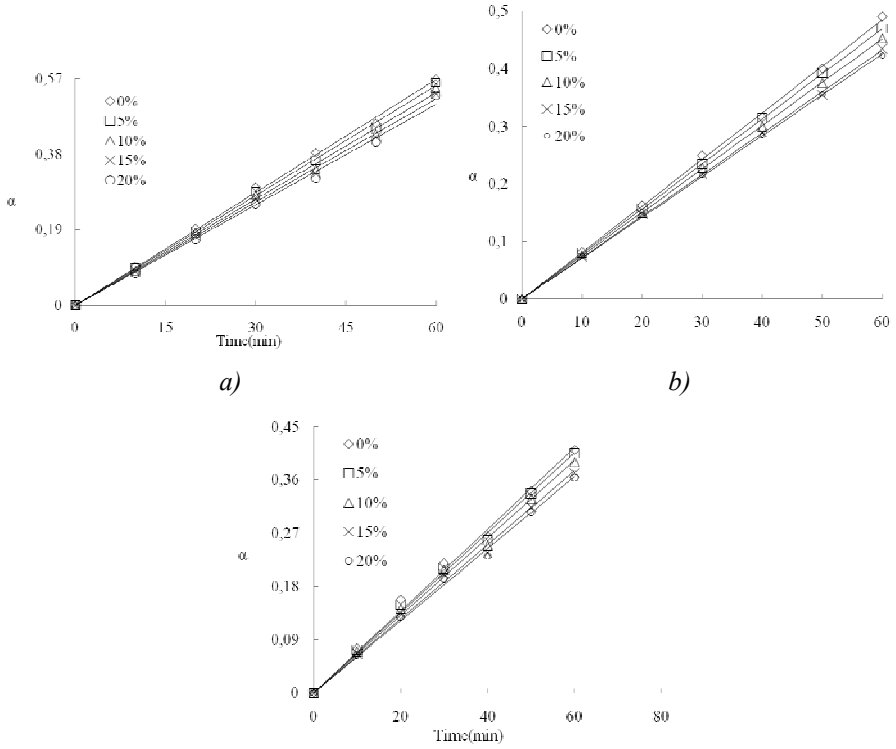

Fig 3 Plot of α against time in a) 0.5N NH_4OH, b) 1.0N NH_4OH c) 1.5N NH_4OH and different percent of glycerol

In the Table 6 the k values are given. The rate of deposition is independent of the zinc ion concentration. The rate constant can be expressed as a function of ammonia concentration and percentage of glycerol as:

$$k = (2c_a - 7) \times 10^{-5} c_g - (0.0026c_a - 0.0018) \qquad (23)$$

Therefore eq. (22) may be written as:

$$\frac{d\alpha}{dt} = \{(2c_a - 7) \times 10^{-5} c_g - (0.0026c_a - 0.0018) \qquad (24)$$

This may be written in terms of rate constants as:

$$\frac{d\alpha}{dt} = \{k1ca\ cg - k2cg - k3ca + k4\} \quad (25)$$

where: $k_1=2\times10^{-5}$, $k_2=7\times10^{-5}$, $k_3=0.0026$ and $k_4=0.0018$.(25)

Since α is related to time, t, α can be written as:

$$\alpha = \{(2c_a - 7) \times 10^{-5} c_g - (0.0026c_a - 0.0018)\}t. \quad (26)$$

Table 6. Reaction rate constants of the electrodeposition kinetics

NH_4OH concentration (M)	Percent of glycerol(%)				
	0%	5%	10%	15%	20%
	Reaction rate constant(min^{-1})				
0.5	0.0095	0.0092	0.0089	0.0086	0.0084
1.0	0.0081	0.0078	0.0075	0.0072	0.0071
1.5	0.0069	0.0068	0.0065	0.0064	0.0061

Avrami-Erofeev kinetics

The chemical kinetics of electrodeposition of zinc is tried to correlate with Avrami-Erofeev kinetics. Avrami-Erofeev kinetics gives some clue about the morphology and size of the particle. The equation is given below:

$$(1-\alpha) = exp(-\kappa t^n) \quad (27)$$

and the logarithmic form of equation is written as:

$$ln\{-ln(1-\alpha)\} = n\ ln\ (t) + ln\ (\kappa) \quad (28)$$

where: n and κ are order of reaction and rate constant of the reaction respectively. Plot of ln{-ln(1-α)} against ln(t) gives a straight line with slope equals to n and intercept equals to ln(κ). The plots are shown in Fig. 4(a-c) for the electrodeposition of zinc in different concentration of ammonium hydroxide and volume percent of glycerol. n and ln(κ) and values are given in Table 7.

Table 7. Avrami-Erofeev kinetic constants

% glycerol	Ammonium hydroxide concentration					
	0.5 M		1 M		1.5 M	
	n	ln(κ)	n	ln(κ)	n	ln(κ)
0	1.145	-4.94	1.345	-5.502	1.07	-5.018
5	1.163	-5.038	1.128	-5.115	1.048	-5.0
10	1.175	-5.129	1.127	-5.164	1.05	-5.04
15	1.171	-5.156	1.105	-5.144	1.044	-5.073
20	1.188	-2.252	1.095	-5.114	1.05	-5.13

Further, n and κ can be expressed as a function of ammonia concentration and percent of glycerol as:

$$n = (0.0078c_a^2 - 0.0189c_a + 0.0091)c_g + (-0.0936\,c_a^2 + 0.1c_a + 1.1296) \quad (29)$$

$$\kappa = (-22.62ca2 + 51.77\,ca - 30.29)10\text{-}5cg + (0.0034ca2 - 0.0071\,ca + 0.0098) \quad (30)$$

However, these equations are not very accurate.

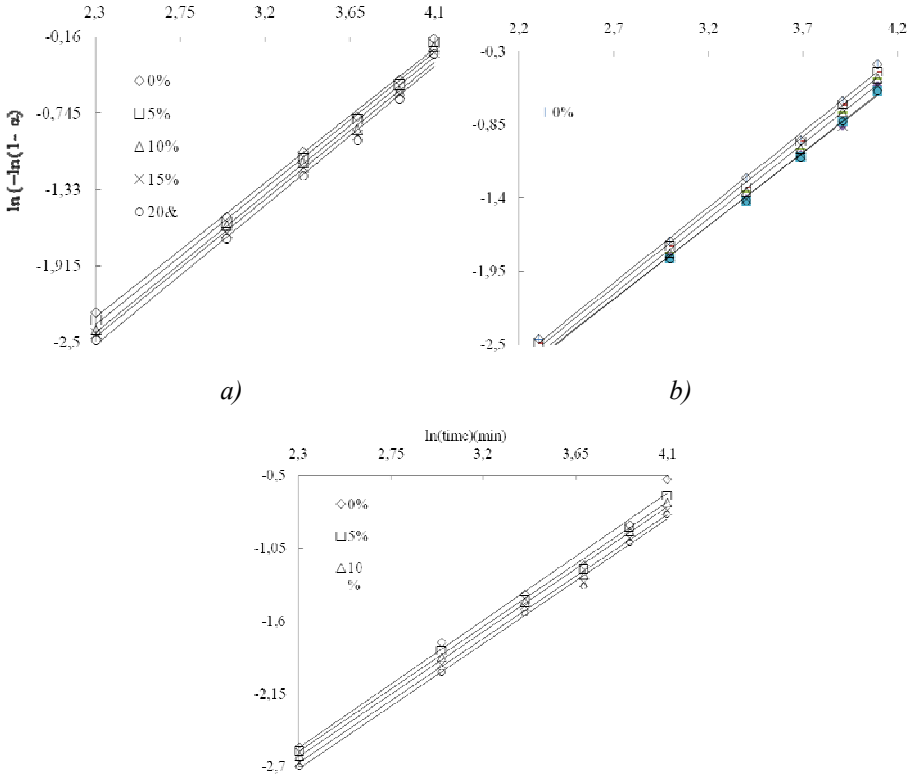

Fig 4. Plot of ln{-ln(1-α)}against ln(time) in a) 0.5M NH_4OH, b) 1.0M NH_4OH c) 1.5M NH_4OH and different percent of glycerol

Discussion

The apparent density decreases with increasing percent of glycerol as well as ammonium hydroxide concentration. The increase in concentration of glycerol and ammonium hydroxide decreases the percent of dendrites in the powder. The Avrami-Erofeev n value is almost 1, and does not vary with the percent of glycerol and ammonium hydroxide concentration. This is an indication that particles are of two dimensional in nature. 0% glycerol and 0.5M ammonium hydroxide concentration produce the powder which contains more of hexagonal and less of weakly bonded dendrites. When the rate of deposition of zinc is slow these types of particles are

produced as is evident from the chemical kinetics as well as from the Avrami-Erofeev kinetics. Decrease in the rate constant in both cases can be attributed to the decrease in the ion environment or low ion strength due to the presence of glycerol molecules in the solution medium. In the electrolysis, all positive ions are aligned and migrate towards cathode, while negative ions migrate towards anode. The metal ions are discharged at the cathode. The solid metal atoms deposited in this manner on the cathode should have a strong metallic bond. When an electrolyte solution containing organic solvents, which are covalent in nature, disturbs this ion environment particularly at cathode causing lose bonding between metal-metal atoms. A large amount of hydrogen liberated at cathode also makes the deposit porous.

When the percentage of glycerol is increased to 5%, the powder contains about 62% of particles with 39.73 μm in size and above 35% of particles with 20.91 μm. However 50% particles have an average size of 33.84 μm. The majority of powder particles are of spherical and hexagonal shape.

It is found that increasing in the percentage of glycerol and ammonium hydroxide in the medium reduces the oxidative stability of the powder .This may be due to the decrease in the particle size of the powder. Generally, spherical particles have small size because of strong interatomic forces holding the particle firmly together. In the present case the particles have small size and large surface area because of the increased percent of spherical particles which accounts for a decrease in the oxidative stability of the powder.

When the concentration of glycerol is increased to 10% and ammonia to 1M there is a considerable decrease in the average size of particles. The size of 70% of particles is 24.55 μm, whereas the size of 30% of particles is only 7.99 μm. However, an average size of 50% of particle is 15.17 μm. SEM studies of these powders revealed that most of particles are spherical in shape along with a low percentage of hexagonal and weakly bonded dendrites.

Keeping the concentration of ammonia at 1M and increasing the medium concentration of glycerol to 20% in bath produces 75% of particles with 33.84 μm size and 25% of particles with size of 9.38 μm. On an average 50% of particles are found to be 20.91 μm size. SEM studies revealed that most of the particles are spherical along with a low percentage of sponge or agglomerates. SEM micrographs show nano-particles in the samples, particularly in those having high percentage of glycerol such as 10 and 20%. The apparent density studies show a decrease with increase in the concentration of glycerol. Decrease in apparent density causes increase in the fraction of nano-particles in the sample as well as a decrease in the nano-particle size. The decrease in cathodic current efficiency is due to electrolysis of water as well as low ionic strength of the medium.

The equation 2 can be used for setting the conditions to prepare a powder of desired density. The equation 23 may be considered as rate law which is the function of ammonia concentration and percentage of glycerol. The equation 24 gives an idea about fraction of powder deposited at a given time.

Conclusions

It may be concluded that electrowinning process in with 10 to 20 % glycerol and 0.5M to 1M ammonium hydroxide produces 99% of particles with size below 100 μm.

The applied current strength should not exceed 0.5 A. The large current densities warm the solution and the bath temperature rises, as well as the deposition of the powder. It may be assumed that the slower rate of deposition of powder is an important factor influencing the deposition of powders with good combination of size and shape.

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