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Effect of pulsating electrolysis parameters on the morphology and structure of Pd–Ag powder

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Results are reported from a kinetic study of single and joint deposition of Pd and Ag, and of the morphology, structure and chemical composition of Pd–Ag powders deposited from aminonitrite electrolyte under potentiostatic and pulsating square-wave overpotential. It was established that the Pd content in the powder reaches 50% with increase in the overpotential amplitude and the pulse/pause ratio. The same conditions are required for the deposition of finely divided powders. The form of the Pd–Ag powder is dendritic, but it is less branched compared to that obtained under steady potentiostatic conditions.

1. Introduction

In the production of electronic elements such as capacitors and integrated circuits, pastes are used containing single and alloy noble metal powders as electroconducting components [1]. Therefore, such powders should satisfy several requirements, such as average particle size (1 to 10 μm), specific surface area (>3 $m^2 g^{-1}$), tap density (>1.5 $g cm^{-3}$) and high chemical purity [2]. The system Pd–Ag is most widely used in the field of conducting pastes [1, 2]. Of practical interest are alloy powders containing 30 to 70% Pd.

A possibility exists of broadening the spectrum of properties of the obtained powders by the potentiostatic application of square-wave pulsating electrolysis. Data exist on the effect of this type of current regime on the morphology of some single-component powders, that is, for Cu [3, 4], Ag [5], Sn [6] and Pb [7]. This effect is accounted for by the concepts of electrocrystallization of metal powders in potentiostatic steady state and pulsating regimes [8–10]. On the other hand, no data are available concerning the effect of pulsation regimes on the morphology, structure and chemical composition of powdered alloys. Our preliminary studies showed that finely divided Pd–Ag powders of a suitable composition can be obtained from an electrolyte based on Ag-ammonia complexes and on mixed aminonitrite complexes of Pd [11].

In this paper results are reported of the morphology, structure and chemical composition of Pd–Ag powder deposited from aminonitrite electrolyte under a pulsating square-wave overpotential regime.

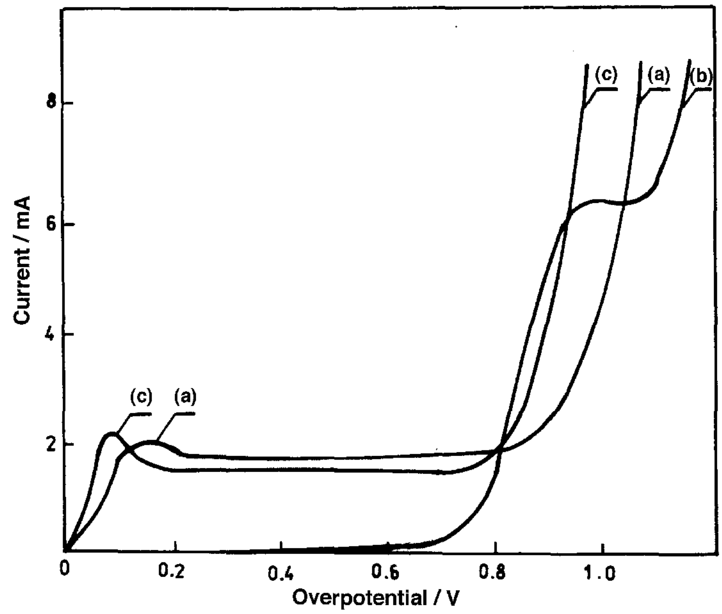

Fig. 1. Potentiodynamic polarization dependencies in electrolytes containing: (a) 7.5 $g dm^{-3}$ Ag; (b) 7.5 $g dm^{-3}$ Pd; (c) 15 $g dm^{-3}$ (Ag/Pd = 1). Electrode surface area 0.2731 cm^2.

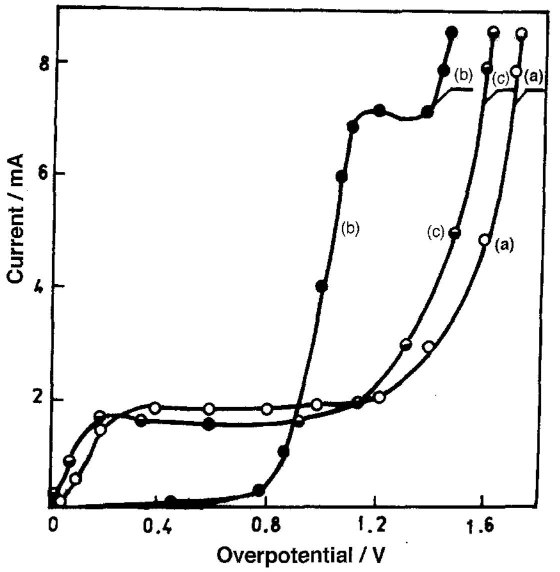

Fig. 2. Polarization dependencies under pulsating conditions at a frequency of 500 Hz and $\tau_p/\tau_z = 1$ in electrolytes with the following composition: (a) $7.5\,g\,dm^{-3}$ Ag; (b) $7.5\,g\,dm^{-3}$ Pd; (c) $15\,g\,dm^{-3}$ (Ag/Pd = 1). Electrode surface area $0.2731\,cm^2$.

2. Experimental details

2.1. *Electrolyte composition*

The electrolyte contained $7.5\,g\,dm^{-3}$ of Pd, $7.5\,g\,dm^{-3}$ of Ag (total concentration of $15\,g\,dm^{-3}$), $15\,g\,dm^{-3}$ of $NaNO_2$ and $20\,g\,dm^{-3}$ of NH_4NO_3. Palladium, in powder form, was dissolved in hot concentrated HNO_3. Silver as $AgNO_3$, and the rest of the components, were introduced as aqueous solutions. pH was adjusted to 9.0 ± 0.1 with the addition of 25% solution of NH_3.

2.2. *Equipment and investigation methods*

The polarization characteristics in the constant and pulsating regimes were recorded by a special combined electrode consisting of a silver working disc with a surface area of $0.273\,cm^2$ and a reference silver electrode spaced concentrically around the WE at a distance of 0.1 cm. Teflon was used as an insulating material between the electrodes. This construction permits the direct reading of the cathodic overpotential. A platinum net was used as counter electrode.

Electrolysis was carried out in a thermostated electrolysis cell of volume $0.150\,dm^3$. All experiments were carried out at $20.0 \pm 0.2\,°C$. The cathode, used for the powder deposition was made of electrolytic silver (with a purity of 99.97%). This was disc shaped with a surface area of $1\,cm^2$. An SCE was used as reference and platinum as counter electrode.

The square-wave pulses were applied by a pulse generator connected to a potentiostat (type OH-405), and their shape was followed by an oscilloscope. The generator provided smooth regulation of the amplitude overpotential, ΔE_p, of the frequency, f, of pulse duration, τ_p, and pause duration, τ_z. The average current value was measured using a milliammeter.

The powders were removed from the cathode by tapping, they were then washed in distilled water and, after being dried in air at ambient temperature, were ground in an agate mortar.

The morphology of the powders was studied using a Philips EM-100 transmission electron microscope (TEM) with an accelerating voltage of 120 kV. The photomicrographs were made by the method of direct observation. The phase identification was carried out using the data from the X-ray diffraction analysis. These were obtained by a TUR-M62 diffractometer

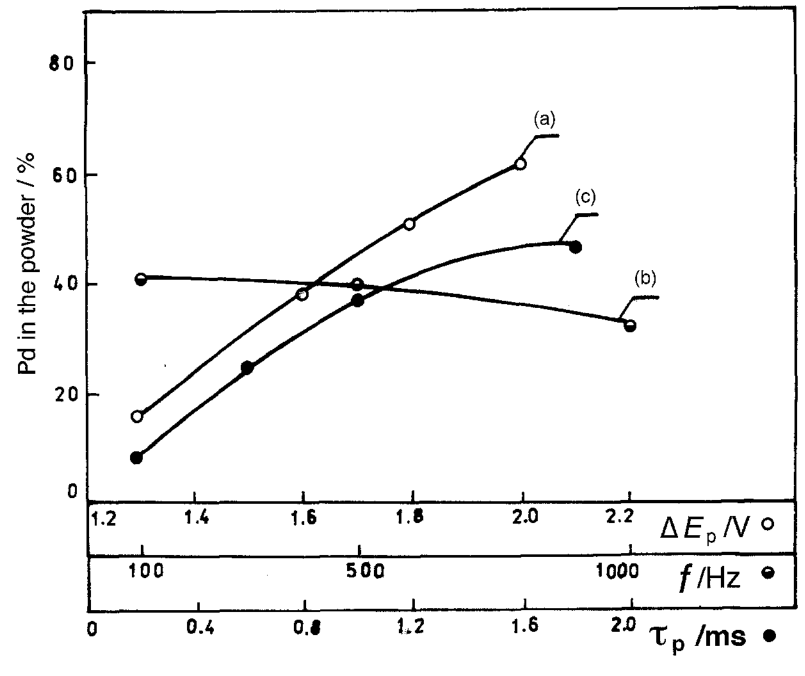

Fig. 3. Chemical composition of Pd–Ag powder as a function of: (a) overpotential, ΔE_p, at a frequency of 500 Hz and $\tau_p/\tau_z = 1$; (b) pulse frequency, f, at $\Delta E_p = 1.6\,V$ and $\tau_p/\tau_z = 1$; (c) pulse duration, τ_p, at $\tau_z = 1.0\,ms$ and $\Delta E_p = 1.6\,V$.

with K_α-emission of the copper anode and nickel selectively absorbing filter. Identification of the phases was carried out with ASTM card index.

The chemical composition of the Pd–Ag deposits and the effect of the pulsating electrolysis parameters was followed by iodometric titration [12]. The Pd–Ag powders were dissolved in hot concentrated HNO_3. The 25% solution of NH_3 was added to achieve a pH value of 9–10. The solution was acidified using glacial acetic acid until a pH of 4–5 was reached. The Ag-ammonia complexes were more unstable than those of Pd under these conditions. This permitted complete precipitation of the Ag and its determination by titration with standard KI solution.

Deposition of Pd–Ag powder was carried out by varying the overpotential amplitude during pulsating deposition from 1.2 to 2.0 V at a frequency of 500 Hz and $\tau_p/\tau_z = 1$; of frequency in the range 100 Hz to 1000 Hz at $\tau_p/\tau_z = 1$ and $\Delta E_p = 1.6$ V; of pulse duration τ_p in the range 0.2 to 1.8 ms ($\tau_z = 1.0$ ms) at $\Delta E_p = 1.6$ V; and of pause duration τ_z in the range 0.2 to 2.0 ms ($\tau_p = 1.0$ ms) at $\Delta E_p = 1.6$ V. The overpotential amplitude, ΔE_p, was determined from the oscillograms.

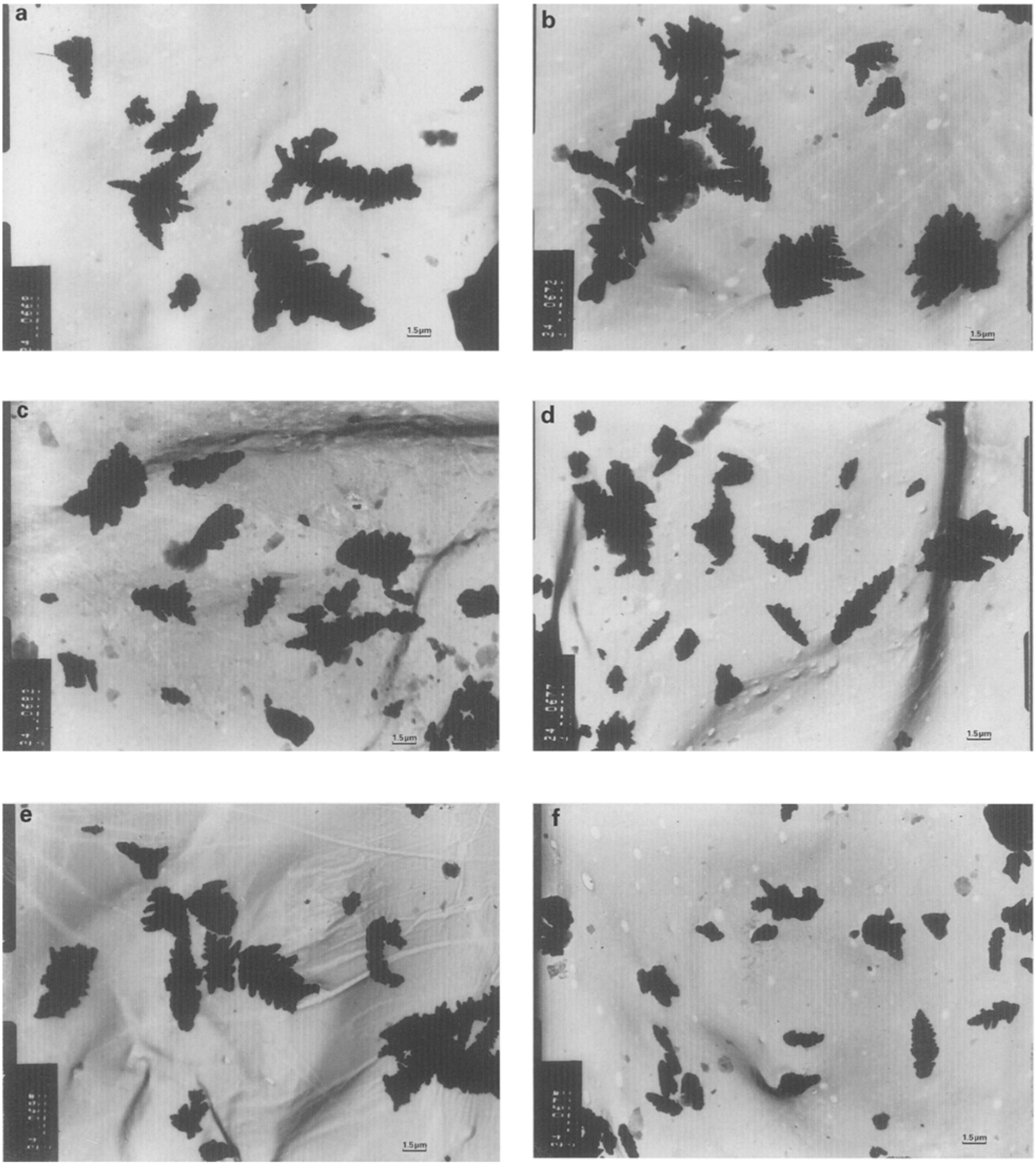

Fig. 4. Electronmicrographs of Pd–Ag powders obtained in (a, b) steady potentiostatic regime at 0.9 V (a) and 1.0 V (b); (c, d) pulsating regime with pulse frequency of 1000 Hz (c) and of 100 Hz (d) at $\Delta E_p = 1.6$ V and $\tau_p/\tau_z = 1$; (e, f) pulsating regime with pulse duration of 0.5 ms (e) and of 1.8 ms (f) at $\tau_z = 1.0$ ms and $\Delta E_p = 1.6$ V.

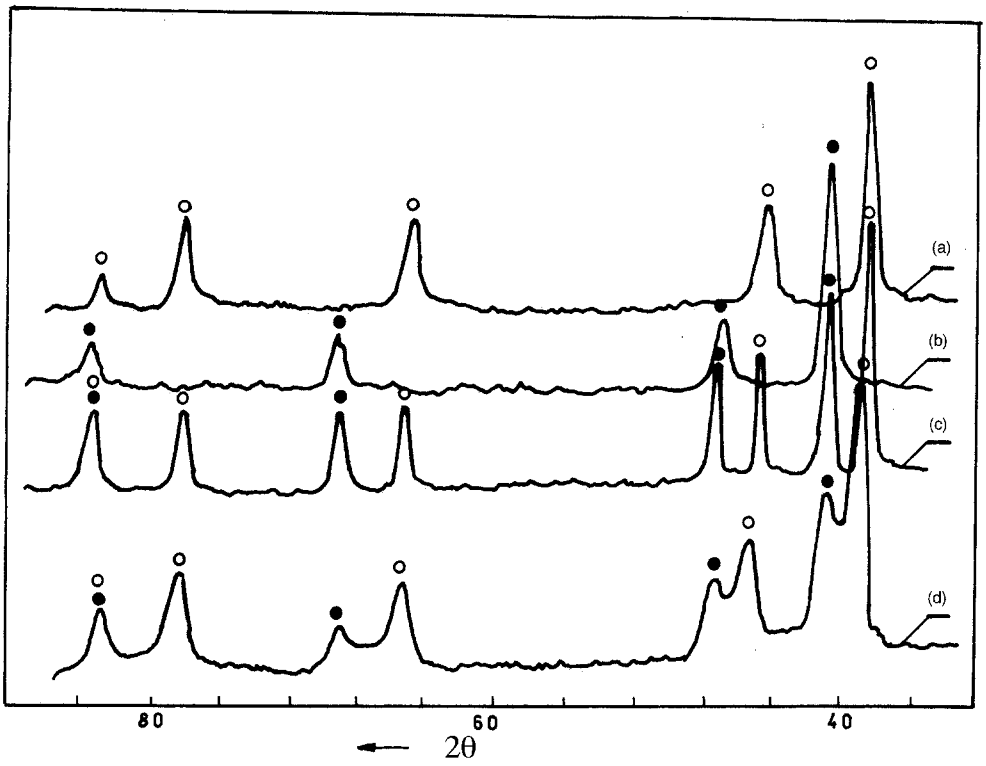

Fig. 5. Diffractograms of (a) Ag (O)-powder; (b) Pd (●)-powder; (c) mechanical mixture of 50% of Ag-powder and of 50% Pd-powder; (d) Pd–Ag powder, obtained in the pulsating regime at $\Delta E_p = 1.6$ V, at a frequency of 500 Hz and at $\tau_p/\tau_z = 1$.

3. Results and discussion

The potentiodynamically recorded polarization dependencies for the deposition and codeposition of Pd and Ag in the potentiostatic regime are presented in Fig. 1. In Fig. 2 the analogous dependencies are plotted based on the oscillograms recorded under a pulsating regime at a frequency of 500 Hz and $\tau_p/\tau_z = 1$.

From the comparison of the curves obtained in the steady and pulsating potentiostatic regimes, it follows that the character of the polarization dependencies remains similar, but the overpotential in the pulsating regime increases. It is seen from Fig. 3 that during deposition under pulsation, when the amplitude of the overpotential grows, the Pd content (%) in the deposit also increases (from 16% at $\Delta E_p = 1.3$ V to 51% at $\Delta E_p = 1.8$ V). When the pulsation frequency is increased from 100 to 1000 Hz, the Pd content decreases from 40 to 32%. The content of Pd in the deposits increases from 8 to 46% when the pulse duration is increased from 0.2 to 1.8 ms at $\tau_z = 1.0$ ms.

The electronmicrographs of Pd–Ag deposits (Fig. 4(a)–(f)) show that the powders obtained under steady conditions are typically dendritic with well developed structure and average particle diameter varying from 0.5 to 3 μm (Fig. 4(a)–(b)). Under pulsating conditions the particles are also dendritic, but with a less branched form and their maximum dimension reaches 2.0–2.5 μm. The average particle diameter increases slightly with increase in frequency (Fig. 4(c)–(d)). When the pulse duration was increased from 0.5 to 1.8 ms the average particle size decreased from 1.5 to 0.8 μm (Fig. 4(e)–(f)).

From the X-ray diffraction analysis data (Fig. 5) it follows that two main phases are present in the powders: cubic Ag and cubic Pd. From the diffractograms the lattice parameters of these phases were calculated and their values are shown in Table 1.

Table 1. Lattice parameter a *and average crystallites size* d *of Pd–Ag powder as related to the conditions of the electrolysis* ($\Delta E_p = 1.6$ *V*)

Regime	*Varying parameter*	*Value*	*Ag-phase*		*Pd-phase*	
			a/pm	*d*/nm	*a*/pm	*d*/nm
Stationary	ΔE/V	0.9	406.81	34.68	388.15	16.28
Pulsating	*f*/Hz	1000	407.18	23.834	388.98	12.184
		500	406.62	22.832	388.52	16.587
	τ_p/τ_z	100	405.96	17.405	388.60	18.228
Pulsating	τ_p/ms	0.4	405.96	23.308	388.52	15.242
	($\tau_z = 1.0$ ms)	1.8	406.82	20.860	389.94	17.231
Pulsating	τ_z/ms	0.2	405.98	20.335	389.16	18.627
	($\tau_p = 1.0$ ms)	1.5	407.34	24.808	390.88	13.495
Thermodynamic value of *a*/pm			408.62		388.98	

The values obtained correspond to lattice contraction for Ag and expansion for Pd. Accounting for the greater atomic radius of Ag, it may be accepted that the diversity of the lattice parameters is due to inclusion of Pd in the lattice of Ag and vice versa, which is thermodynamically probable and corresponds to reference data [13].

The average size of the crystallites was also determined from X-ray diffraction analysis. These data (Table 1) correspond well to those obtained by electron microscopic analysis. They show that decrease in pulse frequency, increase in pulse duration and decrease in pause duration lead to the formation of a more finely divided crystal structure. Under these conditions the size of the Ag-crystallites decreases while that of the Pd-crystallites increases slightly.

Hence, it may be concluded that when pulsating electrolysis is applied Pd–Ag powders with properties corresponding to those required by the electronics industry can be deposited.

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