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ELECTROWINNING OF ZINC FROM AMMONICAL MEDIUM IN PRESENCE OF ACETONE: THE MORPHOLOGY OF THE POWDER AND KINETIC STUDIES OF THE ELECTRODEPOSITION

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Abstract

The electrodeposition of zinc from sulphate bath was studied in ammonical medium. The electrolytic conditions for zinc deposition were optimized at room temperature. The effect of acetone on current efficiency, morphology, stability and particle size of deposited zinc powder was studied. The current efficiency as well as stability of the electrolytically deposited zinc powder was found to decrease with increase in acetone concentration. The distribution of particle size of zinc powder and SEM results were presented for those powders obtained from ammoniac-acetone medium and also with the organic additive, triethylbenzyl ammonium chloride (TEBAC). The optimized operating parameters for powder preparation are presented. The average particle size of the deposited powder was found to decrease with increase in of acetone concentration. The Avrami-Erofeyev kinetic parameters were determined. The kinetic order of the process increases with the increasing concentration of acetone.

Key words: electrowinning, zinc powder, powder metallurgy, electrometallurgy

Introduction

Metal powders are used in wide variety of applications which include dietary supplements in the food processing, as an additive in paints and surface coatings, as pigments in printing and packaging, in solid fuels and cements etc. A number of patents on metal powder fabrication processes have been taken during the early decades of twentieth century. Iron, copper, zinc and titanium are the most studied metals [1-6].

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The research on production of iron and alloy powders with qualitative improvement is at its pace [7]. Zinc has many industrial applications. The practical utilization of zinc powder is related to chemical activity. Zinc powder is mainly consumed in chemical and metallurgical industries. The electrowinning of zinc was carried out in a specially designed EMEW®_cell by Tresure [8]. This has certain advantages like increase in the current efficiency even at low electrolyte concentration. The zinc powder was obtained with purity higher than 99.5%. Saba and Elsherief [9] made an extensive study on continuous electrowinning of zinc from laboratory leached oxidize zinc ore. They have also studied the effect of organic additives like gelatin, thiourea and foreign cations like copper and iron on the current efficiency and morphology of the zinc deposit. Ivanov and Stefanov [10] studied electro-extraction of zinc from sulphate electrolyte containing antimony and hydroxyethylated-butyne-2-diol-1,4 with a specpure aluminum cathode. In our earlier work, we have studied the effect of acetone on production of nickel [11], cadmium [12] and copper [13] powders by electrowinning method

An attempt has been made in this paper to present the electrolytic method of zinc powder preparation from sulphate bath in aqueous ammonical-acetone medium. The paper also describes the effect of acetone at the optimized operating conditions for zinc powder preparation on current efficiency, stability, the particle size distribution and the surface morphology of the deposited powder.

Experimental

The experiments were carried out in a three electrode glass cell without stirring of the electrolyte (800 ml). Stainless steel (1.5 cm × 9 cm × 0.15 cm) served as a working electrode (cathode), graphite electrode (2.5 cm × 2.5 cm × 9 cm) as counter electrode (anode) and saturated calomel electrode as reference electrode. Before electrolysis cathode was polished with emery paper and washed with water and acetone and dried. Constant potential was supplied by using Potentiostat (model 1399) fabricated by CECRI, Karaikudi, (A CSIR Laboratory of India).

The temperature was kept constant at ($30 \pm 1^{o}C$). Bath solution consisted of an alkaline solution of $ZnSO_4.6H_2O$ (0.04M), NH_4OH (~1.4M) and NH_4Cl(0.05). The effect of acetone on the nature of zinc deposition was studied by varying the concentration of acetone from 5 to 30%, volume acetone in 100 ml of solution. The kinetics of deposition of zinc was studied by withdrawing 1ml of bath solution at 10 minutes interval and analyzed for zinc by ethylenadiaminetetra acetic acid (EDTA) titration method using Erichrome Black-T as indicator.

The electrolytic deposition was continued for 90 minutes. The zinc powder was removed from electrode**,** dried at 45 to 50^{o} C in a vacuum oven for about 15 to 20 minutes and kept in a desiccator, then particle size, morphology and stability were analyzed.. The particle size and morphological analysis was performed on Fritsch particle sizer -ANALYSETTE 22 and scanning electron microscope (SEM**)** JEOL, JXA 240A operated at 15 kV respectively at JNARDDC, Wadi, Nagpur, India.

Results

Electrode reactions and zinc powder formation

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

$$4H_2O \rightarrow 4H^+ + 4OH^- \tag{1}$$

$$ZnSO_4 \rightarrow Zn^{2+} + SO_4^{2-} \tag{2}$$

$$2H^+ + SO_4^{2} \rightarrow H_2SO_4 \tag{3}$$

Zinc ion reacts with ammonia and gives complex ion**:**

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

The reactions at cathode are:

$$[Zn\ (NH_3)_4]^{2+} + 4H_2O \rightarrow Zn^{2+} + 4NH_4OH \tag{5}$$

$$Zn^{2+} + 2e^- \rightarrow Zn \tag{6}$$

$$2\ H^+ + 2e^- \rightarrow H_2 \tag{7}$$

The net reaction at cathode is:

$$[Zn\ (NH_3)\ _4]^{2+} + 2H^+ + 4e + 4H_2O \rightarrow Zn + H_2 + 4NH_4OH \tag{8}$$

The reaction at anode is**:**

$$4OH^- \rightarrow 2H_2O + 2O + 4e^- \tag{9}$$

$$2O \rightarrow O_2 \tag{10}$$

The net reaction at anode is:

$$4OH^- \rightarrow 2H_2O + O_2 + 4e^- \tag{11}$$

The overall reaction is**:**

$$[Zn\ (NH_3)4]^{2+} + 2H^+ + 4HO^- + 2H_2O \rightarrow Zn + H_2 + O_2 + 4NH_4OH \tag{12}$$

$$H_2SO_4 + 2NH_4OH \rightarrow (NH_4)_2SO_4 + 2H_2O \tag{13}$$

The rate law follows zero order kinetics. Viswanath and George [14,15] also observed that the kinetic of electrowinning of cadmium and copper from glycerol and sulphuric acid medium follow zero order. Since a large amount of atomic hydrogen is liberated the rate low does not depend on the hydrogen and also independent of the concentration of zinc ions. 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.

The evolution of hydrogen at cathode makes zinc deposition loose and porous, and it can be easily scraped out by water blowing. According to reaction (14) the oxygen evolution at anode oxidizes acetone to acetic acid and formic acid due to which basicity of bath solution decreases as the electrowinning progresses.

$$CH_3COCH_3 \xrightarrow{[O]} CH_3COOH + HCOOH \tag{14}$$

Oxidative stability of zinc powder

The stability of the powder was studied after 15 day of storing in an air tight bottle. stability of zinc powder was determined by dissolving 0.5 g of zinc powder in 100 ml 0.1 M sulphuric acid and dissolved zinc was estimated by complexometric titration using EDTA method. Percent of oxidative stability was calculated by the following equation:

$$\text{Oxidative Stability} = \frac{\text{Weight of zinc taken - Loss in weight of zinc}}{\text{Weight of zinc taken}} \times 100 \qquad (15)$$

The oxidative stability data is presented in the Table 1.When the acetone percent is in the range of 0-15% the stability of the powder is around 97%.. But, with the increase of acetone percent from 20 to 30 in the solution the stability of the powder decreased to 82.86% then to 81.34 % respectively. This may be due to the smaller particles .which have larger surface area. If the surface area of the powder is large the particles are susceptibility to oxidation and hence oxidative stability of the powder decreases. The oxidative stability decrease is presented in Fig.1.

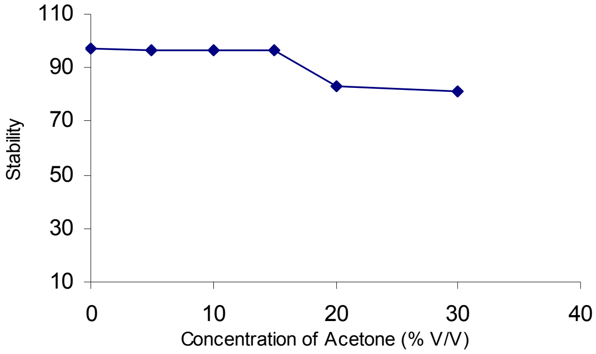


Fig. 1 Plot of stability against % acetone

Cathodic current efficiency

In the Table 1 the current efficiency data is presented. Due to the presence of acetone which is not an electrolyte the ionic environment decreases in solution. The oxidation of acetone forms formic acid and the acetic acid, which are weak electrolytes. The conductance of solution decreases with the increase in percent of acetone. This slows down the movement of the cations towards cathode resulting in low current efficiency. Percent of acetone against the current efficiency plot is shown in the Fig. 2.

Table1. C E and Stability of Zinc Powder

Concentration of acetone, %	Current Efficiency	Stability	Rate Constant, k
0	55.7	97.4	0.0146
5	46.3	96.6	0.0134
10	46.6	96.7	0.0118
15	48.7	96.4	0.0122
20	46.8	82.9	0.0129
30	40.8	81.3	0.0108

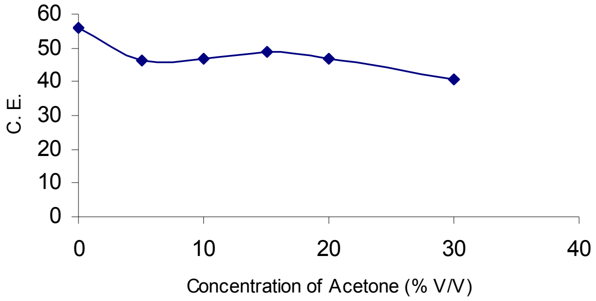


Fig. 2 Plot of current efficiency (C.E.) against % acetone

Particle size analysis

The distribution of particle size of zinc powder is shown in Fig.3 and the particle size distribution data is presented in Table 2. As the concentration of the acetone increases in the bath solution, the average particle size of the zinc powder decreases which is presented in the Fig. 4. Results of Fig. 4 show that the average particle size decreased with the increase in the acetone concentration.

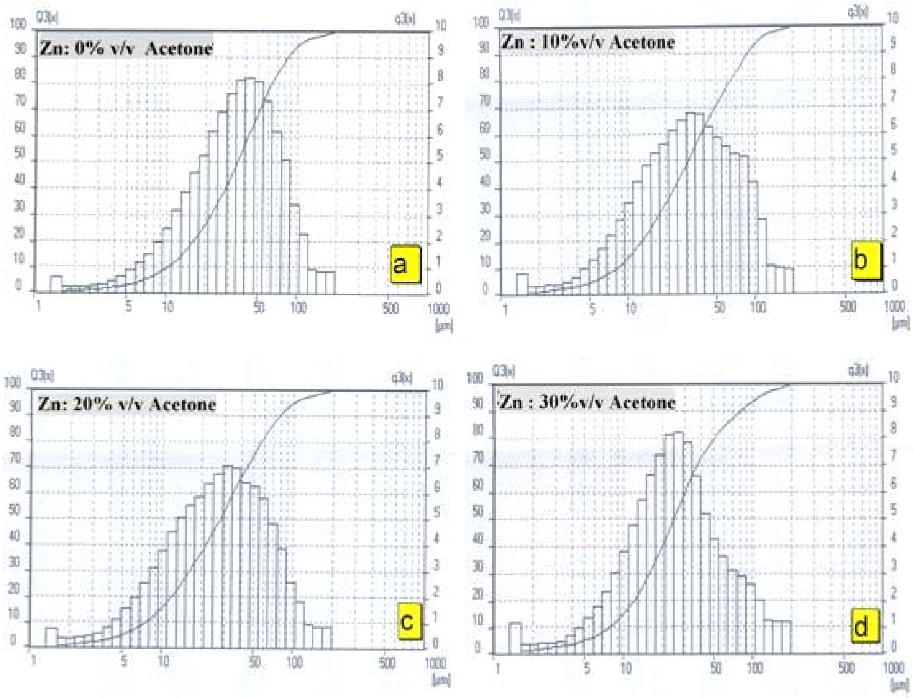


Fig. 3: Distribution of particle size of zinc powder
a) Bath without additive, b) Bath with 10 % acetone, c) Bath with 20 % acetone, d) Bath with 30 % acetone

Table 2. Particle Size Distribution

Acetone concentration, %V/V	Fixed percentage value (undersize), µm					% decrease in average particle size
	10%	20%	50%	70%	90%	
0	10.14	15.14	34.91	47.92	84.27	
10	8.26	12.01	30,05	45.45	88.62	13.9
20	7,61	11.32	27.71	41.44	78.31	20.6
30	7.82	7.88	24.66	35.19	90.75	29.4

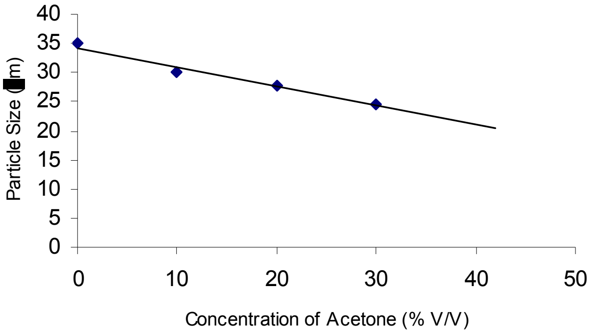
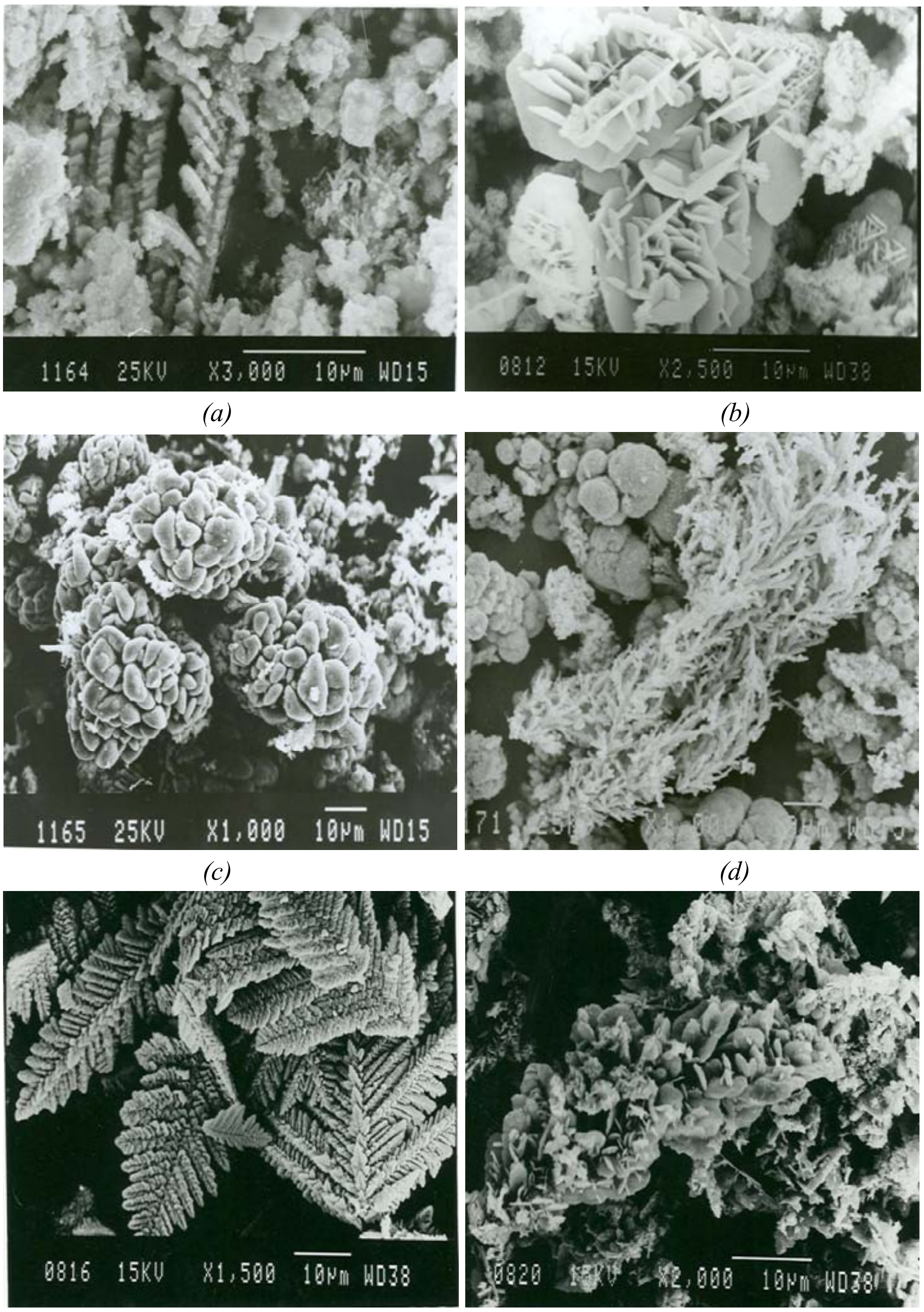


Fig. 4 Plot of average particle size against % acetone

Morphological studies

SEM micrographs of zinc powder obtained from different acetone solution concentrations are presented in Fig 5a-f. It may be observed from Fig.5 that the morphology of the zinc powder changes, upon addition of acetone and triethylbenzyl ammonium chloride (TEBAC) in bath solution. Zinc powder prepared without any additive shown in the Fig. 5a consists of flaky built patterns. For the zinc powder prepared in bath with 10%V/V acetone concentration the shape of powder changes to globular, agglomerated and less flaky as shown in the Fig.5b. Increasing the acetone concentration to 20%, the flaky nature disappears as shown in the Fig.5c. With further increase in concentration of acetone to 30% V/V the formed powder shows dendritic and globular structure (Fig 5d). Thus, a sharp change in morphology was observed with various concentration of acetone. The sequence of change in the morphology of the zinc powder may be described as follows: flaky powder → underdeveloped dentritic → globular → dentritic, when the bath acetone concentration was 0, 10, 20 and 30% V/V respectively.



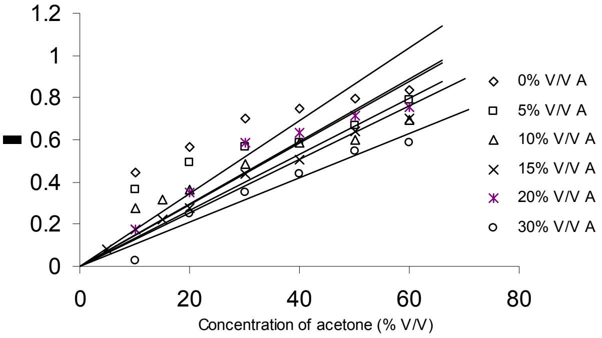
(a) (b)

(c) (d)

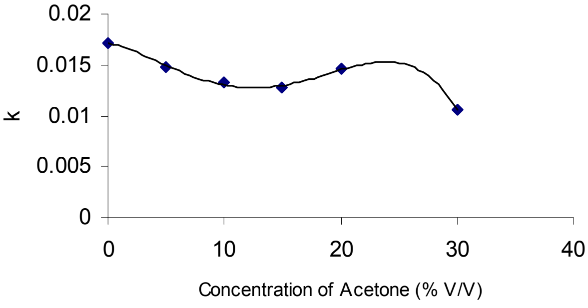
(e) (f)

Fig. 5: Morphology of the zinc powder a) Bath without 0% acetone, b) Bath with 10 % acetone, c) Bath with 20 % acetone, d) Bath with 30 % acetone, e) Bath with 2.5 g/l TEBAC, f) Bath with 5 g/l TEBAC

The morphological changes were also observed for the powder prepared in the presence of TEBAC. With the addition of 2.5 g/l TEBAC to the bath solution the morphology changes from flaky to well defined dendritic structure as observed from the Fig.5e. However, on further increasing in the concentration of TEBAC to 5 g/l, the morphology of zinc was again changed to flaky (Fig. 5f). This indicates that the lower concentration of TEBAC in the bath solution yields well defined dendrite zinc powder.



a)



b)

Fig. 6. a) Plot of α against time in different of acetone %, b) Plot of rate constant against % acetone

General chemical kinetics

The kinetics of the electrodeposition of zinc was studied at different percents of acetone. The plot of α (fraction of Zn removed from the solution) against time t gives a straight line passing through the origin. The linear relationship between the two variables (t and α) may be expressed as:

$$\alpha = (Ci-Ct)/Ci = kt \qquad (16)$$

where, Ci and Ct are concentrations of $ZnSO_4$ initial and at time t, respectively. k is reaction rate constant. The linear relationship indicates that the electrodeposition follows zero order kinetics. The plots α against time at different percent of acetone are presented in Fig. 6a. In Table 1 rate constants are given, Plot of rate constant against percent of acetone are shown in Fig. 6b.If the rate constant (k) is expressed as a function of percent of acetone (c) as

$$k= f(c) = x_1.\ c^4 + x_2.\ c^3 + x_3.c^2 + x_4.c + x_5 \qquad (17)$$

$$k= -9\times10^{-08}c^4 + 4\times10^{-06}c^3 - 4\times10^{-05}x^2 - 0.0001c + 0.0146 \qquad (18)$$

where x_1, x_2, etc are coefficient of the above polynomial If x_1, x_2, and x_3,are very small and may be neglected, then: k is linear function of c

$$k = x_4.c + x_5 \qquad (19)$$

$$k = -0.0001c + 0.014 \qquad (20)$$

where x_4. and x_5 are the slope and intercept of the equation respectively, while c is the percent of acetone. Therefore the relation between α with time and percent of acetone may be written as

$$\alpha = (Ci-Ct)/\ Ci = (x_4c + x_5)\ t \qquad (21)$$

The above equation shows that α depends not only on the time, t but also on the percent of acetone in the solution at a applied potential. In Fig.6b the cure and straight line are shown. The eqs. 18 and 20 represent the cure and line respectively. First few minutes of the kinetics does not obey the zero order. These points are neglected.

Avrami-Erofeyev kinetics

Using Avrami-Erofeyev (AE) equation the electrowinning kinetics of electrodeposition of zinc may be described according to the following equations:

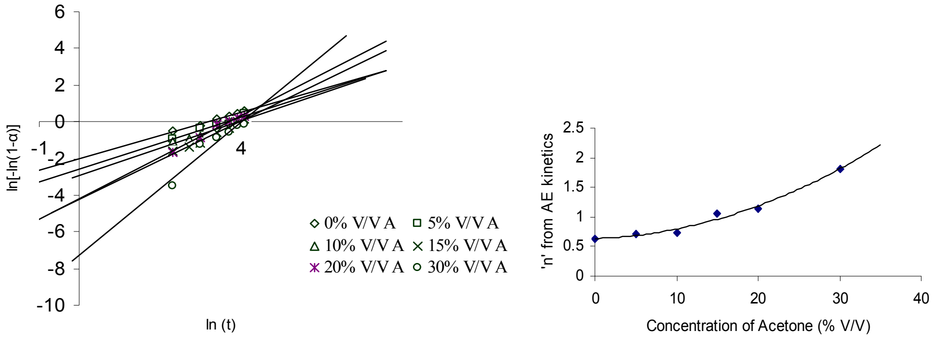
$$(1 - \alpha) = \exp\ (-k't^n) \qquad (22)$$

$$\ln(1 - \alpha) = -k't^n \qquad (23)$$

$$\ln(1 - \alpha) = k't^n \qquad (24)$$

$$\ln\{-\ln\ (1 - \alpha)\} = n\ \ln(t) + \ln\ (k') \qquad (25)$$

where n is order of the reaction and k' is rate constant of the process.



a) b)

Fig. 7. a)Plot of ln(t) against ln[-ln(1-α)] in different % acetone (Avarami-Erofeyev plots) b) n from Avrami-Erofeyev kintetics

The plot of ln{-ln (1- α)} against ln(t) for different percents of acetone give straight lines as shown in the Fig.7. The slop of the line gives n value and intercept gives ln(k') value. A prominent change in morphology of zinc powder is observed when n value increases from 0.633 to 1.133 when acetone percent increases from 0 to 20. But n value falls to 1.051 when acetone percent is 30. As the value of n increases, the morphology of zinc powder changes from flaky to dendrite and globular. Avrami-Erofeyev kinetic constants are presented in Table 3.

Table 3. Relation of n value of Avrami-Erofeyev graphs with morphology of zinc powder

Acetone, %	Avrami- Erofeyev constants n	ln(k)	Morphology of electrodeposited zinc powder
0	0.634	-2.012	Flaky
5	0.703	-2.575	---------
15	1.054	-4.188	Globular, agglomerated, flaky and underdeveloped dentritic
20	1.133	-4.188	Globular and agglomerated
30	1.051	-4.397	Dentritic and globular

Discussion

The deposition of zinc powder is favored by lower concentrations of Zn^{2+} and ammonium hydroxide. When the concentration of acetone in the bath solution is higher, 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 zinc. From the morphological studies, it is observed that acetone free system produces flaky powder. The flaky shape changes with increase in acetone to globular and agglomerated shapes and at higher concentration of acetone it becomes globular and dendritic. At low concentration of TEBAC zinc forms well-defined dendrite shaped powder. However, at higher concentration it becomes flaky again (Table 4.).

Table 4. Effect of TBAC on morphology of zinc powder

Amount of TEBAC, (g/l)	Morphology of powder
0.0	Flaky
2.5	Dentritic
5.0	Flaky

As, the rate constant of chemical kinetics decreases flak formation in the powder reduce. Avrami Erofeyev kinetics indicates that n value increases from 0.6334 to 1.8162 with the increase in acetone concentration to 30% V/V.

The same conclusion may be drawn, *i.e.* the shape of zinc powder changes from dendritic to sponge or porous. The Avrami-Erofeyev kinetic study may also help to find the shapes of electroldeposited powder. The size of particles decreases appreciably with increase in acetone concentration. For example, as the acetone concentration increases from 0% to 30% V/V the particle of 10.4 µm reduced to7.8 µm size. But the larger particle size is not appreciably decreased with increase of acetone concentration. The decrease of the average particle size is 14.36% for 30% V/V increase of acetone concentration.

Conclusions

Good zinc powder can be obtained when the electrolytic solution contains 0.04 M zinc ion ~1.5.M NH_4Cl 0.05N NH_4OH, and 20% of acetone and the potential applied is 4.0 V. The large potential raises the temperature of the bath and causes the evaporation of acetone. Temperature should not exceed 30 $\underline{+}1^{o}C$ since acetone is a volatile solvent.

Acknowledgement

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