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The effect of chelating agents on the cathodic polarization and the electrodeposition of iron powders

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The electrodeposition of iron powders from different baths containing the same major chemical constitutents was studied. The baths were mainly based on aqueous dilute solutions of ferrous sulphate and additives such as oxalic and citric ions. The effect of these additives on the cathodic polarization curves, current efficiency and powder morphology of the electrodeposited iron powders was investigated. It was found that electrodeposition systems with chelating agents were more polarized than a non-chelated system and produced finer powders with no dendrites.

1. Introduction

Iron powder has wide applications in making electronic components and casting tools. There are four methods of producing iron powders: (1) the chemical reduction method [1, 2], (2) atomization [3], (3) the mechanical attrition method, and (4) electrodeposition [4, 5]. The particles of iron powders made by the chemical method are spherical and of low purity. The atomization method is simple in operation but the particle size is usually large. The mechanical attrition method is never directly used to produce powder from raw material. The electrodeposition method can produce needle-like iron powders of high purity, which is of particular interest when magnetic properties are required.

The first industrial attempt to produce electrolytic iron powders can be traced back to 1904 [6]. The metal was deposited from a bath of iron–ammonium sulphate at a current density of $1.07\ \mathrm{A\,dm^{-2}}$ at 30.0 °C. The formation of iron powders by electrodeposition on to a mercury cathode was studied in 1961 [4]. The dendritic iron powders formed were not compact and showed poor magnetic properties.

The electrodeposition process and the properties of the metal deposit depend, to a great extent, on the nature of the additives such as chelating agents and the anions of the metal salts used in the electrolysis [7]. They affect the activity of metal ions and of metal complexes: their effects on the electrodeposition of nickel powders have been studied by Khalil and coworkers [8, 9]. However, no similar information is available for the electrodeposition of iron powders. Thus, the major aim of this study was to investigate the influence of two chelating agents on the electrodeposition of finely divided iron powders, to achieve better control of the process by the adjustment of the bath compositions.

2. Experimental procedure

The electrodeposition experiments were carried out in a 1 litre glass cell which was immersed in a water bath. Pure iron plates were used as anode and cathode. The inter-electrode spacing was maintained at 8 cm. Ferrous sulphate and appropriate chelating agents, including oxalic acid ($H_2C_2O_4 \cdot 2H_2O$ 0.00–0.02 M) and citric acid ($C_6H_8O_7 \cdot H_2O$ 0.00–0.02 M) were the major ingredients of the electrolyte. Stirring the electrolyte was effected with a rotating propeller.

A potentiostat (EG & G Model 173) was used to measure the cathodic polarization relative to a saturated calomel electrode (SCE). The scanning rate was $6.0\ \mathrm{mV\,s^{-1}}$. The morphology of the powders was measured using an electron probe micro-analyser (EPMA, Jeol JXA-733).

3. Results and discussion

3.1. Cathodic polarization

In an acidic solution, hydrogen is easily evolved and the chelating agents cannot completely dissociate. In the present system, the pH range was 4.6–6.0. The complex species of Fe^{2+}–oxalate and Fe^{2+}–citrate are $Fe\,(C_2O_4)$ and $Fe\,(cit)^-$ whose stability constants are $10^{3.05}$ [10] and $10^{4.40}$ [10], respectively.

The cathodic polarization curves obtained for solutions containing 0.06 M $FeSO_4$ and 1.67 M $(NH_4)_2SO_4$ at pH 6.0 with different chelating agents are shown in Fig. 1. The polarization is in the following order: $FeSO_4 < Fe\,(C_2O_4) < Fe\,(cit)^-$. With the addition of chelating agents, the concentration of free Fe^{2+} ions decreases, which causes Curves b and c of Fig. 1 to shift to more negative values.

In 1988, Khalil [9] studied the polarization of nickel ions. The major anions of his baths were sulphate, chloride, iodide, nitrate and acetate. He also found that the chelating anions had significant influence

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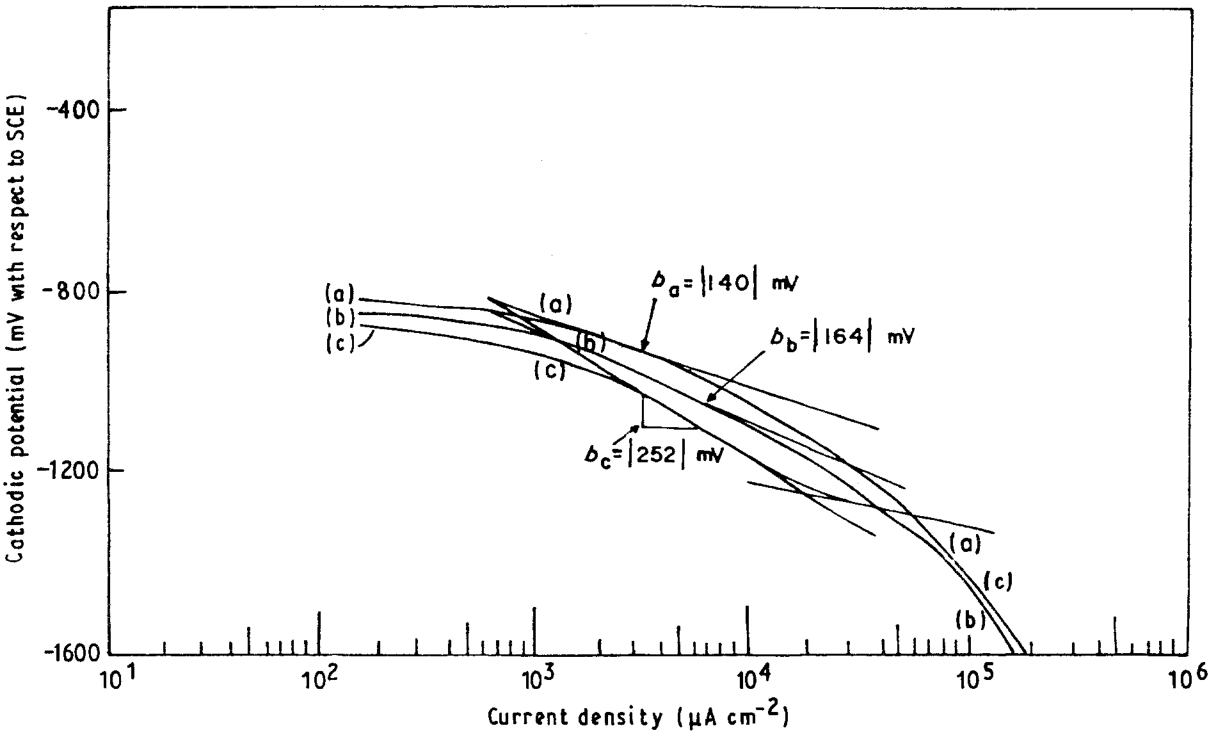

Figure 1 Polarization curves of iron electrodeposition in 0.06 M $FeSO_4$, 1.67 M $(NH_4)_2SO_4$, pH 6.0 solutions containing chelating agents: (a) no chelating agent, (b) 0.02 M oxalic acid, (c) 0.02 M citric acid.

on the polarization pattern. The overpotential was in the following order: $NO_3^- < SO_4^{2-} < Cl^- < I^- < C_2H_3O_2^-$.

Fig. 1a and b have only one Tafel region. The Tafel slope of the oxalic acid system (Curve b) is larger than that without chelating agents (Curve a). The system containing citric acid (Curve c) shows two linear Tafel regions. This is probably due to the concentration polarization effect. The first Tafel region has a slope of 252 mV/decade, which should be considered high, corresponding to value for the Tafel slope of 118 mV/decade of iron electrode in sulphate solution without chelating agent reported by Kelly [11]. The high value for the Tafel slope is probably caused by at least one diffusional effect. The stable Fe^{2+}–citrate complex, which is easily adsorbed on the cathode, results in a decrease in the number of adsorbed sites of free Fe^{2+} ions. Thus the diffusion-limited reaction may be the result of citric acid and/or Fe^{2+} ion diffusion. The other region that has a smaller slope

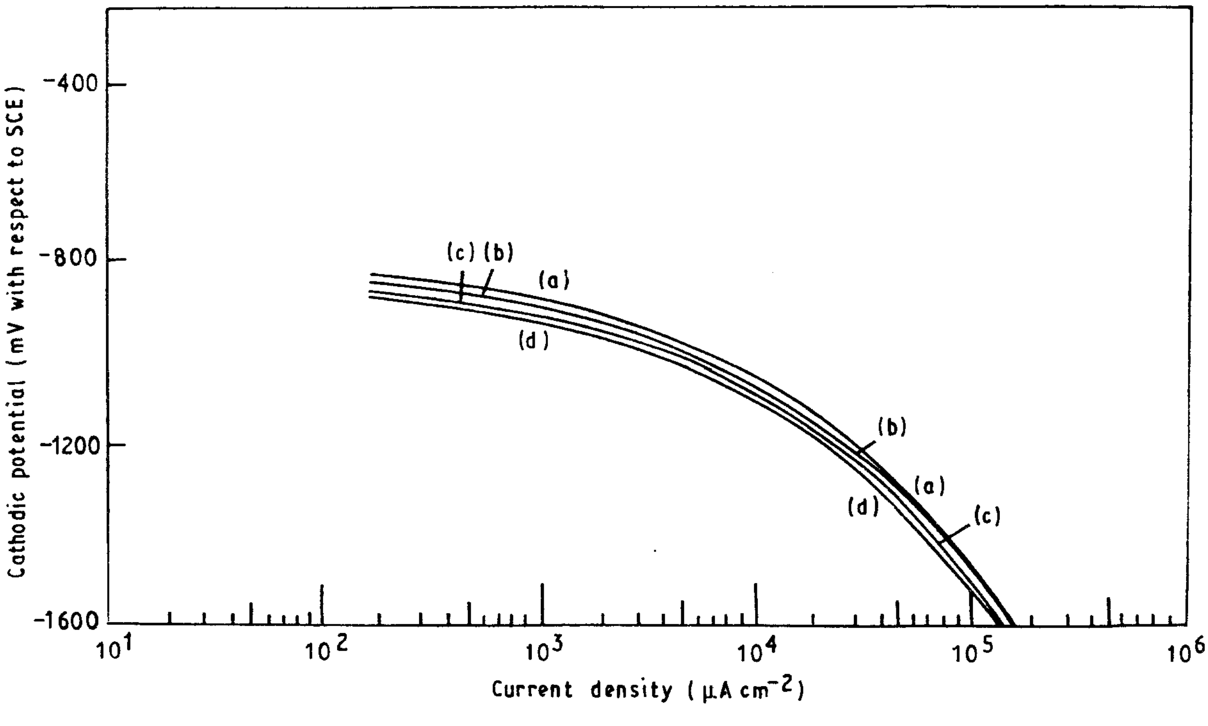

Figure 2 Polarization curves of iron electrodeposition in 0.06 M $FeSO_4$, xM oxalic acid and 1.67 M $(NH_4)_2SO_4$ solutions at pH 6.0. x (M): (a) 0.02, (b) 0.04, (c) 0.06, (d) 0.08.

than the first region may include the decomposition of citric acid and/or the reduction of water to hydrogen gas.

In 1986, Ogundele [12] observed the corrosion of carbon steel in sour gas (H_2S and CO_2) environments. He also found cathodic polarization curves that had two Tafel regions with H_2S.

Figs 2 and 3 show that the potentials shift to the more negative values with increasing chelating agent concentrations, such as oxalic acid and citric acid, due to the decrease of free Fe^{2+} ions. Moreover, there is only one Tafel region with oxalic acid (Fig. 2), but two Tafel regions with citric acid (Fig. 3). Therefore, this polarization character depends on the chelating agents, but not on their concentrations.

Figs 4 and 5 show that the potentials shift to the more negative values with an increase of pH values. Owing to an increase of the hydrogen-ion dissociation from the chelating agents as the pH increases, the concentrations of $C_2O_4^{2-}$ and cit^{3-} increase, as do

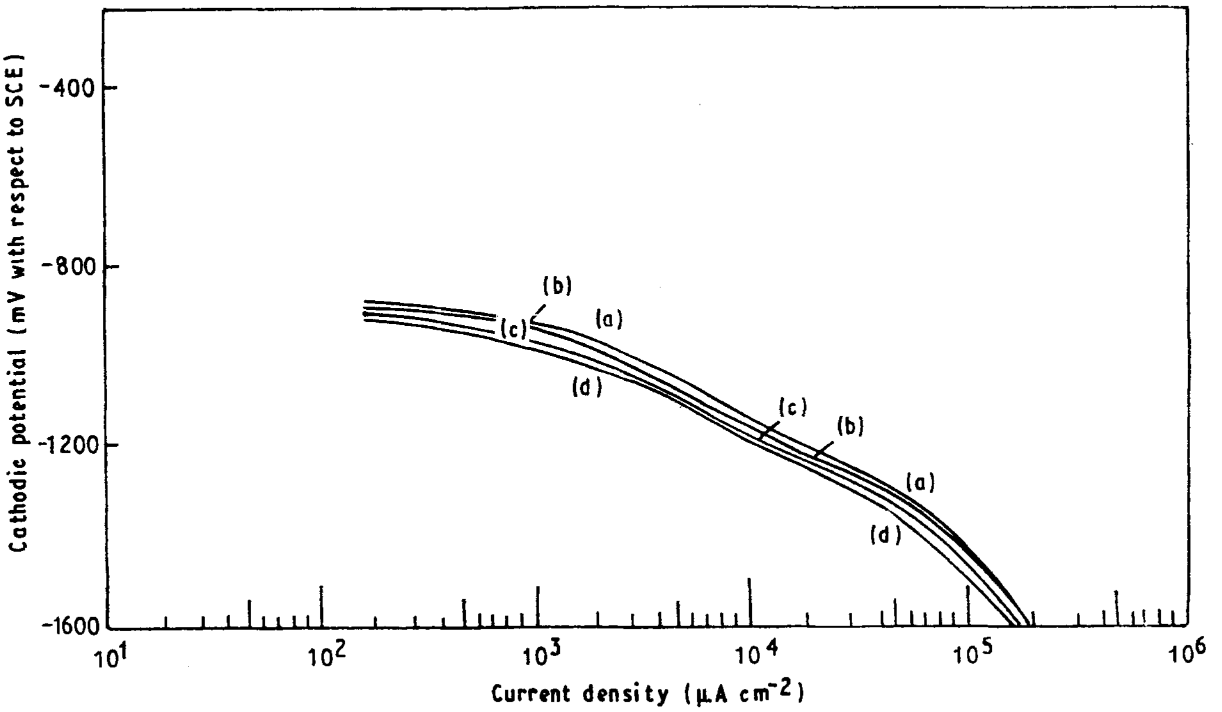

Figure 3 Polarization curves of iron electrodeposition in 0.06 M $FeSO_4$, xM citric acid and 1.67 M $(NH_4)_2SO_4$ solutions at pH 6.0. x (M): (a) 0.02, (b) 0.04, (c) 0.06, (d) 0.08.

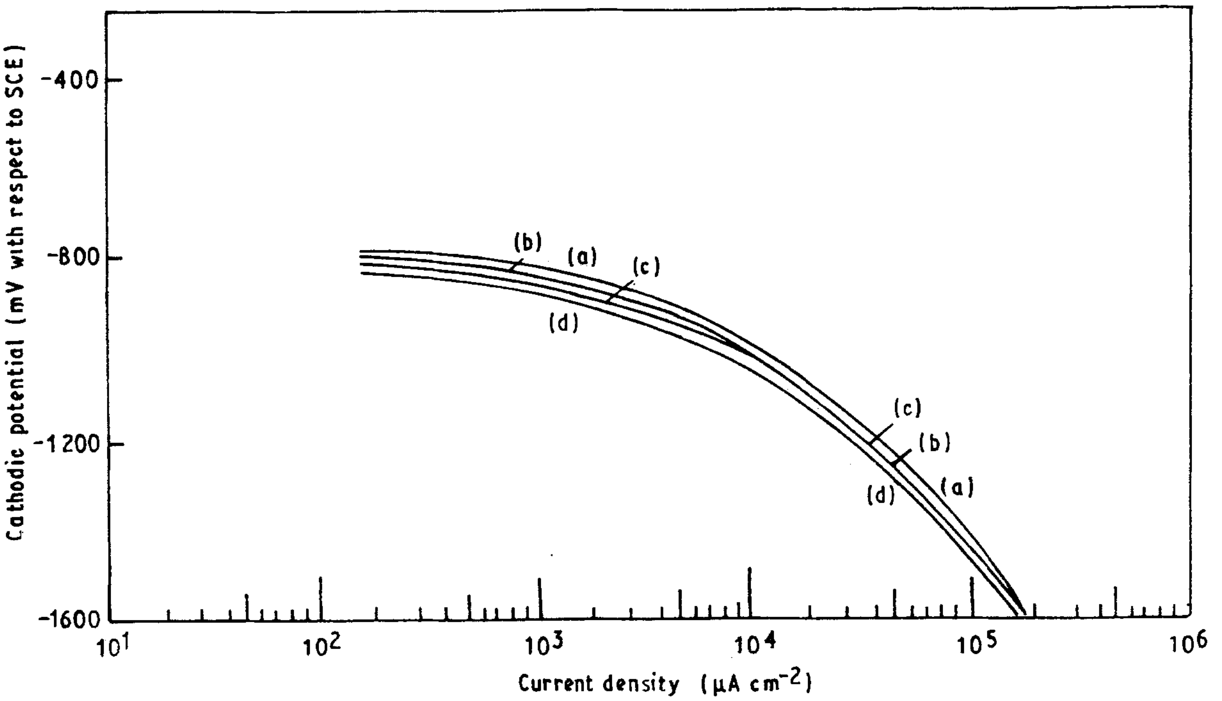

Figure 4 Polarization curves of iron electrodeposition in 0.06 M $FeSO_4$, 0.02 M oxalic acid and 1.67 M $(NH_4)_2SO_4$ solutions, at pH: (a) 4.0, (b) 4.6, (c) 5.3, (d) 6.0.

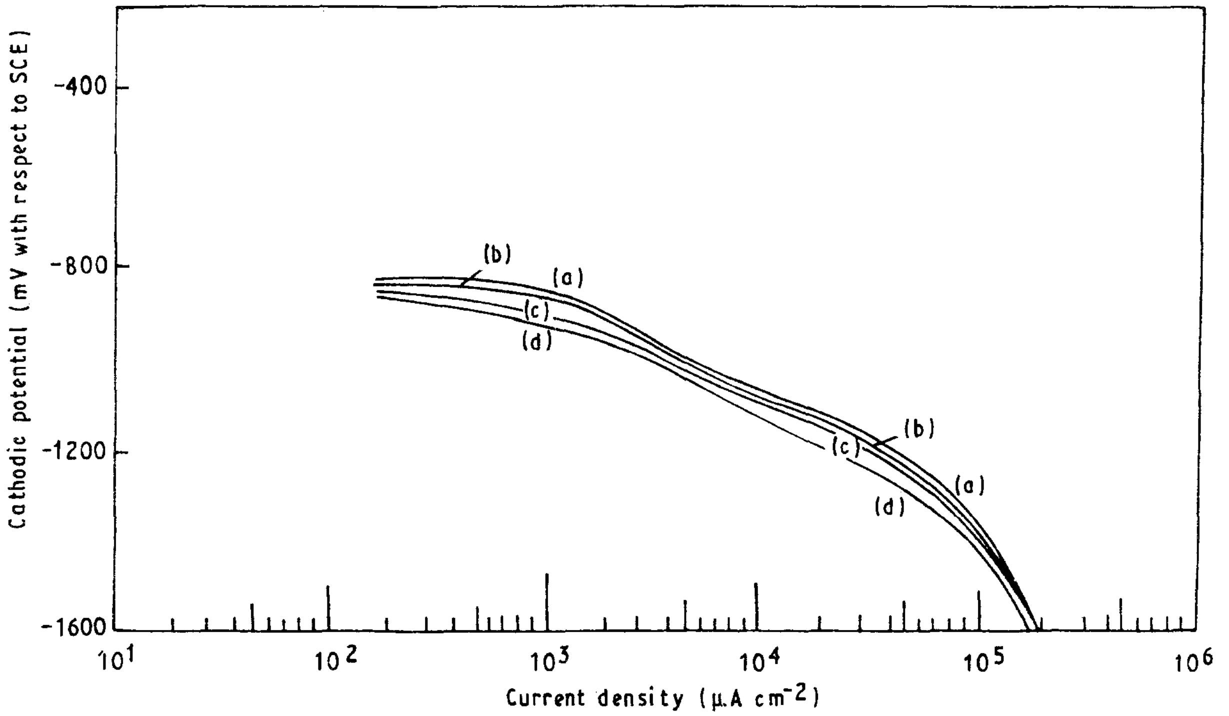

Figure 5 Polarization curves of iron electrodeposition in 0.06 M $FeSO_4$, 0.02 M citric acid and 1.67 M $(NH_4)_2SO_4$ solution, at pH: (a) 4.0, (b) 4.6, (c) 5.3, (d) 6.0.

those of Fe (C_2O_4) and Fe $(cit)^-$. Thus the concentrations of free Fe^{2+} ions decrease as the pH increases. A consequent lowering of free Fe^{2+} ions results in a shift of the cathodic potentials to a more negative value. Like Figs 2 and 3, Fig. 4 has only one Tafel region, but Fig. 5 has two Tafel regions with citric acid. The Tafel slopes decrease less with increasing pH. Thus, the mechanism of the deposition process depends on the nature of the chelating agents, but not on the pH value of the electrolytes.

3.2. Cathodic current efficiency

3.2.1. *Effect of temperature*

In theory, increasing temperature generally favours the complex ion dissociation. Consequently, the concentration of unchelated ferrous ions would increase and result in a decrease of the reduction overpotential [13]. Thus, powders are easily electrodeposited and the cathodic current efficiency increases corresponding to increasing temperature. Our results shown in Figs 6 and 7 and Tables I and II with oxalic acid and citric acid as chelating agents, are consistent with the theoretical prediction.

3.2.2. *Effect of chelating agent concentration and pH*

The system with citric acid as chelating agent is more polarized and has a higher Tafel slope than that with oxalic acid (Fig. 1). Hence, in Fig. 8 the cathodic current efficiency in the citric acid system (Curve b) at 91.37 mA cm^{-2} is lower than that in the oxalic acid system (Curve a); also at 115.73 mA cm^{-2}, that in the citric acid system (Curve d) is lower than that in the oxalic acid system (Curve c).

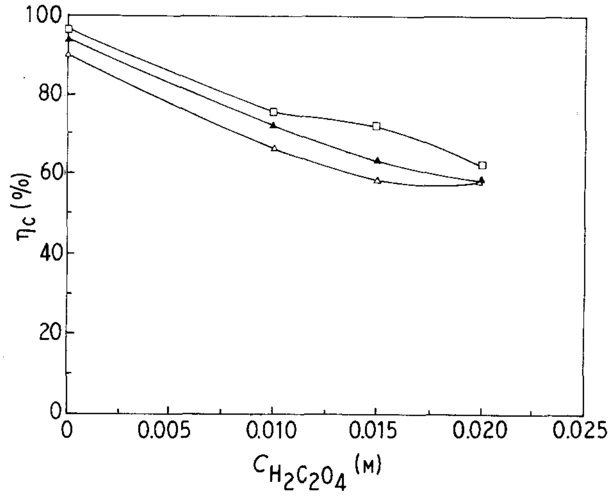

Figure 6 The effect of oxalic acid concentration on the cathodic current efficiency in 0.06 M $FeSO_4$, xM $H_2C_2O_4$ and 1.67 M $(NH_4)_2SO_4$ solutions at pH 4.60, i_c 91.37 mA cm^{-2}. T (°C): (Δ) 50, (▲) 60, (□) 70. x (M): 0–0.020.

The increase in chelating agent concentration, such as oxalic acid and citric acid, increases the concentrations of complex ions, and decreases the concentrations of unchelated ferrous ions, which in turn causes an increase of the cathodic overpotential and a lowering of the cathodic current efficiency. The results are shown in Fig. 6. A similar trend of lowering current efficiency due to a decrease of free Ni^{2+} ion concentration has been observed by Appelt and Paszkiewicz [14].

The complex species are also dependent on the pH value. As the pH value increases, the concentrations of $C_2O_4^{2-}$ and cit^{3-}, as well as those of Fe (C_2O_4) and Fe $(cit)^-$ increase. However, the cathodic current efficiency decreases with a lowering of the acidity at low

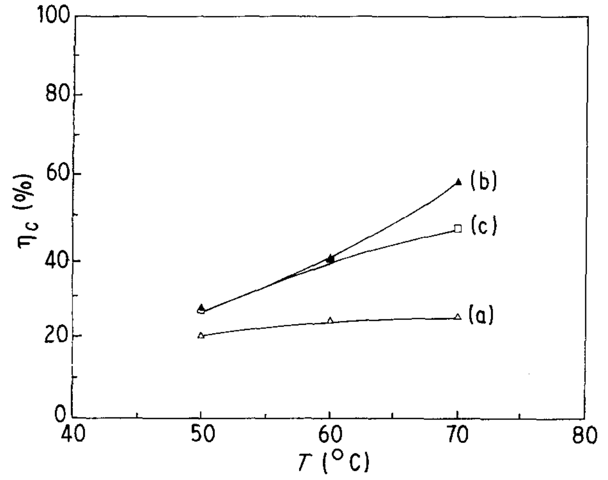

Figure 7 The effect of temperature on the cathodic current efficiency in 0.06 M $FeSO_4$, 0.02 M citric acid and 1.67 M $(NH_4)_2SO_4$ solutions at pH 4.60. i_c (mA cm^{-2}): (a) 91.37, (b) 115.73, (c) 137.59.

TABLE I The effect of oxalic concentration, current density, temperature and pH on cathodic current efficiency. Bath composition: C_{FeSO_4} 0.06M, $C_{(NH_4)_2SO_4}$ 1.67M, C_L 0.000–0.020M, L, oxalic acid.

Curve[a]	C_L (M)	i_c (mA cm^{-2})	T (°C)	pH	η_c (%)
(a)	0.010	91.37	50.0		56.56
			60.0	6.00	66.52
			70.0		86.41
(b)	0.010	91.37	50.0		62.59
			60.0	5.30	68.74
			70.0		78.32
(c)	0.010	91.37	50.0		66.14
			60.0	4.60	71.97
			70.0		75.19
(d)	0.015	91.37	50.0		58.31
			60.0	4.60	62.83
			70.0		72.02
(e)	0.020	91.37	50.0		57.85
			60.0	4.60	58.01
			70.0		62.03
(f)	0.000	91.37	50.0		89.81
			60.0	4.60	93.70
			70.0		96.23

[a] See Figs. 7 and 8.

TABLE II The effect of citric acid concentration, current density, temperature and pH on cathodic current efficiency. Bath composition: C_{FeSO_4} 0.06 M, $C_{(NH_4)_2SO_4}$ 1.67 M, C_L 0.000–0.020 M, L citric acid.

Curve[a]	C_L (M)	i_c (mA cm^{-2})	T (°C)	pH	η_c (%)
(a)	0.020	91.37	50.0		20.19
			60.0	4.60	23.73
			70.0		24.27
(b)	0.020	115.73	50.0		26.58
			60.0	4.60	39.15
			70.0		58.08
(c)	0.020	137.59	50.0		26.43
			60.0	4.60	39.15
			70.0		47.13
(d)	0.000	91.37	50.0		89.81
			60.0	4.60	93.70
			70.0		96.23

[a] See Figs. 7 and 8.

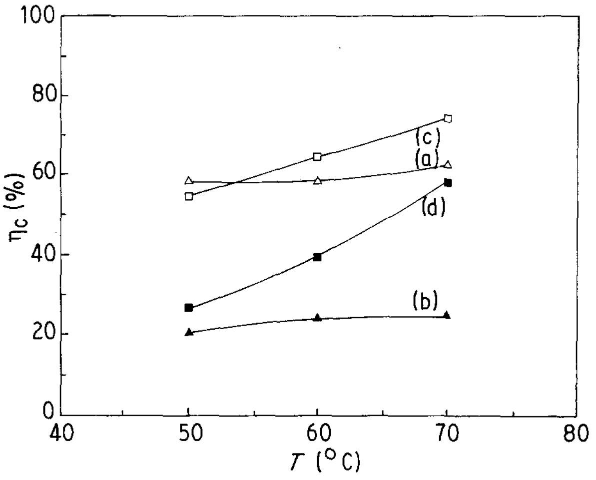

Figure 8 The effect of temperature on the cathodic current efficiency in 0.06 M $FeSO_4$, 0.02 M chelating agents and 1.67 M $(NH_4)_2SO_4$ solutions at pH 4.60. (a) 91.37 mA cm^{-2}, oxalic acid, (b) 91.37 mA cm^{-2}, citric acid, (c) 115.73 mA cm^{-2}, oxalic acid, (d) 115.73 mA cm^{-2}, citric acid.

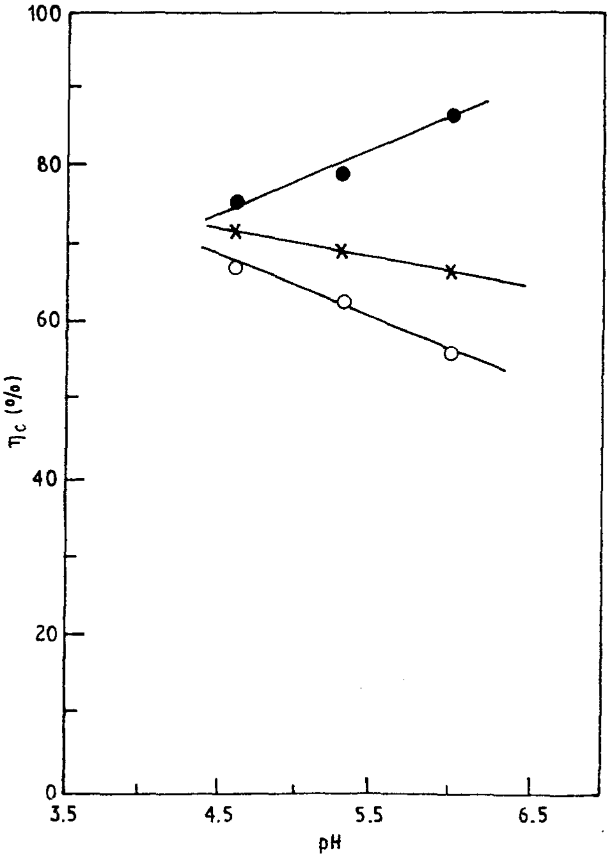

Figure 9 The effect of pH on the cathodic current efficiency in 0.06 M $FeSO_4$, 0.01 M $H_2C_2O_4$ and 1.67 M $(NH_4)_2SO_4$ solutions, at pH: 4.6, 5.3, 6.0. T (°C): (○) 50, (×) 60, (●) 70.

temperature (Fig. 9). Otherwise, at higher temperatures such as 70.0 °C, the effect of temperature is more significant than that of the acidity on the cathodic current efficiency, due to an increase in the degree of dissociation of the complex. Therefore, the cathodic current efficiency increases with decreasing acidity at 70.0 °C (Fig. 9).

3.2.3. Effect of current density

An increase in the current density increases the cathodic current efficiency until a maximum appears; the efficiency then decreases. In Fig. 7 the efficiency of Curve b (at 115.73 $\mathrm{mA\,cm^{-2}}$) is higher than that of Curve a (at 91.37 $\mathrm{mA\,cm^{-2}}$), but the efficiency of Curve c (at 137.59 $\mathrm{mA\,cm^{-2}}$) is lower than that of Curve b (at 115.73 $\mathrm{mA\,cm^{-2}}$). As the current density largely increases, the hydrogen evolution preferentially increases.

3.3. Powder morphology

The shape and size of the iron powders can also be influenced by the presence of chelating agents. As shown from Fig. 10a–e, these baths containing oxalic acid or citric acid produce powders with irregular, elliptical or spherical shape. In a bath without chelating agent, the powders are usually dendritic in form, as shown in Fig. 10f.

The overpotential increases due to a decrease in the concentration of free $\mathrm{Fe^{2+}}$ ions when the chelating agent content is increased. In addition, the formation of new nuclei requires more energy than the growth of already existing ones. It is expected that the nucleation process is preferred, due to enhanced polarization [15]. The system with citric acid is more polarized than that with oxalic acid. Consequently, electro-

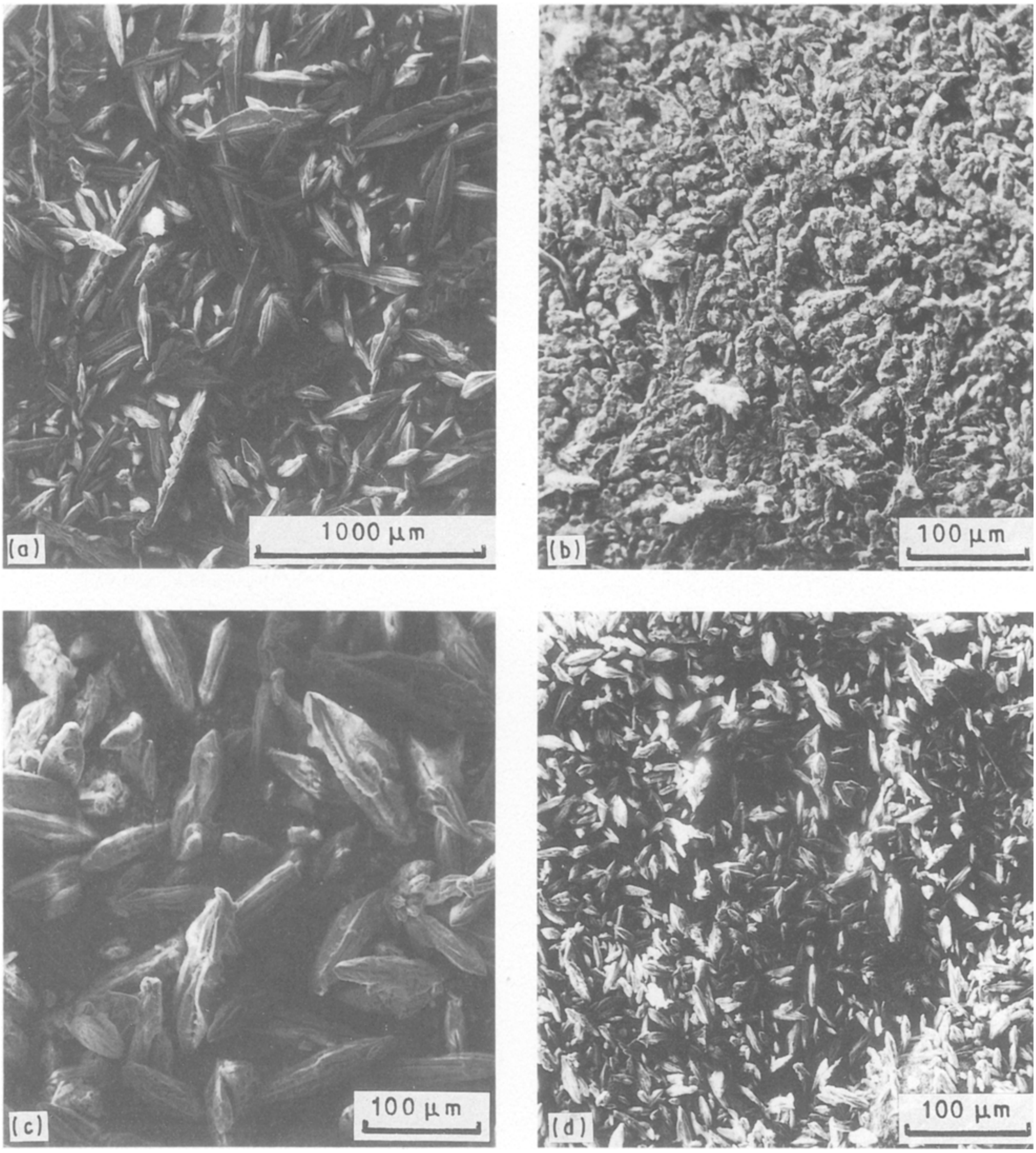

Figure 10 Electron probe microscopy analysis (EPMA) of iron powders. (a) 0.015 M oxalic acid, 70 °C; (b) 0.015 M oxalic acid, 50 °C; (c) 0.020 M oxalic acid, 50 °C; (d) 0.01 M citric acid, 70 °C; (e) 0.020 M citric acid, 50 °C; (f) no chelating agent, 50 °C.

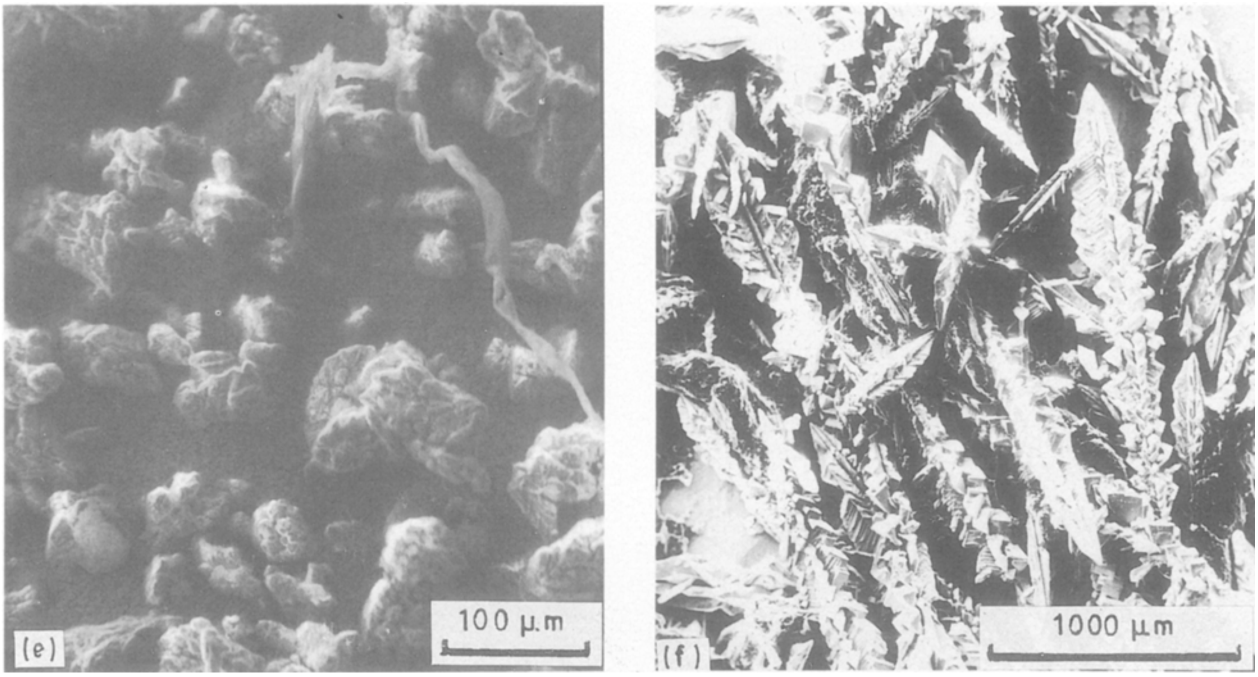

Figure 10 continued.

deposited powders with citric acid, shown in Fig. 10e, are finer than those with oxalic acid, Fig. 10c.

The size of the iron powders is also affected by the bath temperature. The powders are finer in Fig. 10b than those in Fig. 10a, which is because the decrease of crystal supersaturation due to increased temperature causes a decrease in the nucleation rate. Therefore, the electrodeposited powders are finer at low temperature than those at high temperature.

4. Conclusion

It is possible to electrodeposit iron powders from all the baths investigated. The nature of the anions, the salts used in each bath, plays an important role in the electrodeposition process and influences the characteristics of the deposit.

The anion additives, such as oxalic acid and citric acid, easily chelate with ferrous ions to form a stable ferrous complex ion.

Iron powders with a definite shape and size can be produced by carefully controlling the electrodeposition conditions. Spherical and elliptical iron powders can be formed with oxalic acid at low temperature. Moreover, finer powders can be produced with citric acid as chelating agent. Without chelating agents, powders of dendritic form can be produced.

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