Reactive deposition of ultrafine cobalt powders

Part II Effect of preparation conditions

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The particle size distributions of cobalt powders prepared by reactive deposition were examined and correlated with the deposition condition. In reactive deposition, a $Co(OH)_2$ colloid layer was formed at the electrode surface upon reduction of dissolved oxygen. The colloid layer accelerated the decrease in interfacial Co^{2+} concentration and inhibited crystal growth of the metal, and was therefore instrumental in the formation of fine cobalt particles. The powders from reactive deposition were statistically a factor of two finer and of more uniform size distribution than those from normal electrodeposition. It was found that both the reactive deposition of cobalt powders and the reactive deposition of porous cobalt structures were driven by the same kinetic factors, namely the requirement of maintaining an effective presence of the $Co(OH)_2$ colloid layer at the electrode surface. Hence a similar dependence on deposition conditions for both processes was obtained.

1. Introduction

Cobalt powders have many important industrial applications. They are commonly used in alkaline rechargeable batteries, magnetic recording media, heterogeneous catalysis, and, especially, as a pigment in the manufacture of hard metal tools, and grinding and polishing compounds [1].

In previous studies of the reactive deposition of cobalt powders [2], SEM examination showed that ultrafine cobalt powders of $0.4-0.6 \mu m$ minimum particle size could be produced. In addition, due to the formation of a Co(OH)₂ colloid layer at the electrode surface by oxygen reduction prior to the deposition of cobalt (Equations 1-3) the crystal growth of cobalt was inhibited and hydrogen evolution in the deposition process was depressed, and the interfacial Co²⁺ concentration was quickly reduced

$$O_2 + H_2O + 4e^- = 4OH^-$$
 (1)

$$O_2 + H_2O + 2e^- = HO_2^- + OH^-$$
 (2)

$$Co^{2+} + 2OH^{-} = Co(OH)_2.$$
 (3)

As a result, compared with normal electrodeposition, reactive deposition produces purer cobalt powders with less $Co(OH)_2$ over a wider range of working current density.

The advantages of the reactive deposition of cobalt powders are attributed predominantly to the presence of the $Co(OH)_2$ colloid layer at the electrode surface during deposition. In systematic studies on reactive deposition of cobalt [3–6] it was found that the dynamic states of the $Co(OH)_2$ colloid layer were affected by the nature of the bubbling gas, the anion in the deposition solution, the Co^{2+} concentration and the working current density. Gases with different partial pressures of oxygen gas would influence the formation of the colloid layer since oxygen reduction was controlled by the limiting diffusion of dissolved oxygen. It was found [4, 5] that the grain size of cobalt deposits prepared in the presence of different bubbling gases decreased in the following order: bubbling $N_2 >$ bubbling air > bubbling O_2 .

The distribution of 2- and 4-electron oxygen reduction reactions (Equations 1 and 2) in neutral media is strongly dependent on the nature of the anion [3]. HO_2^- from the 2-electron reduction of O_2 has an effect on the change in the dynamic states of the Co(OH)₂ colloid layer at the electrode surface via Equation 4

$$Co(OH)_2 + HO_2^- = CoOOH + 2OH^-$$
(4)

As the preference for the 2-electron oxygen reduction in solutions of different anions decreases in the following order: $CH_3COO^- < SO_4^{2-} < Cl^-$, the grain size of cobalt deposits also decreases in the same order [4]. In addition, operating at high current densities and high Co^{2+} concentration would decrease the effects of the colloid layer and increase the crystal growth process [4].

In this paper, these factors affecting the reactive deposition of cobalt powders will be studied in an attempt to establish the optimum operating conditions and the applicability of the technique.

2. Materials and methods

2.1. Preparation of cobalt powders

The deposition of cobalt powders was carried out in an electrolytic cell as described by Jiang *et al.* [7]. The volume of deposition solution was kept constant at 220 ml. Reactive deposition was carried out in the presence of N_2 , O_2 and air respectively. The gas was bubbled through a sintered glass plug directly onto the working electrode and the flowrate of the gas was regulated by a flowmeter. The working electrode was made of 1 cm² stainless steel foil. A cobalt metal foil (99.5% Co, Cobalt Development Institute) and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The stainless steel was cleaned with washing liquid, then rinsed in a copious amount of deionized water, and dried with tissue paper prior to the deposition of the cobalt powders.

The $CoCl_2 \cdot 6H_2O$ and $CoSO_4 \cdot 6H_2O$ (BDH) were of the AR grade. The deposition solution was prepared by dissolving the cobalt salt in deionized distilled water to reach the desired concentration. Prior to deposition, the gas selected for reactive deposition was bubbled through the solution for 10 min to ensure complete saturation. The reactive deposition was controlled by a computer-driven EG&G model 273 potentiostat/galvanostat. All experiments were performed at room temperature.

The reactivity of electrolytic cobalt powders is in general greater than that of compact metals. Owing to the readiness of cobalt powders to be oxidized by dissolved oxygen, water-free acetone was used as a solvent for the storage of the powders. The powders were scraped off the electrode by a sharp blade, followed by careful washing with acetone, and stored in a glass bottle filled with oxygen-free acetone solvent. An ultrasonic wave was also used to disengage coagulated cobalt particles.

2.2. Particle size distribution

The particle size distribution of the cobalt powders was determined by a Coagulated Instruments Model 2600 laser diffraction particle sizer, controlled through a CBM 4000 computer. The suspension medium was acetone (refractive index 1.359) and a 63 mm focal length lens was used for the measurements. The sample was ultrasonically dispersed prior to the transfer to the suspension medium in a small sample cell. The cell had a volume of 15 ml and provided a beam length through the sample of 14.3 mm. The sample concentration was monitored using the 'obscuration' indicated by the instrument, and its value was kept within the recommended range of 0.2–0.4.

Since cobalt powder is magnetic, a magnetic stirrer was not used for the circulation of the suspension; instead a cycled flow system was employed. In the measurements, the log difference, which indicates the adequacy of particle size measured, was maintained between 4 and 5, showing that the data fit was good and the measurements were performed correctly. Runs were often duplicated for each sample to provide reproducible particle size distribution.

3. Results and discussion

3.1. Nature of bubbling gas

Fig. 1 shows the transient curves obtained from 0.05 M CoCl₂ solution saturated with oxygen at dif-



Figure 1 Transient curves obtained from 0.05 M CoCl₂ solution saturated with oxygen at different current densities.

ferent current densities. During the initial stage the overpotential for the deposition of cobalt increased quickly in the cathodic direction before coming to a plateau after some finite time. Similar phenomena were observed in the solution saturated with either air or nitrogen. If the significant increase in the overpotential was predominantly due to the decrease in interfacial Co^{2+} concentration in the absence of convection then, according to Ibl [8], the transition time τ to reach the potential plateau where the process was under diffusion control of Co^{2+} should have the relationship with current density *i* via Equation 5

$$i\tau^{1/2} = [zF/2(1-n_c)](\pi D)^{1/2} C_0$$
 (5)

where z is the number of electrons exchanged per Co^{2+} in the reaction, n_c is the transference number of Co^{2+} , F is the Faraday constant, D is the diffusion coefficient of Co^{2+} , and C_0 is the concentration of Co^{2+} in the bulk solution. Fig. 2 attests to the logarithmic relationship between transition time τ and current density for the reactive deposition of cobalt powders in 0.05 M CoCl₂ saturated with O₂, air and N₂. The slopes of the straight lines are approximately -1.8, which is in good agreement with the -2 as



Figure 2 Logarithmic relationships between current density and transition time measured in 0.05 M CoCl₂ solution saturated with (\bigcirc) oxygen, (\bullet) air or (\bigtriangledown) nitrogen.

required by Equation 5. Therefore, it is reasonable to assume that the interfacial Co^{2+} concentration fell to zero by the time the potential plateau was reached in the chronopotentiometric curves. At the initial stage, the increase in the overpotential was mainly due to the decrease in the interfacial Co^{2+} concentration, and the effect of increased surface area was negligible. The formation of compact deposit was more likely at this stage, which produced little variation in the surface area. At the later stage, the overpotential was reduced slightly, probably due to the increase in the surface area of deposit resulting from cumulative crystal growth.

An indication of the different behaviour of gases in reactive deposition other than the increase in surface area during deposition can also be inferred from the potential-time curves. Fig. 2 shows also that the transition time is longest in solutions saturated with nitrogen, and shortest in solutions saturated with oxygen. This result could be reasonably understood in terms of a fast decrease of the interfacial Co²⁺ concentration in the presence of oxygen through the high rate of oxygen reduction via Equation 3. In other words the $Co(OH)_2$ colloid layer in solutions saturated with oxygen would be the thickest. The presence of the colloid layer at the electrode surface inhibited the deposition of cobalt. More energy was therefore needed for the reduction of cobalt ions to overcome the inhibiting effect of the colloid layer. Therefore, the value of the transference number n_c in Equation 5 was the lowest in solutions saturated with oxygen, resulting in the shortest transition time. In previous studies [4] the inhibiting effect of the colloid layer was inferred from the more negative nucleation potential required for the deposition of cobalt from a solution saturated with oxygen rather than with nitrogen. On the other hand, the difficulty in the formation of cobalt nuclei will result in finer crystal grains. As a result, the presence of dissolved oxygen in the solution promotes the production of fine cobalt powders in reactive deposition.

3.2. Nature of anions

In the reactive deposition of cobalt, the anions in the deposition medium have a relatively large effect on the formation of porous deposits [3, 4]. In the production of powdery cobalt from both 0.05 ${\mbox{\tiny M}}$ CoCl_2 and $CoSO_4$ solutions saturated with oxygen, the plot of the logarithm of current density against the transition time τ resulted in the parallel straight lines of slope -2 (Fig. 3). Such linearity between the two variables was more extended with respect to the transition time for the chloride solution. This indicates that chloride promotes the formation of Co(OH)₂ colloid layer better under limiting diffusion conditions. In fact, in the studies on oxygen reduction in both chloride and sulphate solutions with or without the presence of Co^{2+} salt [3] it was observed that oxygen reduction was faster in the chloride solution than in the sulphate solution. On the other hand, the cathodic shift in nucleation potential as affected by the $Co(OH)_2$ colloid layer was also more pronounced in the chloride



Figure 3 Logarithmic relationships between current density and transition time measured in either (\bigcirc) 0.05 M CoCl₂ or (\bigcirc) 0.05 M CoSO₄ solutions saturated with oxygen.

solution [4]. Therefore, the formation of cobalt powders by reactive deposition is facilitated by the presence of chloride.

3.3. Cobalt powder particle size distribution

Fig. 4 shows the particle size distribution of the cobalt powders deposited from 0.05 M CoCl_2 solution at a current density of 20 mA cm⁻² in the presence of bubbling nitrogen and bubbling oxygen (30 ml min⁻¹), respectively. The powder prepared in the presence of bubbling oxygen was obviously smaller in size than the powder prepared in the presence of bubbling nitrogen. In previous studies on the reactive deposition of cobalt electrode [3–5] it was found that due to the formation of the Co(OH)₂ colloid layer at the electrode surface and the change of the dynamic states of the colloid layer prior to the deposition of cobalt, the reactive deposition of cobalt was characterized by localized nucleation and limited crystal growth processes. The Co(OH)₂ colloid layer at the electrode



Figure 4 Size distributions of cobalt powders prepared from 0.05 M CoCl₂ solution in the presence of either bubbling nitrogen or bubbling oxygen (30 ml min⁻¹) at a current density of 20 mA cm⁻².

depressed the nucleation to a more negative potential. Individual Co particles could be isolated and their extensive crystal growth inhibited due to the continuous formation of the $Co(OH)_2$ colloid layer around the grain boundaries [4, 9], resulting in the generation of a high surface area and a highly porous deposit of ultra-fine grain structure. The reactive deposition of powdery cobalt as studied here exhibited the same behaviour, confirming once again the significance of colloidal formation and its inhibiting effect on crystal growth.

A common parameter to use in particulate characterization is the Sauter mean diameter as defined by

$$D(M, N) = \int_{D_0}^{D_m} D^M n(D) \, \mathrm{d}D \Big/ \int_{D_0}^{D_m} D^N n(D) \, \mathrm{d}D \, (6)$$

where D is particle diameter and n(D) the number of particles in a sample. The Sauter mean diameter D(3, 2), which is a measure of the total volume of particles relative to the total surface area, is therefore representative of the statistical average diameter of the particles. In addition, the span of the particle size distribution can be described by

$$Span = [D(90) - D(10)]/D(50)$$
(7)

where D(10), D(50) and D(90) are the particle diameters below which 10, 50 and 90 vol% of the distribution belongs respectively. A small span is indicative of a narrow particle size distribution.

The Sauter mean diameters of powders deposited reactively from $0.05 \text{ M} \text{ CoCl}_2$ solution in flowing oxygen (at 30 ml min⁻¹) were computed from their respective particle size distributions and plotted against current density in Fig. 5. In the low current density range the Co(OH)₂ colloid layer at the electrode surface formed upon the reduction of oxygen exerted the most influence on cobalt deposition. The crystallization of cobalt in the neutral solutions is known to proceed via progressive nucleation and



Figure 5 Dependence of Sauter mean diameters of cobalt powders on current density. The powders were prepared from 0.05 M CoCl_2 solution in the presence of bubbling oxygen (30 ml min⁻¹).

crystal growth regardless of the absence or presence of a Co(OH)₂ colloid layer [5, 10]. However, the increase in current density below 30 mA cm⁻² brought about mainly the increase in nucleation, and the crystal growth of cobalt was inhibited by the colloid layer. As a result, cobalt particles of the smallest dimension of D(3, 2) (3.0 µm) were formed at 30 mA cm⁻². Further increase in current density, however, enhanced the crystal growth process which eventually overwhelmed the inhibition by the Co(OH)₂ colloid layer. Therefore, the size of cobalt particles increased when the current density was higher than 30 mA cm⁻².

The removal of the inhibiting effects of the colloid layer with increasing current density was also evident in the particle size distribution of powders prepared with different flowing gases (Table I). When a current density as high as 60 mA cm⁻² was used, all powders showed nearly the same Sauter mean diameter irrespective of the nature of the gas (oxygen, nitrogen or air) used in the deposition. At such a high current density the Co²⁺ concentration at the electrode surface was not high enough to sustain the current demand and hydrogen evolution superseded as the main charge transfer reaction at the electrode. The generous liberation of hydrogen wore down the persistence of the Co(OH)₂ colloid layer at the electrode surface, and the inhibiting effects of the colloid layer were curbed. In the end, some of the $Co(OH)_2$ could even be precipitated without reduction and be present in the cobalt powders. On the other hand, when a low current density of 20 mA cm⁻² was used, the inhibiting effect of the colloid layer at the electrode surface was maintained, and the size of powders prepared with different bubbling gases decreased in the same order as reactively deposited cobalt bulk, i.e. bubbling N_2 > bubbling air > bubbling O_2 . It was also noted that at this current density the Sauter mean diameter of powder prepared in the presence of bubbling oxygen was a factor of two smaller than powder prepared in the presence of bubbling nitrogen. Therefore, the $Co(OH)_2$ colloid layer in the reactive deposition was only effective in inhibiting of cobalt crystal growth at lower current densities. The oxygen in air could also produce a $Co(OH)_2$ colloid layer at the electrode surface to inhibit the crystal growth, albeit understandably less efficiently than pure oxygen. Hence the powder particles prepared in bubbling air were smaller than those prepared in bubbling nitrogen. In addition, the span of the particle size distribution of powders prepared in the presence of bubbling oxygen was also narrower, indicating that the inhibiting effects of

TABLE I Size characteristics of cobalt powders prepared in 0.05 M CoCl_2 solution in the presence of bubbling gas (30 ml min⁻¹)

	Oxyg	en	Air		Nitro	gen
Current density (mA cm ⁻²)	20	60	20	60	20	60
Sauter mean diameter (µm)	7.4	8.3	12.3	8.6	16.3	8.5
Span	1.4	1.8	1.7	2.2	2.0	3.1

the colloid layer also led to cobalt powders of more uniform dimensions.

Fig. 6 compares the Sauter mean diameters of powders prepared in chloride solutions of varying Co²⁺ concentrations in the presence of bubbling oxygen (30 ml min^{-1}) at a current density of 40 mA cm⁻². The spans of the particle size distribution of the powders are also indicated. The Sauter mean diameter was found to increase with Co²⁺ concentration when the latter was higher than 0.05 M. Hence larger powder particles were formed in solutions of high Co²⁺ concentrations. The kinetics of electrodeposition is known to proceed via electron transfer/diffusion control [5, 10]. As the Co^{2+} concentration increases, the electron transfer process becomes rate-controlling and the inhibiting effects of the Co(OH)₂ colloid layer which was formed upon limiting diffusion of Co^{2+} are suppressed. The experimental results also concurred with the disappearance of the cathodic peak in the reverse scan of the cyclic voltammogram of high Co²⁺ concentration [4]. Similarly, cobalt powders of more uniform sizes, i.e. small span values, were produced in solutions of low Co²⁺ concentration where the Co(OH)₂ colloid layer exercised effective control on the deposition of powdery cobalt. It can therefore be concluded that fine cobalt powders are only produced under conditions where the $Co(OH)_2$ colloid layer at the electrode surface can effectively inhibit cobalt crystal growth. In previous studies [4] it was found that the colloid layer was most effective in producing a highly porous cobalt structure only in the reaction region where the kinetics of cobalt deposition was mutually controlled by diffusion of interfacial electron transfer processes. The results of varying current density of Co²⁺ concentration reported here for an effective presence of Co(OH)₂ colloid layer at the electrode surface were also similar. Hence the same deposition kinetics could also be extended to reactive deposition of cobalt powders in addition to the deposition of porous cobalt metal.

The characteristics of the powders prepared from the chloride or the sulphate solutions containing



Figure 6 Dependence of Sauter mean diameters of cobalt powders on bulk Co^{2+} concentration. The powders were prepared from chloride solutions in the presence of bubbling oxygen (30 ml min⁻¹) at a current density of 40 mA cm⁻². The spans of size distribution of the powders are also shown.

TABLE II Size characteristics of cobalt powders prepared in different solutions with 0.05 M Co^{2+} concentration in the presence of bubbling oxygen (30 ml min⁻¹)

Nature of anion	Chloric	le solution	Sulphate solution		
Current density (mA cm ⁻²)	20	40	20	40	
Sauter mean diameter (µm)	7.4	6.2	12.1	10.4	
Span	1.4	1.5	1.9	2.0	

 $0.05 \text{ M} \text{ Co}^{2+}$ in the presence of bubbling oxygen (30 ml min^{-1}) are given in Table II to highlight the effect of anions. It can be seen that finer powders of more uniform sizes are produced by reactive deposition from the chloride solution. A similar observation was also reported previously in the reactive deposition of highly porous cobalt deposits [4]. With reference to the role of the $Co(OH)_2$ colloid layer on cobalt crystal growth, the inhibiting effects of the colloid layer are therefore greater in the chloride solution than in the sulphate solution. In the presence of chloride, the dynamic state of the colloid layer as affected by HO_2^{-1} from oxygen reduction leads to a unique crystallization characteristic via localized nucleation and limited crystal growth [5]. Hence the reactive deposition of fine cobalt powders is facilitated in the chloride solutions. In summary, the reactive deposition of cobalt powders and the preparation of porous cobalt deposits display similar dependence on deposition variables such as Co²⁺ concentration, current density, and nature of anions and bubbling gases, as both processes rely on the effective presence of the Co(OH), colloid layer to inhibit extensive crystal growth of cobalt.

4. Conclusions

The particle size distribution of cobalt powders deposited in different gases was studied as a function of deposition variables including Co²⁺ concentration, current density, nature of anions and gases. A Co(OH)₂ colloid layer was formed at the electrode surface upon oxygen reduction. The colloid layer accelerated the decrease in the interfacial Co²⁺ concentration, suppressed extensive crystal growth of the depositing phase, and was therefore instrumental in the production of fine cobalt powders. The powders formed by reactive deposition were generally a factor of two smaller and of more uniform size distribution than those obtained by normal electrodeposition. The production of fine cobalt powders by reactive deposition also displayed a dependence on deposition variables similar to that in the reactive deposition of porous cobalt. The similarity was due to the common requirement of maintaining an effective presence of the $Co(OH)_2$ colloid layer at the electrode surface, which inhibited crystal growth. The inhibiting effects of the colloid layer were most effective when the kinetics of deposition were controlled by a combination of diffusion and interfacial electron transfer which resulted in the unique crystallization characteristic of localized nucleation and limited crystal growth. Therefore, in

either high Co^{2+} concentrations or at high current densities where the deposition kinetics were predominantly under diffusion or electron transfer controls, respectively, large powder particles were produced. Finer cobalt particles with more uniform size distribution were also produced in reactive deposition from chloride solutions than from sulphate solutions.

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