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ELECTRODEPOSITION OF COBALT POWDERS WITH NOVEL THREE-DIMENSIONAL STRUCTURE

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Abstract

Novel three-dimensional cobalt powder structures were successfully prepared by electrodeposition. Electrodeposited cobalt powder was characterized by scanning electron microscopy (SEM) and light microscopy. It was possible to control the morphology and structure of cobalt particles by adjusting process parameters of electrodeposition such as current density and type of working electrode. The morphology and structure of cobalt powders were investigated and the formation mechanism of agglomerate was also discussed.

Key words: electrodeposition, cobalt powder, 3D structure, particle, morphology

Introduction

Metal powder production techniques are used to manufacture a wide spectrum of metal powders designed to meet the requirements on large variety of applications. Powders of virtually all metals can be produced. Suitable methods for powder production depend on required production rates, powder properties and the physical and chemical properties of the materials. Electrodeposition is a viable method to produce pure powders with an ultrafine structure [1, 2].

From electrochemistry point of view, metals can be divided into three groups by melting points and exchange current densities: normal, intermediate and inert. Normal metals (Cd, Zn, Sn,) have low melting points ($320^{\circ}\text{C} < t_m < 420^{\circ}\text{C}$) and high exchange current densities ($j_0 > 1 \text{ A dm}^{-2}$). Intermediate metals (Au, Cu, Ag) possess moderate melting points ($960^{\circ}\text{C} < t_m < 1090^{\circ}\text{C}$) and medium exchange current densities (j_0 between 10^{-2} and 1 A dm^{-2}). Inert metals (Fe, Ni, Co, Pt, Cr, Mn) exhibit high melting points

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($1240^{\circ}\text{C} < t_m < 1870^{\circ}\text{C}$) and low exchange current densities (j_0 between 10^{-2} and 10^{-12} Adm^{-2}) [1, 3].

Morphology is probably the most important property of electrodeposited metals. It depends mainly on the kinetic parameters of deposition process and deposition current density. Obviously, the morphology of electrodeposited metal also depends on deposition time and on the final form of the deposit before its separation from the electrode surface [4]. Electrodeposition has two stages, i.e. nucleation and growth. In the case of smooth cathodes the growth process is enhanced through nucleation, but the growth process is dominant for powder production where each nucleus is a powder particle. Therefore, the obtainment of a proper particle size of the powder is strongly dependant on the relative rates of nucleation and crystal growth [5, 6].

In recent years, one of the important goals of material scientists is to develop ways of producing the structure of materials with unusual and novel forms using different technology [7-9]. Also, large-scale self-assembly of misro/nanostructured building components with highly specific morphology and novel properties are of great interest to chemists and material scientists not only for their role in better understanding concept of self-assembly, but also for their great potential for technological application. It is still a big challenge to develop simple and reliable methods for hierarchically self-assembled architectures with novel and interesting morphologies, which would lead to novel properties of micro/nanomaterials. Cobalt has been extensively studied as an important magnetic material not only due to its multiple crystal structures (hexagonal-close-packed, hcp and face-centered-cubic, fcc), but also because of its structure-dependent magnetic and electronic properties [7-13]. In the usual aqueous electrolytes, cobalt electrodeposition is accompanied by the hydrogen evolution reaction (HER), and therefore, in such circumstances, a quantitative evaluation of kinetic parameters of the cobalt electrocrystallization process, is almost impossible [10, 11, 14-16]. In the present study the morphology and structure of cobalt powders galvanostatically deposited on different electrodes were investigated.

Experimental

All chemical reagents in this work were of analytical grade purity. Electrolytes were made from chemicals and pure water (EASY pure UV, 18.3 M Ω , Barnstead).

Electrodeposition. All details of process of electrodeposition of cobalt powders, current density, and time of deposition and dimension of working electrodes as a function of electrode material are given in Table 1.

Table 1. Dimension of working electrode, current density (j) and time of electrodeposition as a function of electrode material.

Electrode material	Dimension of working electrode	j [mA cm^{-2}]	Time of electrodeposition [min]
Glassy carbon	$d = 0.5 \text{ cm};$ $S = 7.5 \text{ cm}^2$	500	250
		770	70
Cobalt wire	$d = 0.11 \text{ cm};$ $S = 1.5 \text{ cm}^2$	770	70
Nickel wire	$d = 0.18 \text{ cm};$ $S = 2.3 \text{ cm}^2$	770	90

Cobalt powder samples were electrodeposited at the room temperature in the cylindrical glass cell of the total volume of 1 dm³ with the cone-shaped bottom of the cell in order to collect powder particles. During the deposition process powder was not removed from the electrode surface, but it was left to be detached spontaneously. After deposition, powder was washed with EASY pure UV water and alcohol and left to dry in the air at room temperature.

Characterization

To observe the internal structure of cobalt powder particles a loose powders were mounting by the epoxy resin. Sample was polished several times and the cross-section structure was observed in a non-etched state using a Zeiss Axiovert 25 light microscope. The morphology of the electrodeposited powder was examined using scanning electron microscope (SEM), Philips, model XL30.

Results and discussion

The influence of current density on the morphology of cobalt powders

In the powder sample deposited at $j_{Co} = 500 \text{ mA cm}^{-2}$ onto a glassy carbon, generally two types of particles are detected: 1. dendrite particles and 2. different types of agglomerates. These agglomerates are further divided into three groups: (i) compact agglomerates; (ii) spongy-like agglomerates of different shapes and (iii) balls-shaped agglomerates. All types of agglomerates contain deep cavities with the fern-like dendrites formed on the bottom of most cavities. In our previous paper [17] some details of morphology of cobalt powder were given.

Cross-section analysis (Fig. 1) is very useful method for observation of particles and for explanation mechanism of their growth [17, 18]. For some reason, and probably due to the tendency of powder particles to grow in condition of low surface energy [19], the agglomerate started to grow as a ball from disperse and finished as a compact deposit on the surface. With the time of growth the disperse agglomerate is branching in different directions and at the tip of each branch spherical diffusion prevails over the planar diffusion. This provides conditions for compact deposition as a consequence of decrease of the local current density on the tip of each branch.

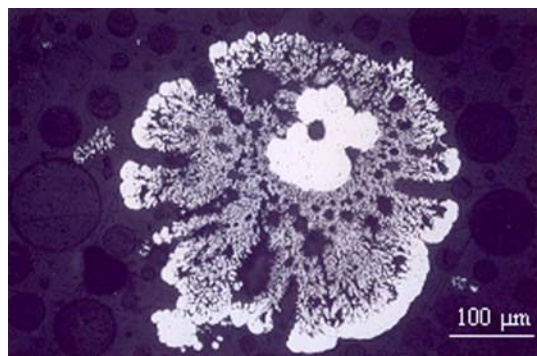


Fig. 1. Light microscope microphotograph of cross-section ball-like agglomerate in cobalt powder electrodeposited at $j_{Co} = 500 \text{ mA cm}^{-2}$.

Quite unique feature of all agglomerates detected in cobalt powder deposit is the presence of deep cavities on their surface and the fern-like dendrites on the bottom of most of these cavities (Fig. 2). As can be seen in Fig. 2a agglomerate is composed of closely connected rounded parts. Each rounded part is composed of needles of average length of about 1 μm and thickness of about 0.1 μm . Surface of compact agglomerate is shown in Fig. 2b.

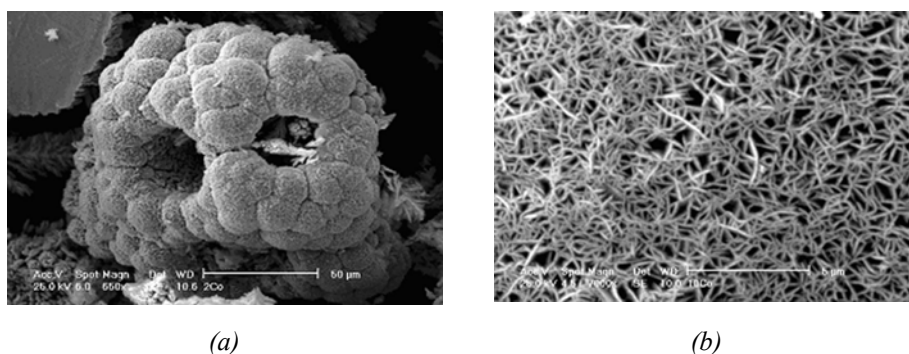


Fig. 2. SEM microphotograph of the (a) compact agglomerate, (b) surface of cobalt powder particle electrodeposited onto glassy carbon at $j_{\text{Co}} = 500 \text{ mA cm}^{-2}$.

Increased current density deposition of cobalt powder reduces the number of observed types of particles. Investigation of the morphology of cobalt powder particles deposited at diffusion limiting current density ($j_{\text{L}(\text{Co})} = 770 \text{ mA cm}^{-2}$) onto glassy carbon (Fig. 3) indicates the existence of only two types of particles: (a) compact agglomerate (Fig.3a) with clearly visible cylindrical cavities (without fern-like dendrites on their bottom) with nodular endings, which have needle dendrites on its surface (detail Fig.3a), and (b) spongy particle (Fig.3b).

There was no presence of ball-shaped agglomerates as was the case with cobalt powder deposited at the $j_{\text{Co}} = 500 \text{ mA cm}^{-2}$ from the same electrolyte. Spongy particles have narrow and deep cavities (Fig.3b), while the surface changes from smooth to the needle (detail in Fig.3b). The shape of cavities of both types of particles indicates that the release of hydrogen bubbles occurs before the separation particles from the surface electrodes. On the surface of particles open cavities may be seen with diameters ranging from small, about 2 μm (detail in Fig.3a), to larger diameters measuring approximately 20 μm (Fig. 3a). Morphology and surface of both types of particles dictate the moment of separation of particles from the surface of electrode. Needle dendrites on the surface of particles probably represent the initial phase of growth in the second generation of dendrites, while smooth areas are compact deposit.

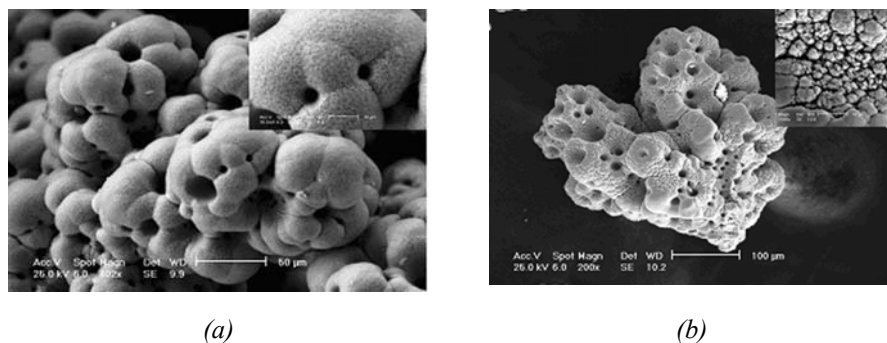


Fig. 3 SEM microphotographs of cobalt powder particles deposited at $j_{L(\text{Co})} = 770 \text{ mA cm}^{-2}$ onto glassy carbon electrode; (a) the agglomerate and detail of surface, (b) spongy-like particle with detail of surface.

The influence of working electrode material on the morphology of cobalt powders

Cobalt powder deposited at diffusion limiting current density $j_{L(\text{Co})} = 770 \text{ mA cm}^{-2}$ onto the cobalt electrode (Fig. 4a,b), have similar morphology as cobalt particles deposited onto glassy carbon. Agglomerate (Fig. 4a) with nodular endings is covered with needle dendrites (detail in Fig. 4a) and contains only cylindrical cavities. In addition to the narrow and deep cavities spongy particles (Fig.4b) contain slightly wider, conical cavities. It is very likely that the morphology of hollow particles dictate the moment of separation from the surface of the electrode, i.e. the degree of development of bubbles in the moment of separation of particles from the surface of electrode. The appearance of these conical cavities, which are not observed in cobalt powder particles deposited at $j_{\text{Co}} = 500 \text{ mA cm}^{-2}$ and $j_{L(\text{Co})} = 770 \text{ mA cm}^{-2}$ onto the glassy carbon, is a consequence of higher speed of formation of hydrogen bubbles. Cavities do not contain fern-like dendrites, indicating that the separation of particles from surface of the electrode occurs before the establishment of conditions for planar diffusion inside cavities. At higher magnification it could be seen that the spongy particles have needle dendrites on their surface instead of smooth areas (Fig.4b). The lack of smooth areas is a consequence of deposition with slightly higher density and the range of mixed deposition control.

Cobalt powder deposition at diffusion limiting current density onto the nickel electrode causes the appearance of only spongy particles (Fig.5) with size ranging from 200 to 300 μm. In samples of cobalt powder electrodeposited onto glassy carbon and cobalt electrodes the presence of agglomerates was observed (Fig.5a). Characteristic of these particles is that they have deep cavities which are the result of intensive hydrogen evolution. Higher magnification (Fig. 5b) reveals the surface with nodular endings, but without needle dendrites. It is likely that the particles show the same characteristic transformation from disperse to the compact parts with increasing their size. According to the surface morphology of the cavity (white arrows in Fig.5b) it seems that the transition occurs from disperse to compact area.

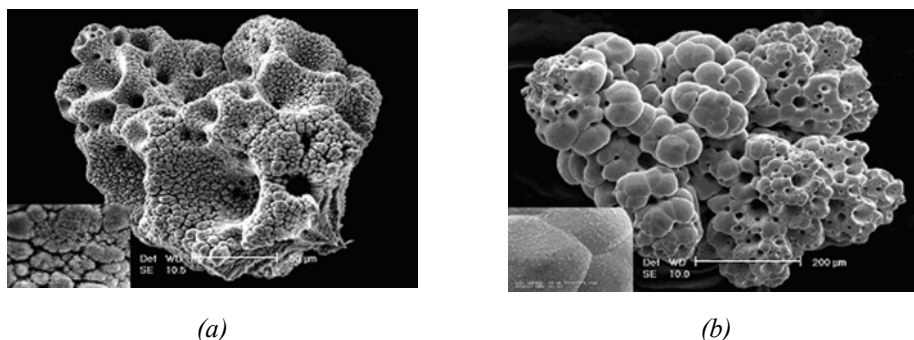


Fig. 4. SEM microphotographs of cobalt powder particles deposited at $j_{L(Co)} = 770 \text{ mA cm}^{-2}$ onto cobalt electrode; (a) agglomerate, (b) spongy-like particle, with details of their surface.

Unlike the cobalt powder particles deposited at $j_{Co} = 500 \text{ mA cm}^{-2}$ in these cavities fern-like dendrites do not appear on their bottom, or, they are not created under the conditions for planar diffusion in these hollows. In general, the type of used electrodes does not substantially affect the morphology of cobalt powder particles electrodeposited at diffusion limiting current density. It is known that the surface where the metal precipitates may affect the formation of the first few layers of deposit in two ways: (a) providing a strong force of attraction allowing a strong adhesion between deposited metal and the substrate, (b) providing its own regulated grid that defines the layout and structure of the newly formed crystals [20].

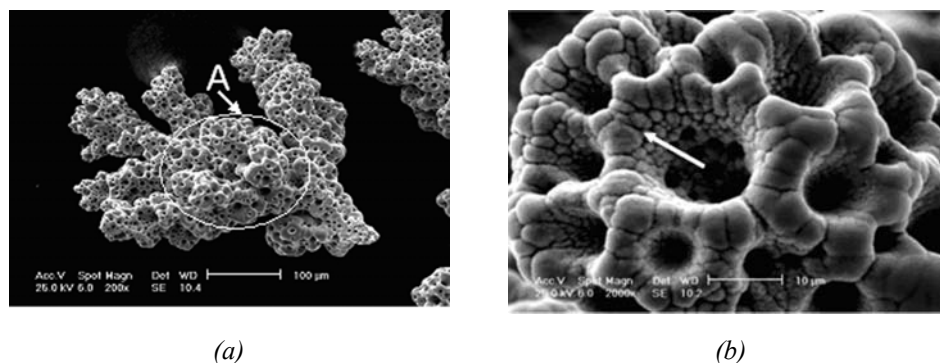


Fig. 5. SEM microphotographs of cobalt powder particles deposited at $j_{L(Co)} = 770 \text{ mA cm}^{-2}$ onto nickel electrode; (a) spongy-like cobalt powder particles, (b) details of (A) spongy-like particle.

Cobalt with hcp lattice needs to keep crystal structure of nickel substrate with fcc crystal structure, creating an error in the order of several layers [21]. Cobalt deposition on nickel electrode suppresses the appearance of agglomeration and needle dendrites. This phenomenon is not only conditioned by the different properties of the electrolyte-electrode, but the primary distribution of current, speed and method of transport of adatoms to the electrode surface must also be considered [20].

Conclusion

The experimental results demonstrated that it is possible to control the morphology and the structure of cobalt powder particles by adjusting process parameters of electrodeposition such as current density and type of working electrode. It was found that all formed particles (agglomerates and spongy-like) show the presence of deep cavities on their surfaces as a consequence of intensive hydrogen evolution. With increasing of size particles show the characteristic transformation from disperses to the compact parts. Electrodeposition can be a simple and a reliable method for production of novel and interesting morphologies of cobalt powder particles.

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