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Extended abstract

EXTENDED ABSTRACT

Metal powder electrolysis: The shape of powder particles as a function of the exchange current density and overpotential for hydrogen evolution reaction•

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Abstract: The short survey of the dependence of the shape of electrolytically produced powder particles on the exchange current density for metal deposition and overpotential for hydrogen evolution reaction is presented. The decrease of the exchange current density leads to a branching of dendrites and their transformation from needle-like and the two-dimensional (2D) fern-like to the three-dimensional (3D) pine-like shapes. Vigorous hydrogen evolution inhibits the dendritic growth leading to a formation of cauliflower-like and the spongy-like particles. The very thin needles were obtained by molten salt electrolysis. Mechanisms responsible for the formation of both the dendritic (the general theory of disperse deposits formation) and the cauliflower-like and the spongy-like particles (the concept of „effective overpotential“) were also mentioned.

Keywords: electrolysis; powder; particles; scanning electron microscope (SEM).

INTRODUCTION

Electrolysis is one of a common way for a production of metals in the powder form. The advantages of electrolysis relative to the other methods of powder synthesis can be summarized as follows: low equipment and product costs, one-step, environmentally friendly, formation the high purity products, *etc.*[1] Metal powders can be obtained by both electrolysis from aqueous electrolytes and molten salt electrolysis.[2] The both constant (potentiostatic and galvanostatic) and periodically changing (pulsating overpotential (PO), pulsating current (PC) and reversing current (RC)) regimes of electrolysis are used for the formation of

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powdered deposits. The parameters of electrolysis affecting a shape and size of powder particles are type and composition of electrolytes, temperature and time of electrolysis, the type of working electrode, stirring of electrolyte, the presence of additives, *etc*.

Although all above mentioned regimes and parameters of electrolysis affect the final shape of electrolytically synthesized particles, the shape of particles is primarily determined by the parameters like the exchange current density (j_0), overpotential for hydrogen evolution reaction and melting point (T_m).[3] According to these parameters, metals are classified into three groups:

a) normal metals, like Pb, Sn, Cd, Ag, Zn; this group of metals is characterized by high values of j_0 ($j_0 > 1$ A dm^{-2}) and overpotential for hydrogen evolution reaction, and low T_m,

b) intermediate metals, like Cu, Ag (ammonium electrolyte), Au; this group of metals is characterized by medium values of j_0 ($10^{-2} < j_0 < 1$ A dm^{-2}) and lower overpotentials for hydrogen evolution reaction than the normal metals, and

c) inert metals, like Ni, Co, Pt and Fe; this group is characterized by the low values of both the exchange current density and the overpotential for hydrogen evolution reaction, and high T_m.

Although dendrites are the most common shape of powder particles, some other forms like spongy, needles, cauliflower, fibrous, *etc*., can be obtained by electrolysis.[2]

METAL POWDERS OBTAINED BY ELECTROLYSIS FROM AQUEOUS ELECTROLYTES

The normal metals

For the group of normal metals, the exchange current density decreases in the following row: Pb < Ag < Zn.[4] Pb and Zn represent the limiting cases for this group of metals, since the estimated value of j_0 for Pb tends to infinity, while the j_0 value for Zn brings it closer to the group of the intermediate metals. The needle-like and the 2D (two-dimensional) fern-like dendrites are the typical shapes of powder particles characterizing this group of metals (Fig. 1).

The decrease of j_0 led to a shifting of formation of dendritic particles towards the higher overpotentials of electrodeposition. The branching of dendrites increases by both the process of complex formation with metal ions (Fig. 1c) and the decrease of j_0 value (Fig. 1d).

The intemediate metals

The two types of powder particles characterize the group of intermediate metals: the 3D (three-dimensional) pine-like dendrites constructed from the corn-cob-like forms like the basic element (Fig. 2a) and the cauliflower-like particles (Fig. 2b). The cauliflower-like particles are obtained by removing the deposit from the honeycomb-like structure (Fig. 2c). The honeycomb-like type of structure, and hence, the cauliflower-like particles are obtained in the conditions of vigorous hydrogen evolution, which inhibited a dendritic growth. The hydrogen evolution as a parallel reaction to Cu electrolysis commences inside the plateau of the limiting diffusion current density, and the increasing overpotential intensifies this reaction causing a complete inhibition of dendritic growth at overpotentials outside the plateau of the limiting diffusion current density.

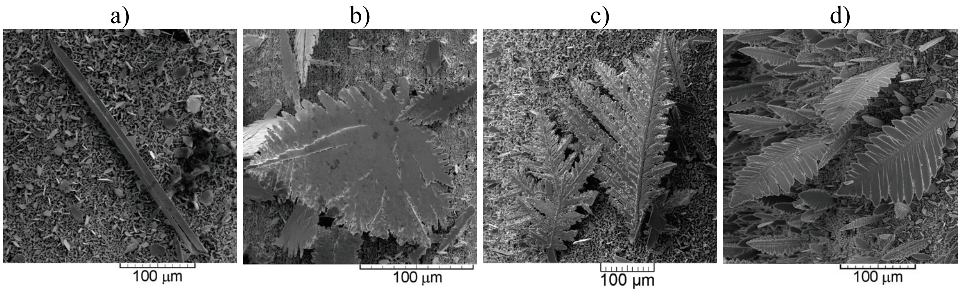

Fig. 1. The typical shapes of powder particles characterizing the group of the normal metals (Pb and Zn): a) the needle-like dendrite of Pb (0.10 M $Pb(NO_3)_2$ in 4.0 M $NaNO_3$; overpotential (η) = 50 mV)[5], b) the compact 2D fern-like dendrite of Pb (0.10 M $Pb(NO_3)_2$ in 0.50 M $NaNO_3$; η = 80 mV)[5], c) the branchy 2D fern-like dendrite of Pb (0.10 M $Pb(CH_3COO)_2$ in 1.5 M $NaCH_3COO$ in 0.15 M CH_3COOH; η = 60 mV)[6], and d) the 2D fern-like dendrite of Zn (0.40 M ZnO in 6.0 M KOH; η = 225 mV).[7]

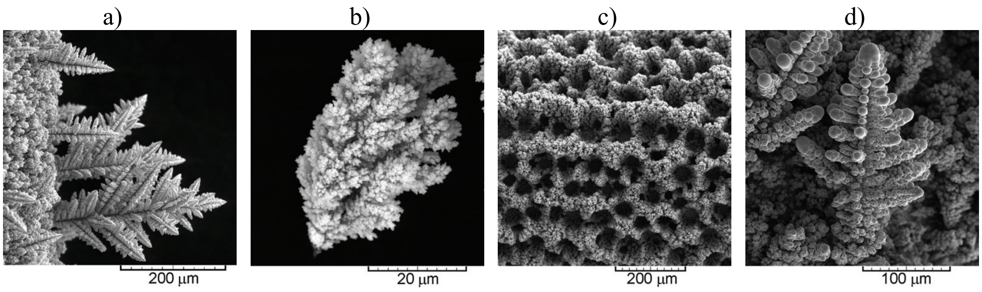

Fig. 2. The typical shapes of Cu powder particles: a) the 3D pine-line dendrite with the sharp tips,[8] b) the cauliflower-like particle,[8] c) the honeycomb-like structure,[8] and d) the 3D pine-line dendrite with globules.[9] Electrolyte: 0.10 M $CuSO_4$ in 0.50 M H_2SO_4; a) η = 625 mV; b) and c) η = 925 mV and d) current density, j = 14.4 mA cm^{-2}.

The shape of pine-like dendrites of Cu was very similar to the shape of dendrites of the other representatives of the group of intermediate metals, like Au and Ag when ammonium electrolyte was used.

In the galvanostatic regime of electrolysis with higher deposition charge applied, it is possible to obtain modified shape of the 3D pine-like dendrite where the tips of both stalk and branches are finished by globules (Fig. 2d), instead of the sharp tips (Fig. 2a).[9]

The inert metals

For this group of metals, there is parallelism between metal electrodeposition and hydrogen evolution in the whole range of overpotentials and current densities.[2] The spongy-like particles (Fig. 3) are the typical shape of the particles characterizing the group of the inert metals. This particle type, with the honeycomb-like structure, is obtained in the conditions of vigorous hydrogen evolution. There is no difference in the shape of the spongy-like particles of Ni, Co and Fe.[2] It is understandable because this particle type is only determined by vigorous hydrogen evolution as a parallel reaction. Formation of the 3D dendritic particles is possible for this group of metals, but the strong effect of hydrogen evolution on their shape is clearly visible.[2]

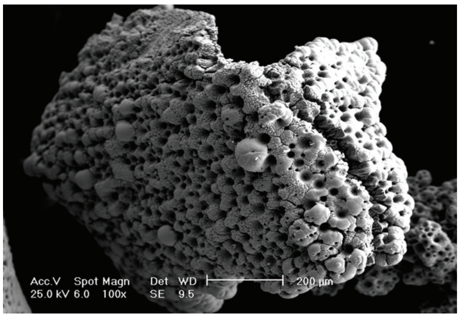

Fig. 3. The spongy-like Co powder particle electrodeposited onto glassy carbon electrode from the solution containing 0.1 M $CoSO_4$ in 1M $(NH_4)_2SO_4$ in 0.70 NH_4OH at j = 0.5 A cm^{-2}.[10]

MOLTEN SALT ELECTROLYSIS

The very thin needles of $MgO/Mg(OH)_2$ are formed by the electrolysis from magnesium nitrate hexahydrate melt (Fig. 4). These very thin needles are often grouped into the flower-like aggregates. Aside from very thin needles, holes formed from detached hydrogen bubbles can be also formed by this molten salt

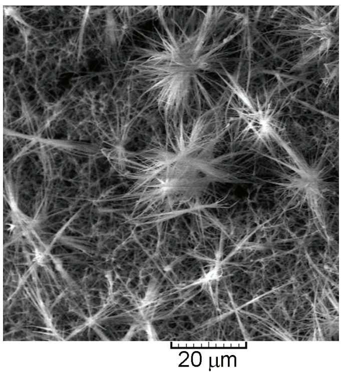

Fig. 4. The very thin needles of $MgO/Mg(OH)_2$ obtained by electrolysis of magnesium nitrate hexahydrate melts at j = 4 mA cm^{-2}.

electrolysis process.[4,11] There is no any difference in the shape of thin needle-like forms between those obtained by potentiostatic and galvanostatic regimes of electrolysis.

DISCUSSION

Formation of all types of dendritic particles can be explained by the application of the general theory of disperse deposits formation.[2,12] The basis of this theory is a formation of the spherical diffusion layer around the tip of surface protrusion formed in the initial stage of electrolysis and buried deep into the diffusion layer of the macroelectrode. It follows from this theory that the tip of the protrusion grows under the activation control, while simultaneously electrolysis to the flat part of the macroelectrode is under the diffusion control.

Formation of a cauliflower-like (Fig. 2b) and the spongy-like (Fig. 3) particles in conditions of vigorous hydrogen evolution can be explained by the concept of the "effective overpotential".[2,13] The basis of this concept is a strong effect of vigorous hydrogen evolution on the hydrodynamic conditions in the near-electrode layer. Vigorous hydrogen evolution causes a stirring of the electrolyte in the near-electrode layer leading to an increase in the limiting diffusion current density, the decrease in the thickness of the diffusion layer, and consequently, to the decrease of the degree of the diffusion control. The formation of cauliflower-like particles (Fig. 2b) instead of well-defined dendrites (Fig. 2a) really proves the lower degree of diffusion control at the overpotential outside than at the overpotential inside the plateau of the limiting diffusion current density.

CONCLUSION

The typical shapes of powder particles obtained by electrolysis processes are identified. The decrease of the exchange current density leads to the change of shape of dendrites from the needle-like and the 2D fern-like dendrites to the 3D pine-like dendrites. The cauliflower-like and spongy-like particles are formed under strong hydrogen evolution, as a parallel reaction to the metal electrolysis inhibiting dendritic growth.

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ИЗВОД

ФОРМИРАЊЕ МЕТАЛНИХ ПРАХОВА ЕЛЕКТРОЛИЗОМ: ОБЛИК ЧЕСТИЦА КАО ФУНКЦИЈА ГУСТИНЕ СТРУЈЕ ИЗМЕНЕ И ПРЕНАПЕТОСТИ ЗА РЕАКЦИЈУ ИЗДВАЈАЊА ВОДОНИКА

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Приказан је кратак преглед зависности облика електролитички произведених металних прахова од густине струје измене таложења метала и пренапетости за реакцију издвајања водоника. Смањење густине струје измене доводи до гранања дендрита и

њихове трансформације од игличастих и дводимензионалних (2Д) налик папрати, до тродимензионалних (3D) дендрита налик стаблу бора. Интензивно издвајање водоника инхибира дендритични раст доводећи до формирања карфиоластих и сунђерастих честица. Веома фине игле су добијене електролизом из растопа. Такође су разматрани механизми одговорни за формирање и дендритичних (општа теорија формирања дисперзних талога) и карфиоластих и сунђерастих честица (концепт „ефективне пренапетости“).

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