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## Investigations on the electrochemical preparation of gold–nanoparticle composites

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**Abstract** The role of electrical charges in the double layers of the electrode and in particles during the electrochemical preparation of dispersion coatings was studied for the systems Au/diamond and Au/Al<sub>2</sub>O<sub>3</sub>. The surface charge of the electrode under the conditions of electroplating will depend on the potential of zero charge (p.z.c.). For the nanoscaled particles the sign of the surface charge was estimated from the zeta potential in dilute solutions. Successful inclusion of Al<sub>2</sub>O<sub>3</sub> and diamond nanoparticles was observed when the particles and the electrode were oppositely charged. The Vickers hardness of the layers was increased by the codeposition of Al<sub>2</sub>O<sub>3</sub>, whereas it decreased in the case of nanodiamond.

**Keywords** Aluminum oxide · Diamond · Electroplating · Gold · Nanoparticles

### Introduction

The modification of metal layers by the inclusion of particles has found great interest in obtaining functional coatings with tailored properties. To improve the hardness and wear resistance of the metal layers, the codeposition of particles from hard materials is a well-established technique (dispersion coating). Mechanisms have been proposed taking into account the wetting

behaviour of the particles [1] and the hydrodynamic conditions in front of the electrode [2, 3]. In most cases the validity of the corresponding models has been shown for relatively large particles (sizes in the region of some micrometers). In the case of relatively large particles, the optical properties of the surface of the dispersion coating can be negatively influenced. For obvious reasons, only the codeposition of nanoparticles will give smooth and homogenous surfaces. This is even more important for layers with thicknesses in the nanometer range. However, fundamental investigations on the mechanism of codeposition of nanoscaled particles are scarce. The electrochemical preparation of nanostructured dispersion coatings often proceeds on a highly empirical level. It is known that the surface charge of the nanoparticles is important for the stability of the dispersions [4]. So far, the role of surface charges in the codeposition process has been mostly neglected.

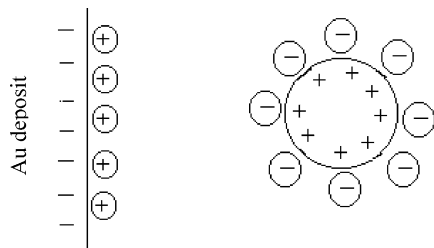
This work emphasizes and investigates the role of electrical charges in the electrical double layers of both the nanoparticle and the electrode. To study the effects at a system of technological relevance, the codeposition of nanosized Al<sub>2</sub>O<sub>3</sub> and diamond particles in an Au matrix was chosen. Au layers with included hard particles are promising candidates as replacements for classical hard gold coatings (e.g. Au-Co alloys).

### Theory

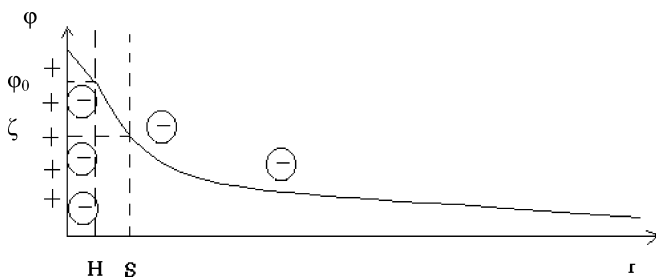
As the size of a nanoparticle approaches the dimensions of the electrical double layer surrounding it, the importance of the charge distribution is obvious. Therefore, in an electrochemical codeposition process, the structures of the electrical double layers of both the particle and the electrode may play an important role for the inclusion of the particle into the growing metal layer (Fig. 1). In dilute solutions (i.e. low ionic strength) the structure of the electrical double layer (i.e. the distribution of the electrical charges) around the particle is reflected by the zeta potential,  $\zeta$  (Fig. 2). The zeta potential is the

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**Fig. 1** Schematic representation of the charge distribution during cathodic codeposition of nanoparticles in a typical plating electrolyte with high ionic strength



**Fig. 2** Galvani potential  $\phi$  as a function of the distance  $r$  from the surface of the particle.  $H$ , Helmholtz plane;  $\phi_0$ , galvani potential within the Helmholtz plane;  $S$ , shear layer in the experimental determination of the  $\zeta$  potential

potential drop between the shear layer  $S$  and the bulk of the solution. In dilute solutions,  $\zeta$  corresponds to the galvani potential  $\phi_0$  at the end of the Helmholtz plane  $H$ . According to the theories of the structure of the electrical double layer [4], the absolute value of the zeta potential decreases with the ionic strength of the electrolyte. In an electrolyte of high concentration (such as a typical electrolyte used for electroplating) the zeta potential tends towards zero. In other words, the diffuse electrical double layer has collapsed, and the particle only bears a compact layer of ions in the Helmholtz plane. If specific adsorption is absent, zeta potential measurements in dilute electrolytes with compositions as close as possible to the real plating electrolyte will reveal information about the sign of the charge of the compact layer. However, specific adsorption of electrolyte components can reverse the sign of the excess charge in the electrical double layer of the particle.

The charge distribution in front of the electrode to be coated is governed by the position of the deposition potential with respect to the potential of zero charge (p.z.c.) [5]. At the p.z.c. the electrical excess charge on the metal,  $\sigma_M$ , is zero. At potentials positive to the p.z.c.,  $\sigma_M$  is positive; at negative potentials,  $\sigma_M$  is negative. The p.z.c. can be determined by measuring the potential dependence of the double layer capacity,  $C_{DL}$ , of the electrode (e.g. by impedance spectroscopy) in an electrolyte of low concentration ( $10^{-4}$ – $10^{-2}$  M). At the p.z.c. the  $C_{DL}$  vs.  $E$  curve will show a minimum. In most cases of cathodic deposition the electrode potential will be cathodic from the p.z.c. and the electrode will bear a

negative charge, compensated by positive charges in the electrolytic part of the double layer (Fig. 1).

Taking into consideration the compensating effects of the electric charges, the codeposition of nanoparticles in a cathodically growing metal matrix should be favoured by a negative zeta potential (i.e. a negatively charged electrolytic side of the double layer) of the particle in a dilute solution of the plating electrolyte (Fig. 1).

In addition to the electrostatic prerequisites for incorporation, it has been shown that the adsorption of metal cations can have an important effect [9].

## Experimental

All solutions were prepared from analytical grade chemicals and highly purified water. All characterizations and depositions were performed with  $Al_2O_3$  (synthesized by a low-temperature/high-frequency plasma process, average size 32 nm) and diamond particles (PL-D-G from PlasmaChem, detonation synthesis, average size 4 nm). A commercial gold electrolyte (Siemens, Berlin) was used, containing 12 g/L potassium dicyanoaurate(I), and citric acid, boric acid, phosphoric acid and Titrplex III (disodium ethylenediaminetetraacetate dihydrate) in their usual concentrations. Electrochemical depositions of pure Au and dispersion coatings were performed on copper substrates ( $0.04 \text{ dm}^2$ ) at  $62 \pm 2 \text{ }^\circ\text{C}$ ,  $1 \text{ A/dm}^2$  (if not otherwise specified). The pH of the electrolyte (500 mL) was adjusted to 5.8–6.0. The deposition time was 4.5 min, yielding gold films of ca.  $2 \text{ }\mu\text{m}$  thickness.

The zeta potential of the particles was determined with a Zetasizer 3 (Malvern Instruments, Herrenberg, Germany). The measuring principle is based on the determination of electrophoretic mobility by laser anemometry. The zeta potential was measured in  $10^{-3}$  M KCl (base electrolyte) in the pH range 3–11 (adjusted with HCl or KOH). To mimic actual plating conditions, the individual electrolyte components were added in a concentration of  $10^{-3}$  M as well as 4–5 mL/L of the commercial electrolyte. The concentration of the particles was 0.2 g/L ( $Al_2O_3$ ) and 0.1 g/L (diamond), respectively. The particle concentration was adjusted empirically, taking into account the average size of the particles and their density. The number of particles per mass is much higher for the nanodiamond.

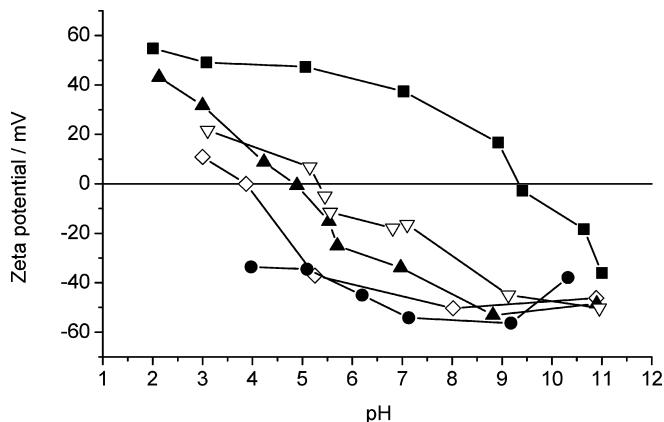
The p.z.c. of the layer was determined from the potential dependence of the double layer capacitance ( $-200$  to  $+1000 \text{ mV}$ ,  $50 \text{ mV}$  steps,  $0.5 \text{ Hz}$ – $10 \text{ kHz}$ ), which was measured by electrochemical impedance spectroscopy (Zahner IM6, Germany). Electrodeposited gold layers (area  $0.125 \text{ cm}^2$ , thickness  $2 \text{ }\mu\text{m}$ ) were used in  $0.02 \text{ M Na}_2\text{SO}_4$  and in an aqueous solution ( $4 \text{ mL/L}$ ) of the commercial gold electrolyte. Reference measurements were made at polished gold sheets in  $0.02 \text{ M Na}_2\text{SO}_4$ . If not otherwise stated, all potentials refer to the saturated calomel electrode (SCE).

The content of  $Al_2O_3$  in the gold film was determined by EDX. The microhardness was determined with a FischerScope H100C according to ISO 14577. The reported values are the average results of 4–6 measurements.

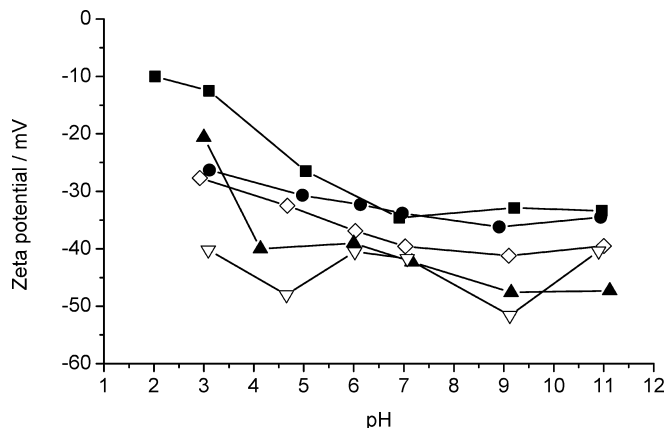
## Results

### Zeta potential of the particles and potential of zero charge of the gold layer

In accordance with the literature [6], the  $Al_2O_3$  particles showed a positive zeta potential in  $1 \text{ mM KCl}$  in the pH range from 2 to 9. In the presence of the gold electrolyte the zeta potential shifted to negative values (Fig. 3),



**Fig. 3** Zeta potential of 0.2 g/L  $\text{Al}_2\text{O}_3$  nanoparticles in different electrolytes as a function of pH (all concentrations  $10^{-3}$  M if not otherwise specified). *Solid squares*: KCl; *open diamonds*: KCl+citric acid; *solid up-triangles*: KCl+phosphoric acid; *open down-triangles*: KCl+Titriplex III; *solid circles*: KCl+dilute gold electrolyte (5 mL/L)



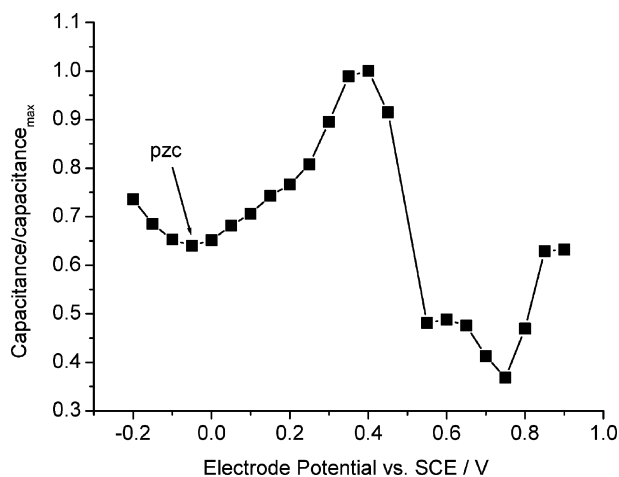
**Fig. 4** Zeta potential of diamond nanoparticles (0.1 g/L) in different electrolytes (all concentrations  $10^{-3}$  M if not otherwise specified). *Solid squares*: KCl; *open diamonds*: KCl+citric acid; *solid up-triangles*: KCl+phosphoric acid; *open down-triangles*: KCl+Titriplex III; *solid circles*: KCl+dilute gold electrolyte (4 mL/L)

probably because of the adsorption of anions. The electrolyte components boric acid and the gold cyanide complex had no influence on the zeta potential of the  $\text{Al}_2\text{O}_3$  particles (not shown). In contrast, the components Tritriplex III, phosphoric acid and citric acid shifted the zeta potential to negative values and the isoelectric point to lower pH values. This finding is in accordance with the literature, where phosphoric acid and citric acid are described as peptizers for pharmaceutical applications [7]. Adsorption of these substances at the particle surface gives rise to a large negative surface charge, which leads to electrostatic stabilization of the dispersion.

In the investigated range the diamond particles had a negative zeta potential (Fig. 4). Boric acid and the potassium dicyanoaurate(I) had almost no influence on the zeta potential (not shown). The value of the zeta potential increased with the addition of citric acid, phosphoric acid and Titriplex III. The citric acid electrolyte stabilized the dispersion of nanosized diamond in the acid pH region, as can be seen by a shift of the zeta potential to more negative values. At higher pH values it had no influence.

The p.z.c. of a polished gold surface is reported to be  $-0.01$  V in 0.02 M  $\text{Na}_2\text{SO}_4$  [8]. In this electrolyte there will be only minor adsorption of sulfate ions at the gold surface. In the present work the minimum of the double layer capacitance in 0.02 M  $\text{Na}_2\text{SO}_4$  was detected at  $-0.05$  V. In the dilute (4 mL/L) gold electrolyte the double layer capacitance showed a minimum at  $-0.1$  V for polished gold and at  $-0.05$  V for electroplated gold (Fig. 5). When comparing these values it must be born in mind that the error of the measurement is ca. 0.03 V. Minima at higher potentials can be related to the formation of surface oxides.

The open circuit potential of the gold electrode in the gold electrolyte was  $-0.92$  V (SCE). Gold plating with a

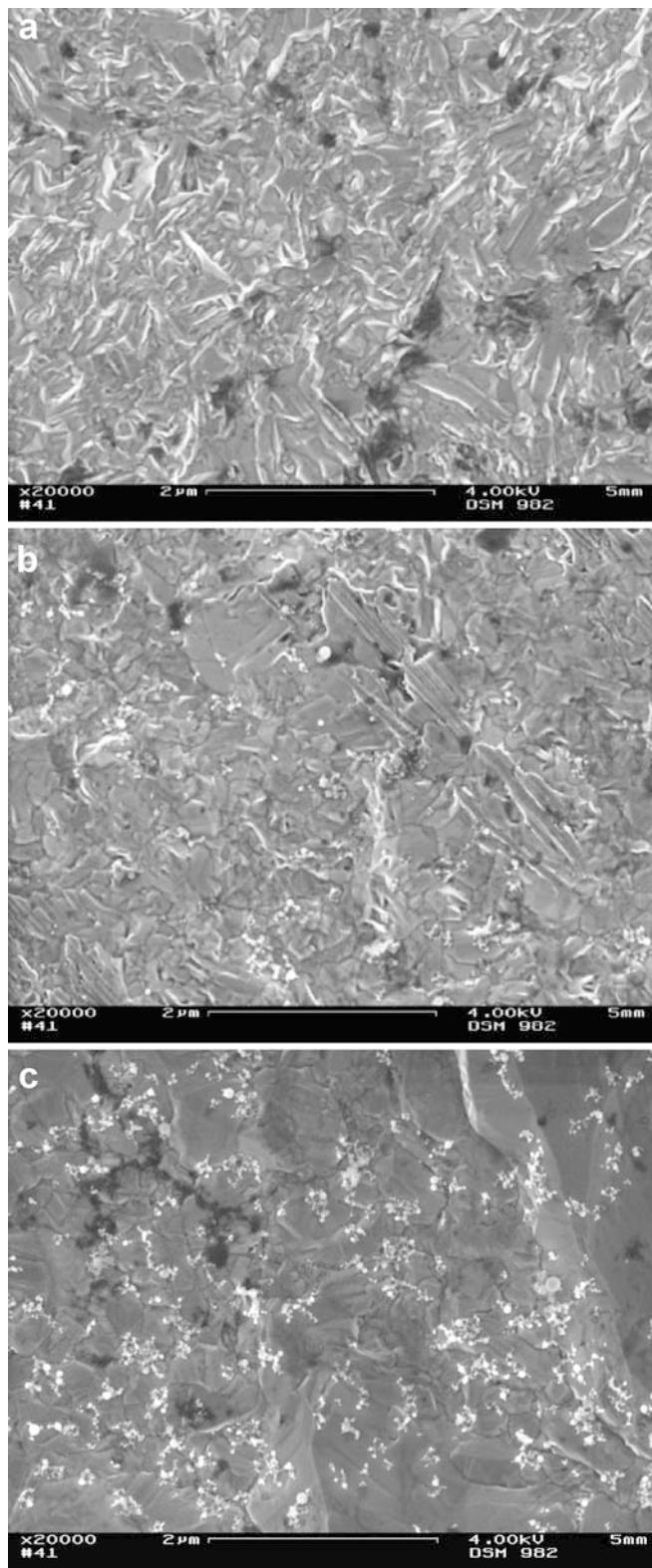


**Fig. 5** Potential dependence of the double layer capacitance of a pure electroplated gold layer in the diluted gold electrolyte (4 mL/L)

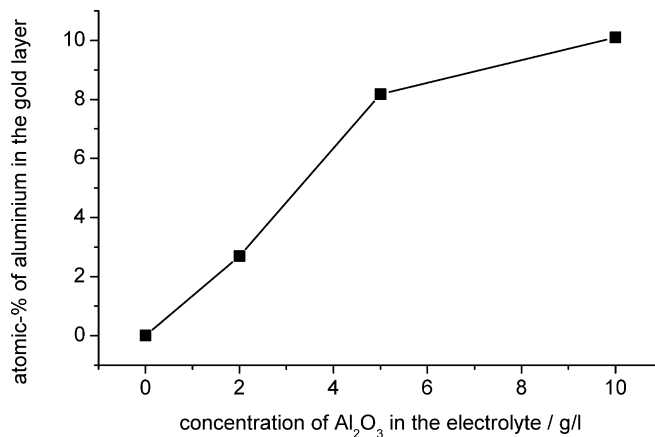
current density of  $1 \text{ A/dm}^2$  took place at ca.  $-1.0$  V. As the deposition potential is cathodic with respect to the p.z.c., the metal electrode bears negative charges under the conditions of gold electroplating. For reasons of electroneutrality there will be an excess of cations at the solution site.

#### $\text{Al}_2\text{O}_3$ codeposition

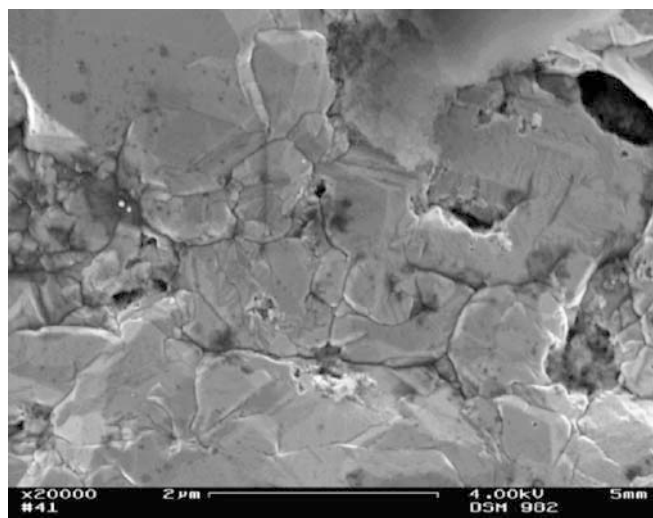
SEM showed that the  $\text{Al}_2\text{O}_3$  particles are codeposited with the gold as single non-agglomerated particles at a current density of  $1 \text{ A/dm}^2$  (Fig. 6b) and as agglomerates at  $0.5 \text{ A/dm}^2$  (Fig. 6c). The morphology of the gold with nano- $\text{Al}_2\text{O}_3$  did not differ from that of the pure gold (Fig. 6a).



**Fig. 6** SEM images of the pure gold layer and gold dispersion layers: (a) pure gold; (b) 10 g/L  $\text{Al}_2\text{O}_3$ , 1  $\text{A}/\text{dm}^2$ ; (c) 10 g/L  $\text{Al}_2\text{O}_3$ , 0.5  $\text{A}/\text{dm}^2$



**Fig. 7** Correlation between the Al content in the layer and the concentration of  $\text{Al}_2\text{O}_3$  in the electrolyte



**Fig. 8** SEM image of gold layer prepared from the gold electrolyte containing 3 g/L nanodiamond, 1  $\text{A}/\text{dm}^2$

The content of  $\text{Al}_2\text{O}_3$  in the layer increased with the concentration of  $\text{Al}_2\text{O}_3$  in the electrolyte up to 10 at% (10 g/L  $\text{Al}_2\text{O}_3$  particles in the electrolyte, Fig. 7).

#### Nanodiamond codeposition

The codeposition of diamond with gold caused a change in the surface morphology. The surface roughness increased and the crystals were larger (Fig. 8). One possible explanation is that impurities in the diamond suspension act like additives.

The codeposition of nanosized diamond caused an increase of the carbon content from 33 at% in the pure gold layer to about 60 at% in the gold layer with diamond. Increasing the diamond content of the electrolyte did not increase the carbon concentration in the layer significantly. Because of the high background concentration of carbon, it was not possible to give exact values for the concentration of nanodia-

mond in the layer. Furthermore, it was not possible to visualize the particles in the scanning electron micrographs.

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## Discussion

The model sketched in Fig. 1 is based on the assumption that for a successful codeposition the particles and the electrode must be oppositely charged. Under these conditions the particles can invade the electrical double layer of the electrode. In the next step the adsorbed ions desorb and the particle is incorporated into the growing metal matrix. Pictorially speaking, the adsorbed ions at the particle have a "Trojan horse" effect. The experimental data given above are in accordance with this assumption, for  $\text{Al}_2\text{O}_3$  as well as for nanodiamonds.

The microhardness of the gold layer decreased from  $280 \pm 60$  HV for pure gold to  $250 \pm 110$  HV for low concentrations of  $\text{Al}_2\text{O}_3$  in the electrolyte. At higher concentrations (10 g/L) it increased to  $440 \pm 180$  HV, which seems to correspond to a dispersion hardening. Although the layer deposited at  $0.5 \text{ A/dm}^2$  with 10 g/L  $\text{Al}_2\text{O}_3$  showed many particles at the surface (Fig. 6c), the microhardness decreased to  $120 \pm 20$  HV, which is less than pure gold.

The presence of diamond in the electrolyte decreased the microhardness to  $100 \pm 10$  HV. This can be explained with the increased grain size seen in Fig. 8.

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## Conclusions

It was shown that it is possible to prepare dispersion coatings of gold with nanoscaled  $\text{Al}_2\text{O}_3$  and nanodia-

mond. The investigations show that the adsorption of citric acid gives rise to a strongly negative zeta potential. The electrode potential will be negative relative to the p.z.c. under most cathodic plating conditions. Therefore, careful tuning of the surface charge of the particles seems to be a crucial point for the inclusion of nanoscaled particles in metal matrices. Furthermore, it was shown that the codeposition of nanoscaled  $\text{Al}_2\text{O}_3$  increased the microhardness of the electroplated gold layers.

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