

ELECTROWINNING OF CADMIUM POWDER FROM GLYCEROL AND SULPHURIC ACID – STUDY OF MORPHOLOGY AND NANO-NATURE OF THE POWDER

S.G. Viswanath^{1*}, Sajimol George¹

¹ Department of Chemistry, Laxminarayan Institute of Technology, R.T.M Nagpur University, Nagpur-440033, India

Received 19.02.2010

Accepted 12.03.2010.

Abstract

Electrowinning of cadmium with glycerol and sulphuric acid concentrations varying from 0 to 15% and 0 to 1.5N respectively, were studied. Morphology and particle size of cadmium powder formed by this process were studied. The particles appeared as dendrite, but their shape might also be hexagonal, acicular, sponge-like etc. In 1N acid and 15% glycerol average size of 61.52% particles was in the range from 1.77 to 62.26 μm and also nano-particles were found in the range from 247 to 456nm. A method for determination of approximate density of cadmium powder which might be correlated to the particle size was suggested. The stability of the powder and current efficiency were also studied.

Key words: Electrowinning, cadmium, stability, SEM, particle size, Avrami-Erofeev kinetics

Introduction

Powder metallurgy is one of the oldest and yet the most modern branch of metallurgy for fabricating metal products. A number of patents have been filed on powder fabrication since the early decades of the twentieth century. Electrolytic preparation of powders of iron, copper, nickel and zinc are among the most extensively studied metals [1-6].

Osborn *et al.* [7] and Smith [8] studied the electrolytic preparation of copper powder. Horhersall and Gardam [9] gave a method for the commercial preparation of copper powder by electrodeposition. Electrolytic nickel powder was studied by Levin [10], while cathodic preparation of finely dispersed nickel was presented by Lashkarev

* Corresponding author: S.G. Viswanath gortiviswanath@yahoo.com

[11]. Electrolytic preparation of zinc dust was studied by Morgan and Raston [12, 13] and Eckardt [14]. Hanseland and Passer [15, 16], performed experiments on electrolytic preparation of zinc powder and described the influence of the variation of the conditions of the electrolysis on the form of deposits.

Cadmium has many industrial applications. Dutra *et al.* [17] studied cadmium removal from a diluted aqueous solution by electrorefining technique in a flow cell. Elsherief [18] studied the efficient removal of cadmium from a dilute acid solution in a flow cell using rotating glassy carbon and spiral wound steel electrodes. Borikar, Umare and Viswanath [19, 20] studied the effect of acetone on the electrowinning process to obtain copper [19], nickel [20] and cadmium [21] powders.

In the present work an attempt has been made to study the influence of glycerol and H_2SO_4 concentrations on electrowinning of cadmium powder as well as its morphology and particle size. A method has been suggested for the determination of approximate density (apparent density) of cadmium powder. This density may be correlated with the particle size. Standard electrode potentials of cadmium were determined in different concentrations of H_2SO_4 and glycerol media. An attempt was made to study Avrami-Erofeev general kinetics to relate kinetic constants to the shape of the particles.

Experimental procedure

Instruments

The particle size analysis and scanning electron microscopy (SEM) studies were performed on Fritsch particle sizer-ANALYSETTE 22 and JEOL JAX240A microscope operated at 15kV, respectively, at JNARDDC, Wadi, Nagpur.

The bath solution ($CdSO_4$, H_2SO_4 and glycerol) was added into a single compartment of two-electrode cell. The electrowinning experiments were performed by using cadmium plate ($6 \times 1.5 \times 0.1$ cm) as cathode and gold plate as anode. The current was supplied by regulated digital DC Power Supplier Model L3202 (Aplab). All experiments were carried out at room temperature. The temperature of the bath was maintained almost constant during the experiment. Current of 0.5A was applied with variation 0.01A.

Procedure

All chemicals used were of AR grade and bath solutions were prepared in double distilled water. The glycerol was added in the volume percent, *i.e.* volume/volume. During electrowinning process 2 ml of bath solution was taken from the bath in 10min interval and analyzed for cadmium. The kinetics of cadmium deposition was studied by titration the solution against 0.01N EDTA using Eriochrome black T as indicator. The deposition was continued for 4 hours to get sufficient quantity of powder for different types of analysis. The cadmium concentration initially taken was 0.1N for all experiments. The collected powder was thoroughly washed several times with distilled water and then with acetone. The powder was dried in air oven at $110^\circ C$. After drying the powder was stored in an air-tight container.

Determination of apparent density of cadmium powder

The mass of the empty dry density bottle was determined (W_1). Then the bottle was filled with distilled water and weighed again (W_2). The volume of bottle (V_1) is given by $(W_2 - W_1)/D$, where D is the density of water at the working temperature. Approximately 1g of cadmium powder was added into the same dry empty bottle and weighed (W_3). W_4 was the weight of the bottle filled with water. The weight of the water was $(W_4 - W_3)$ and the volume (V_2) of water in the presence of cadmium powder was changed into $(W_4 - W_3)/D$. Thus, the volume of the cadmium powder is $(V_1 - V_2)$ and apparent density of cadmium powder is given by $(W_3 - W_1)/(V_1 - V_2)$. Apparent densities of cadmium powder obtained at different concentrations of sulphuric acid and glycerol are presented in Table 1.

Table 1. Apparent densities of cadmium at various concentrations of H_2SO_4 and glycerol

H ₂ SO ₄ concentration (N)	Percent of glycerol (%)				
	2.5	5	7.5	10	15
	Apparent densities of cadmium (g/ml)				
0.0	8	7	6.75	5.7	3.8
0.5	7.6	5.75	5	3.5	2.25
1.0	6	4.2	2.5	2	2.1

Cathodic current efficiency (C.E.)

Based on the current used for the particular period of electrolysis, the theoretically expected weight of cadmium deposition was calculated using Faraday's law:

$$W = Z I t \quad (1)$$

where W , Z , I and t are theoretically expected weight of cadmium deposition, electrochemical equivalent of cadmium, current and time, respectively.

The C.E. was calculated using the relation:

$$C.E. = (w/W) \times 100 \quad (2)$$

where w is the weight of the cadmium deposited during experiment. The data are presented in Table 2.

Table 2. Cathodic current efficiency of cadmium electrowinning process at different concentrations of H_2SO_4 and glycerol

H ₂ SO ₄ concentration (N)	Percent of glycerol(%)				
	2.5	5	7.5	10	15
	Cathodic current efficiency (%)				
0.0	78.7	62	46.3	42.62	42.5
0.5	71.54	57.24	43.57	40	40.5
1.0	66.6	52.5	41.66	38.7	38.9

Determination of stability of cadmium powder

Cadmium powder was kept for 45 days in an air-tight sealed bottle and then it was studied for its stability. Accurately weighed cadmium powder (0.7 ± 0.3) was taken in 100ml 0.05N sulphuric acid. The solution was stirred with a magnetic stirrer for one hour. The solution was filtered and the dissolved cadmium in the filtrate was estimated by titrating the filtrate, against EDTA (0.01N) using Eriochrome black T indicator. Cadmium powder is susceptible to oxidation and forms cadmium oxide (CdO). The oxide reacts with acid forming corresponding salt. The stability of cadmium was estimated using the formula:

$$\text{Stability} = \frac{\text{Weight} \cdot \text{undissolved} \cdot \text{metallic} \cdot \text{powder}}{\text{Weight} \cdot \text{of} \cdot \text{metallic} \cdot \text{cadmium} \cdot \text{experimentally} \cdot \text{obtained}} \times 100 \quad (3)$$

The data are presented in the Table 3

Table 3. Stability of cadmium powder obtained at various concentrations of sulphuric acid and glycerol

H ₂ SO ₄ concentration (N)	Percent of glycerol(%)				
	2.5	5	7.5	10	15
	Stability of cadmium powder (%)				
0.0	90.7	81.4	73.6	70.7	66.4
0.5	89.4	76.4	72.4	69.2	64.87
1.0	86	75.8	71.65	68.7	62.35

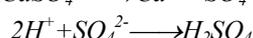
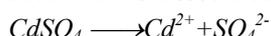
Results

Mechanism of reactions during electrodeposition of cadmium

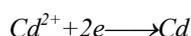
The important electrode reactions during the electrowinning process are given below. The water molecule dissociates according to the following reaction:



Being a strong electrolyte cadmium is dissociated completely, *i.e.*:



The reaction at cathode is:



The net *cathodic* reaction is:



H⁺ ions combine with SO₄²⁻ to form sulphuric acid. Therefore OH⁻ ions obtained from dissociation of water undergo the reaction at anode



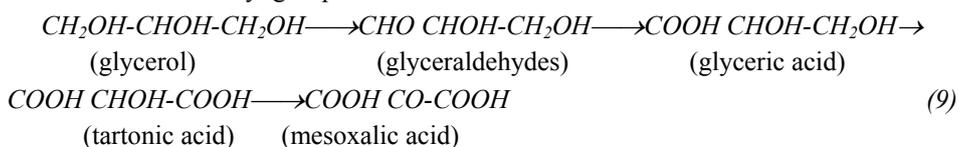
The net *anodic* reaction is



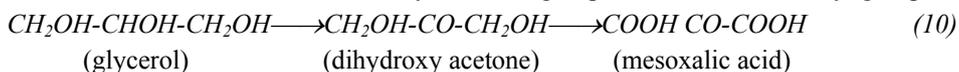
The net cell reaction is:



While released 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:



On the other side, the secondary alcoholic group is oxidized to carbonyl group:

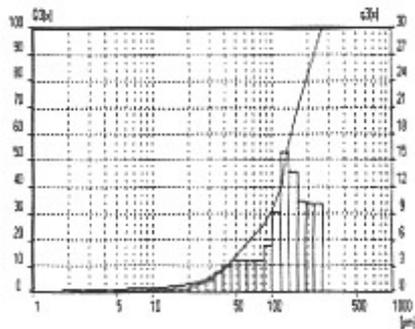


When the electrowinning process is completed the acid concentration reaches almost double the initial concentration. The formation of different carboxylic acids is one of the important reasons for the increase in the acid concentrations. Also sulphate ions from cadmium salt increase the concentration of sulphuric acid.

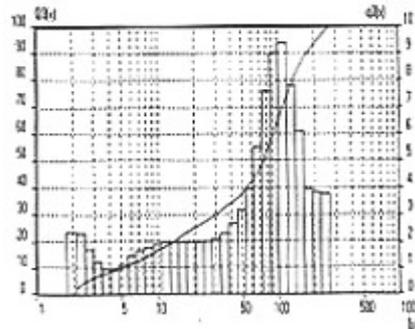
It is well known that during electrolytical processes all positive ions migrate towards the cathode while negative ions move to anode. The metal ion is discharged at the cathode. The solid metal atoms deposited on the cathode should have a strong metallic bond. A large amount of hydrogen released at the cathode creates a porous deposit, whereas the solution containing organic solvents, which are covalent in nature, disturbs this ion environment particularly at the cathode causing a loose bonding between metal-metal atoms. The result of this process is the formation of metallic powder.

Particle size analysis

The distribution of cadmium particle size is shown in Fig. 1 and the data of distribution are given in Table 4.



(a)



(b)

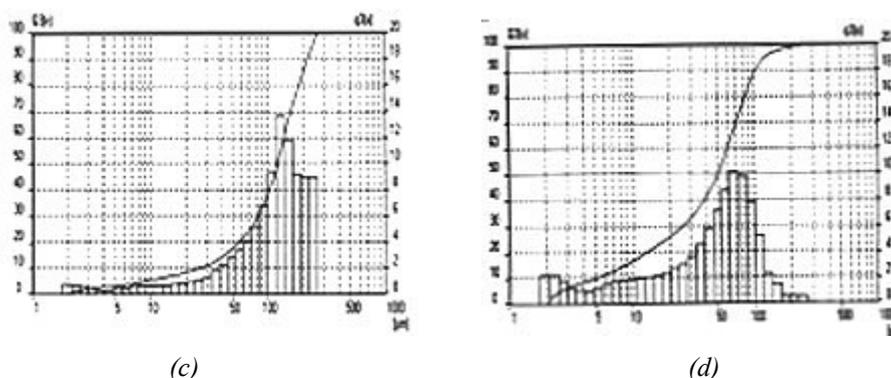


Fig. 1. Distribution of particle size of cadmium powder obtained from different media (a) 5% glycerol, (b) 10% glycerol, (c) 1N H_2SO_4 +10% glycerol and (d) 1N H_2SO_4 +15% glycerol

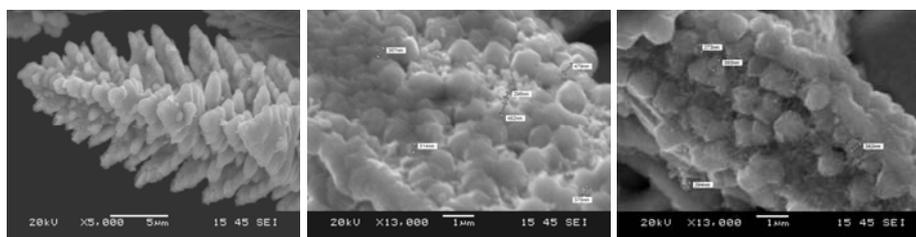
Table 4 Particle size of cadmium in different concentration of H_2SO_4 and glycerol

Concentration H_2SO_4 (N) + glycerol (%)	Particle size of Cd (μm) with cumulative frequency (%)				
	1.77- 12.52	12.52- 38.48	38.48- 62.54	62.54- 118.28	118.28- 263.81
0 N+ 5%	2.05	6.38	10.22	21.42	59.93
0 N+ 10%	19.16	14.2	9.72	31.48	25.44
1 N+ 10%	6.21	7.26	8.47	25.41	52.65
1N+ 15%	19.34	20.54	21.64	33,03	5.45

With 10% glycerol in the bath solution the cumulative frequency of partial size decreases by about 10%. It is also observed that the concentration of sulphuric acid in the range from 0 to 1.0 N and glycerol in the range from 5 to 10% produce nano-sized powder particles, which is well documented from SEM studies.

Morphological investigation

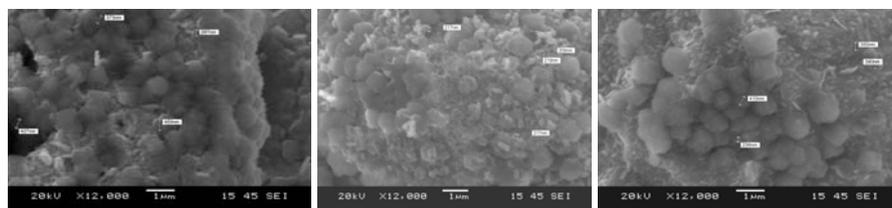
SEM micrographs of cadmium powder are presented in Fig. 2. In the Table 5 relevant physical data of respective powders were presented. These results show that lower is the apparent density smaller is the particle size of electrodeposited powders



1

2

3

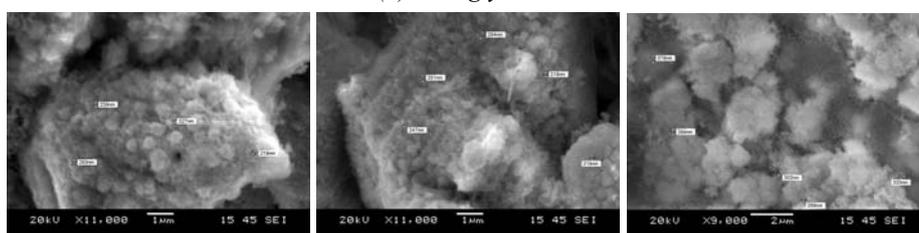


4

5

6

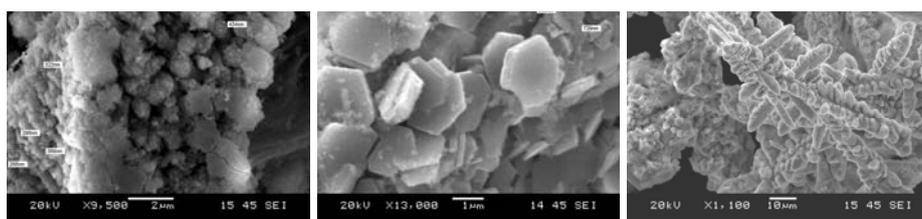
(a) 5 % glycerol



1

2

3

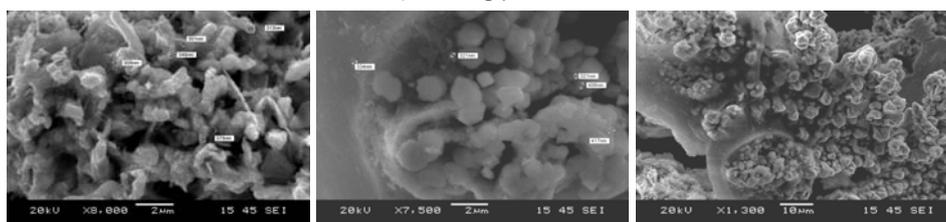


4

5

6

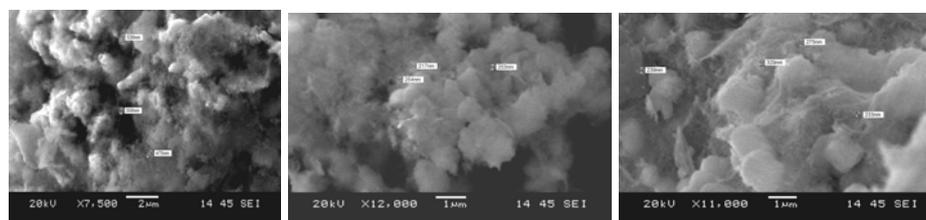
b) 10 % glycerol



1

2

3



4

5

6

c) 1M H₂SO₄+10 % glycerol

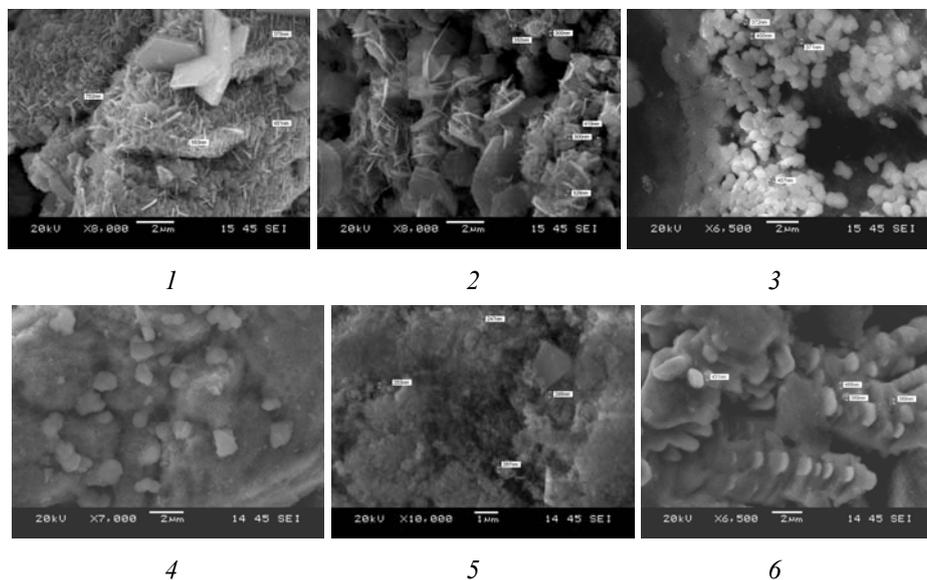
d) 1M H₂SO₄ + 15 % glycerol

Fig. 2. SEM microphotographs of cadmium powder obtained from different media

Table 5. Morphology of copper powder and related data

Concentration H ₂ SO ₄ (N)+ glycerol (%)	Apparent Density (gm/ml)	Current Efficiency (%)	Stability of powder (%)	Range of particle size (nm)	Morphology of electrodeposited powder
0+5	7	62	81.4	208-482	Hexagonal, dendrite,
0+10	5.7	42.62	70.7	247-434	Hexagonal, dendrite, sponge, aggregate
1+10	2	40	68.7	203-475	Hexagonal, sponge, acicular, aggregate
1+15	2.1	38.9	62.35	247-456	Hexagonal, acicular, sponge.

Kinetics of electrodeposition of cadmium

Chemical kinetics

The kinetics of electrodeposition of cadmium in the presence of different concentration of sulphuric acid and glycerol was studied. α , the fraction deposited is defined as:

$$\alpha = C_t / C_i \quad (11)$$

where C_i and C_t are initial concentration and concentration of Cd²⁺ at any time t , respectively. The rate of change of concentration with respective time is expressed as:

$$d\alpha/dt = k(1-\alpha)^n \tag{12}$$

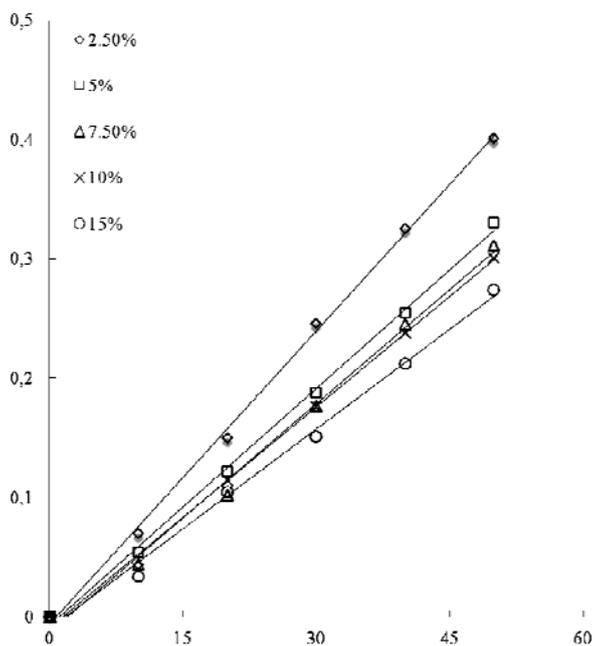
where n and k correspond to the order of reaction and reaction rate constant, respectively. (1- α) is the fraction of cadmium metal deposited. For zero order reaction the integrated form of the above equation is written as:

$$\alpha = kt \tag{13}$$

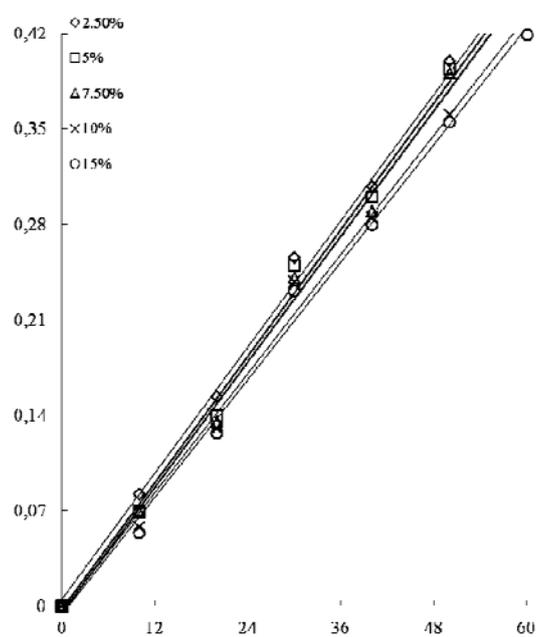
Plot of α vs. time gives a linear plot passing through the origin with the slope equals to k. Fig. 3(a-c) represents the zero order plots for the electrodeposition of cadmium in different concentrations of sulphuric acid and glycerol and in the Table 6 values of k are given.

Table6. Reaction rate constants of the electrodeposition kinetics

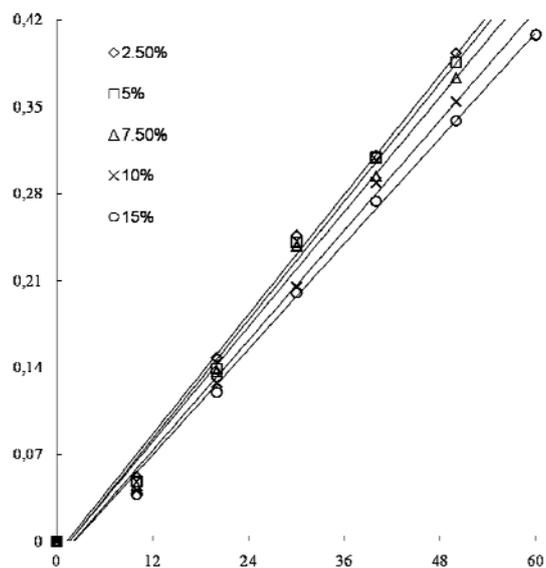
H ₂ SO ₄ concentration, (N)	Reaction rate constant (min ⁻¹)				
	2.5%	5%	7.5%	10%	15%
0.0	0.0082	0.0066	0.0064	0.0062	0.0056
0.5	0.0077	0.0078	0.0077	0.0073	0.0072
1.0	0.0080	0.0079	0.0077	0.0074	0.0071



a)



b)



c)

Fig. 3. Plots α - t in different conditions ($y=\alpha$ and x =time). a) Plots of α against time in different percent of glycerol, b) plots of α against time in 1.0 N H_2SO_4 and different percent of glycerol, c) plots of α against time in 1.5 N H_2SO_4 and different percent of glycerol

Avrami-Erofeev kinetics

There was an attempt to correlate the chemical kinetics of electrodeposition of cadmium with Avrami-Erofeev kinetics. Avrami-Erofeev kinetics gives some clue about the morphology and size of the particle as we found in our earlier work [19,20]. Thus, the equation is given below:

$$(1-\alpha) = \exp(-kt^n) \tag{14}$$

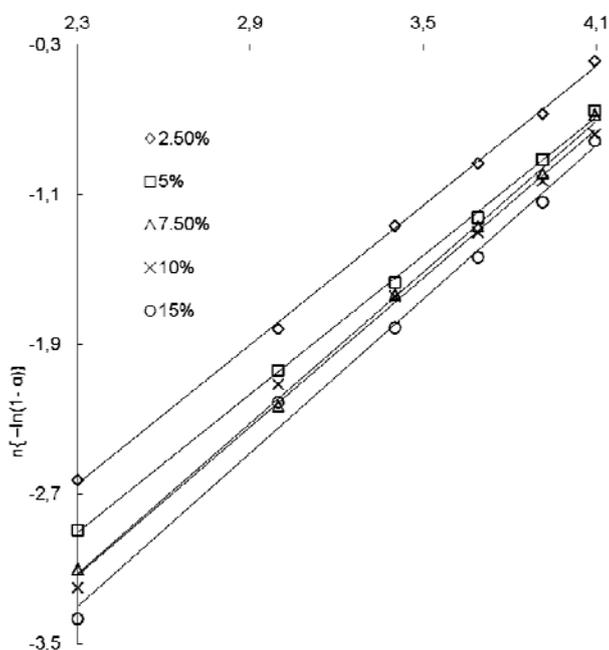
The logarithmic form of equation is written as:

$$\ln\{-\ln(1-\alpha)\} = n \ln(t) + \ln(k) \tag{15}$$

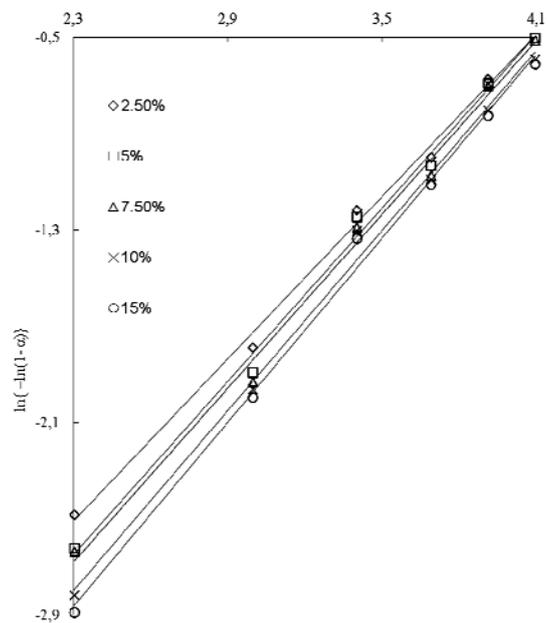
where, n and k are order of reaction and rate constant of the reaction, respectively. Plot of $\ln\{-\ln(1-\alpha)\}$ vs. $\ln(t)$ gives a straight line with slope equals to n and intercept equals to $\ln(k)$. The plots are shown in Fig. 4(a-c) for the electrodeposition of cadmium in different concentrations of sulphuric acid and glycerol. In Table 7 n and $\ln(k)$ values are given.

Table 7. Avrami-Erofeev kinetic constants

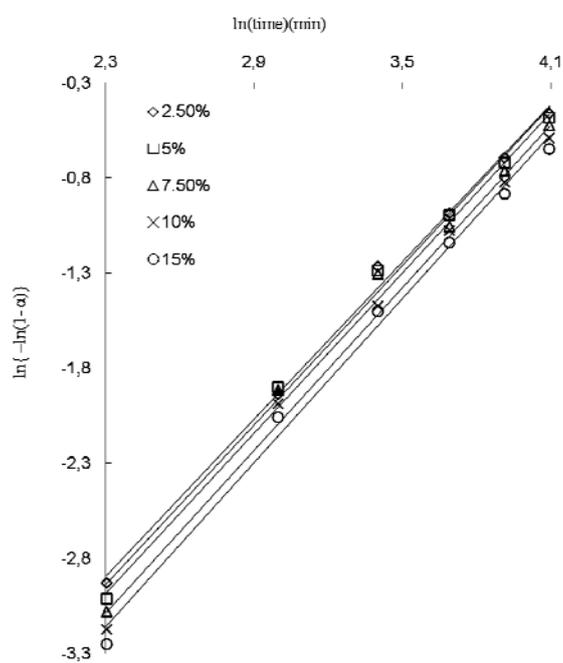
Glycerol (%)	Sulphuric acid concentration					
	0.0N		0.5N		1.0N	
	n	ln(k)	n	ln(k)	n	ln(k)
2.5	1.2413	-5.5017	1.1244	5.0972	1.3801	6.0701
5.0	1.2368	-5.7519	1.2005	-5.4115	1.4002	-6.159
7.5	1.3463	-6.2255	1.2045	-5.4511	1.4062	-6.2189
10	1.3271	-6.1876	1.2491	-5.674	1.4284	-6.3755
15	1.3717	-6.4577	1.277	-5.8027	1.4398	-6.4734



a)



b)



c)

Fig. 4. Plots $\ln\{-\ln(1-\alpha)\}$ for the electrodeposition of cadmium in different concentrations of H_2SO_4 and glycerol, a) 0.0 N H_2SO_4 , b) 1.0 N H_2SO_4 , c) 1.5 N H_2SO_4

Discussion

The electrodeposition of metal follows zero order reaction and hence the rate of deposition is independent of metal ions. The increase in the concentrations of sulphuric acid and glycerol decreases the amount of dendrites in the powder. Therefore, the decrease in the cadmium apparent density may be correlated to decrease of dendrites in the powder. The Avrami-Erofeev n value is between 1 and 2 and does not vary with concentrations of sulphuric acid and glycerol. This is an indication that the most number of particles are two-dimensional with hexagonal, sponge-like, acicular or polygonal shape. When the rate of deposition of cadmium is slow two-dimensional particles are produced. Decrease in the rate constant in both cases can be attributed to the decrease in the ion environment or ion strength due to the presence of glycerol molecules in the solution medium.

The C.E. and the oxidative stability (oxidation by atmospheric oxygen) decrease with increase in concentrations of sulphuric acid and glycerol. The decrease in the C.E. is obviously due to decrease in the conductivity of the solution. The decrease in the oxidative stability and C.E. may be attributed to the formation of large number of smaller particles.

The percent of average particle size of 49.10 μ m in 5% glycerol and 0.0 N sulphuric acid increases from 14.97 to 52.75% in 15% glycerol and 1.0N sulphuric acid. It clearly indicates that as the concentrations sulphuric acid and glycerol increase the percent of smaller particles should also increase. This is mainly due to the large evolution of hydrogen gas which makes deposit porous as well to the low ionic concentration of the solution which does not allow the strong metallic bonding between metal atoms..

The large current densities warm the solution and the bath temperature increases along with the rate of deposition of the powder. Thus, the lower rate of deposition is another important parameter which indicates that obtained powder deposits possess good properties.

It was also found that powders obtained from 1.0N sulphuric acid and 10% glycerol mixture correspond to nano-particles with average size in the range from 247 to 456nm. This observation may help to obtain large amount of nano-particles from this mixture. The SEM studies show that in all cases a large amount of nano-particles was observed. However, in some cases, when glycerol concentration is below 15% f nano-particles ranging from 500 to 750nm were also obtained.

Conclusion

In 1.0 N sulphuric acid and 15% glycerol medium More than 60% particles are below 62.54 μ m and nano-particles are in the range of 247-456nm.

Acknowledgement

The authors are indebted to the Director and staff of JNARDDC, Wadi, India, for particle size and SEM analysis.

References

- [1] D.Primavesi. Fr.Patent, 976,453 (1951).
- [2] C.F. Burgess and D.Hambucehm, Trans, Am. Electrochem. Soc., 5(1904)201.
- [3] T.Kikuchi and K. Yamaguchi, Jap. Patent, 1514/50(1950)
- [4] H.R. Copson, A. Wesley and T.H. Wickenden, Can. Patent ,475/886 (1951)
- [5] M.Kurodea and G.Ito, Jap, Patent, 5166/53 (1953).
- [6] N.Fujise, Jap. Patent, 2363/57 (1957).
- [7] W.H. Osborne and S.B. Tuviner, Trans. Electro. Chem. Soc., 85(1944)107.
- [8] G.B. Smith, Iron Age, 153(1944)779.
- [9] A.W. Hothersall and G.E. Gardam, Metal Ind. (London) 66(1945)234.
- [10] A.J. Levin J. App. Chem. (USSR) 19(1946)779.
- [11] M. Loshkarev, A. Krukova and O. Gornostaleva, J. Appl. Chem., USSR 19 (1946) 46.
- [12] H.J. Morgan and O.C. Ratson, Trans. Am. Electrochem. Soc., 30 (1916) 229.
- [13] H.J. Morgan and O.C. Ratson, Met. Chem. Eng., 15(1916) 465.
- [14] W. Eckardt, US. Bur. Mines Inform Cir., 7466(1948)6.
- [15] G. Hanesland and M. Passer, Wiss. Veroffentl Siemens-Werk, Weerstoff Sanderheft, 9(1940)124.
- [16] G. Hanesland and M. Passer, Chem. Zentr, (II)112(1941)1252.
- [17] A.J.B. Dutra, E. Espinola and P.P. Borges, Miner. Eng. 13(2000) 1139.
- [18] A.E. Elsherief, Electrochim. Acta , 48 (2003) 2667.
- [19] D.K. Borikar, S.S. Umare and S.G. Viswanath, Trans. SAET 39 (2004) 9.
- [20] D. K. Borikar, S.S. Umare and S.G. Viswanath, Metallurgija 45(2006)3
- [21] D.K. Borikar, S.S. Umare and S.G. Viswanath, Bul. Electro. Chem. 21(2006)423.