

Structure of Electrolytically Deposited Pd–Ag Powders

K. Ignatova,[†] L. Nikolova,* and W. Dimov[‡]

University of Chemical Technology and Metallurgy, Sofia, Bulgaria, and Institute of Applied Mineralogy, Bulgarian Academy of Sciences, Sofia, Bulgaria

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The present paper reports results from the study of morphology, phase composition, and microstructure of Pd–Ag alloy powder obtained by potentiostatic pulsating electrolysis. Several independent physical methods (electron microscopy, X-ray diffraction and electronographic probe analysis) were applied. It was found that the powder contained two basic types of particles: the first one, enriched in Pd (Ag/Pd ratio less than 1) were of a dendritic form, monocrystal cubic structure and smaller average particle size (0.1–0.6 μm); the second type of particles, enriched in Ag (Ag/Pd ratio greater than 2), were of a nearly isometric form, polycrystal structure of cubic silver and greater average particle size (0.6–1.5 μm). It was shown that Pd–Ag alloy powder consisted of two types of solid solutions of Pd and of Ag.

1. Introduction

Alloy metal powders deposited electrochemically are strongly inhomogeneous from the structural point of view. Metastable structures, intermetallic compounds and phases which do not correspond to the phase diagrams, are found in them more often than in the compact alloy coverages.¹ The reason is connected with the highly nonequilibrium conditions of electrodeposition (high current densities and overpotentials, joint deposition of hydrogen and metals) and with the peculiar topography of the surface, which is constantly changing in the course of deposition.^{1,2}

There are data^{1–3} on the conditions of production of some powder alloys of Cu, Ag, Bi, Cd, Ti, Fe, Ni, and Co, but information on their structure is in general scarce.

A dependence of the macrostructure (morphology, chemical, and phase composition) of the alloy Pd–Ag powder on the conditions of deposition under potentiostatic stationary⁴ and pulsating⁵ regimes was found by us. But an interrelation of the data obtained with the structure and composition of the individual powder particles, i.e., with the powder microstructure was not elucidated.

The present paper reports results from the study of morphology, phase composition, and microstructure of alloy Pd–Ag powder obtained by potentiostatic pulsating electrolysis. Several independent physical methods (electron microscopy, X-ray diffraction, and electronographic probe analysis) were applied.

2. Experimental Section

2.1. Electrolyte and Equipment. The electrolyte composition, as well as the parameters of pulsating electrolysis applied for deposition of alloy Pd–Ag powders, was optimized aiming to reach a maximum dispersion (average particle size of about 1 μm). Aminonitrite electrolyte was used. Unlike that applied in,⁵ it contained 0.5 g dm^{−3} of gelatin. The deposition was carried out on a silver electrode (of a surface area $S = 1 \text{ cm}^2$) at an amplitude overpotential (ΔE_p) ranging from 1.4 to 2.2 V. The pulse frequency (f) was of 500 Hz while the pause/pulse ratio (τ_z/τ_p) was equal to 1.0. The application of a potentiostatic pulsating regime was realized by an equipment previously described.⁵

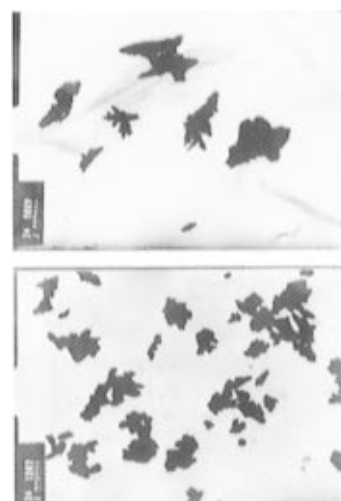


Figure 1. Electronmicrographs of Pd–Ag powder deposited under pulsating regime at an overpotential $\Delta E_p = 1.6 \text{ V}$: (top) in gelatin absence, (below) in gelatin presence.

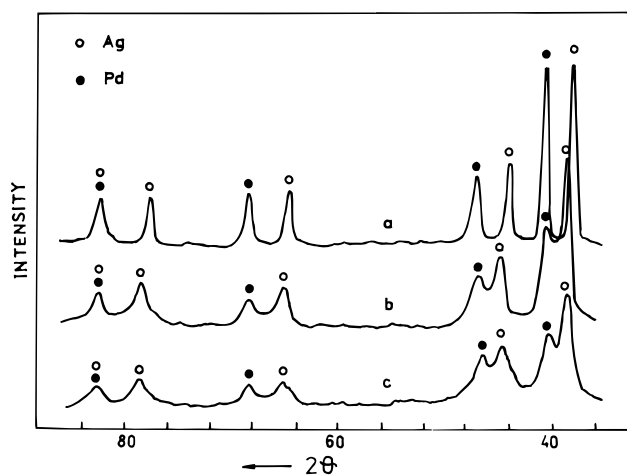


Figure 2. X-ray diffractogram of a mechanical mixture of 50% Pd and 50% Ag (a) and X-ray diffractograms of Pd–Ag powder-deposited under pulsating regime at an overpotential $\Delta E_p = 1.6 \text{ V}$: (b) in gelatin absence, (c) in gelatin presence.

2.2. Investigation Methods. The study of powder morphology was carried out using Philips EM-420 transmission electron microscope (TEM) with an accelerating voltage of 120 kV, with

[†] University of Chemical Technology and Metallurgy.

[‡] Institute of Applied Mineralogy.

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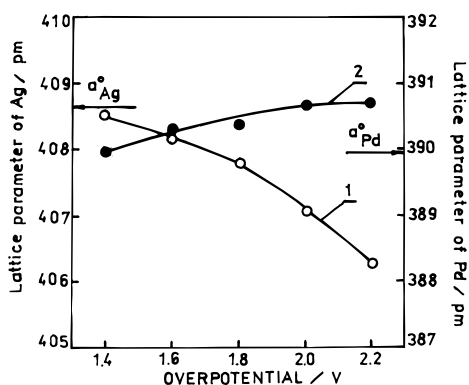


Figure 3. Variation of lattice parameters of the components of Pd-Ag powder deposited under pulsating regime in an electrolyte containing gelatin as an additive with changing the applied overpotential: curve 1, for Ag; curve 2, for Pd.

a 0.35 nm point resolution, and with a 0.2 nm line resolution at maximum magnification of 820 000. The electronograms were obtained by the same microscope in a chamber of 100–6500 nm length. It was equipped with an X-ray microanalyzer with a Si-Li detector for semiquantitative elementary microanalysis of elements from Na to U with sensitivity of tenths of the percentage. Weight and atomic and oxide percentage ratios were obtained.

The phase identification was carried out on the basis of data from the X-ray diffraction analysis; the electronograms parameters obtained and data concerning 9 phases of Ag, Pd, and

oxygen, i.e., cubic and hexagonal Ag, monoclinic and cubic Ag_2O , monoclinic Ag_3O_4 , cubic Pd, tetragonal PdO , and tetragonal PdO_2 , which were previously summarized.

3. Results and Discussion

3.1. Morphology of Pd-Ag Powder. Electronmicrographs of Pd-Ag powder deposited in the absence (Figure 1, top) and in the presence of gelatin (Figure 1, bottom) are shown. The comparison of both pictures shows that the introduction of gelatin to the solution brings about a significant decrease of the average particle size. The latter varies in a limited range (about 1 μm). The powders deposited in the presence of gelatin contain particles of irregular form, close to the isometric one for some and to the dendritic one for most of them.

3.2. Phase Composition of Pd-Ag Powder. A picture of the general phase composition of Pd-Ag powders is shown in the diffractograms presented in Figure 2(b, c). In the absence (b), as well as in the presence of gelatin as an additive (c), the electrochemically deposited Pd-Ag powders give a diffraction picture which differs from that of a mechanical mixture of Pd and Ag powders (Figure 2a). The difference observed lies in a more significant shift of the lattice parameters of both metals in the electrochemically deposited Pd-Ag powder when compared to the thermodynamic data.

As it is seen from Figure 3, the increase of the applied overpotential from 1.4 to 2.2 V leads to a decrease of Ag lattice parameter from 408.52 to 406.24 pm while that of Pd slightly increases from 389.90 to 390.75 pm. It is found as well that

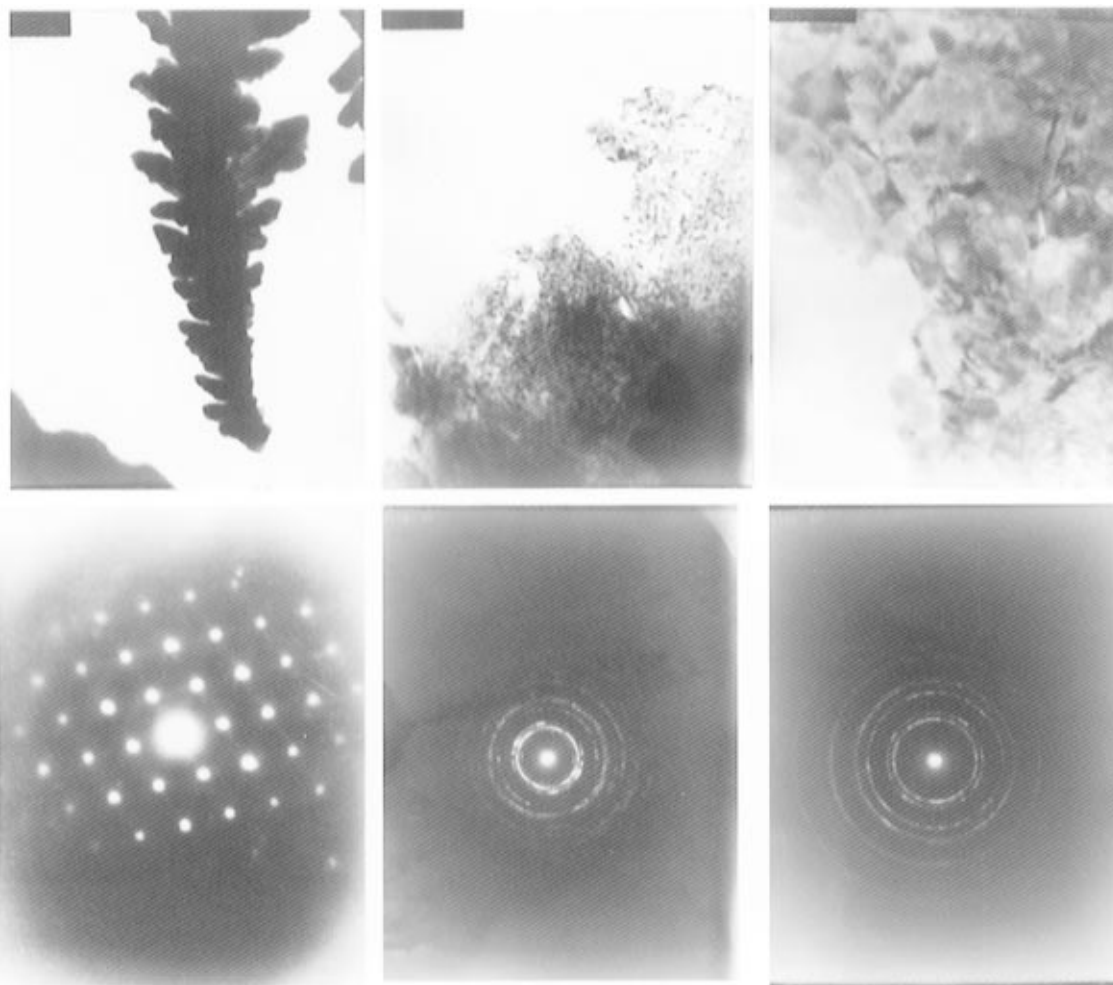


Figure 4. Electronmicrographs (top row) and electronograms (bottom row) of electrochemically deposited Pd-Ag alloy powder in an electrolyte containing gelatin under pulsating regime at an overpotential of 1.6 V.



Figure 5. Element distribution in individual particles of electrochemically deposited Pd–Ag powder from an electrolyte containing gelatin under pulsating regime at an overpotential of 1.6 V: (top) Ag, (middle) Pd, (bottom) simultaneous distribution of both Ag and Pd.

the Pd content of the powder grows from 10 to 65%⁵ with the increase of the applied overpotential. The same result is obtained when the Ag content of the solution decreases: the pulses frequency grows and the pause/pulse ratio decreases. In fact, this change of the experimental conditions draws the deposition overpotentials of both metals nearer. Taking in consideration the result discussed and the fact that Ag is characterized by a greater atomic radius than Pd: $r_{\text{Ag}} = 144.4$ pm, $r_{\text{Pd}} = 137.6$ pm,⁶ it can be concluded that Pd–Ag powder

is a system containing two types of solid solutions of Ag and of Pd with a different content of the solute when compared to that of the solvent: a solution of Pd in Ag with Pd content which reaches 15% depending on the conditions and a solution of Ag in Pd of maximum content of 8%. This result is in an agreement with the phase diagram of this two-component system⁷ which shows that formation of a continuous series of solid solutions is thermodynamically favorable.

3.3. Electronographic Microprobe Analysis. The results discussed above give a general idea of Pd–Ag powder structure. The application of combined electron microscopy, X-ray diffraction and electronographic microprobe analysis provided the characterization of powder microstructure and the relation of the morphology of individual powder particles to the phase and chemical composition as well as to the degree of crystallinity.

Figure 4 shows electromicrographs (top row and the corresponding electronograms (bottom row of various fields of the powder particles chosen to illustrate the general dependencies characteristic for the sample as a whole.

It is seen that Pd–Ag powder contains two types of particles. The first one are of a dendritic form (Figure 4, top left) and a smaller average particle size (from 0.1 to 0.6 μm). The chemical microanalysis shows deviations in Ag/Pd ratio from 0.9 to 1.06 for the various dendrites and insignificant one for the various fields of each dendrite. The electronograms show monocrystal cubic structure (Figure 4, bottom left).

The second type of particles are relatively isometric, they have grain structure and average particle size ranging from 0.6 to 1.5 μm (Figure 4, top, middle and right). The isometric particles whose Ag/Pd ratio is in the range of 1.97–2.40 give a diffraction picture comprising discrete point maxima (Figure 4, bottom middle), while those of predominating Ag content (Ag/Pd in the range of 2.40–2.72) give a diffraction picture consisting of better outlined polydiffraction maxima (Figure 4, bottom right) of cubic silver.

3.4. Distribution of Pd and Ag in the Powder Particles.

To provide a visual image of the results obtained, the distribution of Pd and Ag in the individual particles of Pd–Ag powder is presented in Figure 5. The different intensity of coloring is explained with a difference in Ag (Figure 5, top) and in Pd concentration (Figure 5, middle) for the individual powder particles. If the data for both components are superimposed, a picture is obtained which illustrates the simultaneous presence of Pd and of Ag in the particles of the alloy powder (Figure 5, bottom). It is seen that Pd–Ag alloy powder is not a mechanical mixture of both metals. Thus the conclusion derived on the basis of general X-ray diffraction and electronographic probe analysis is in fact verified.

4. Conclusions

Pd–Ag alloy powder obtained by potentiostatic pulsating electrolysis is not a mechanical mixture of both metals but consists of more or less uniformly distributed solid solutions of Ag and of Pd whose ratio is different both for the individual powder particles and for the different fields in them.

The dependencies found valid for Pd–Ag alloy powder, as well as the verified correlation between morphology, phase and chemical composition, and degree of crystallinity of individual powder particles could also be applied other similar systems, the components of which form a continuous series of solid solutions.

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