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Homogeneous Ni-P/Al_2O_3 nanocomposite coatings from stable dispersions in electroless nickel baths

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ABSTRACT

The dispersion stability of aluminum oxide colloidal particles stabilized with comb-polyelectrolytes in an electroless nickel (EN) solution was studied under plating conditions (80–90 °C). The nanodispersions which were stable at room temperature for several weeks flocculate rapidly as the temperature approached ∼65 °C. Hydrotropes such as propylene glycol and urea are found to induce stability under plating conditions. A dependency of the critical flocculation temperature (CFT) on additives, comb-polyelectrolyte polyether side chain, and particle morphology is found. The codeposition of stabilized and nonstabilized nanoparticle dispersions resulted in very different particle density and distribution in the composite coatings. Highly homogeneous Ni-P/alumina nanocomposite coatings plated from stabilized baths with up to 50 vol% particle incorporation have been demonstrated.

1. Introduction

Composite electro and electroless nickel (EN) research is receiving increased attention lately [1–11]. This stems from new prospects for improving the tribological properties of the coatings by the incorporation of nanometer size hard particles such as diamond, SiC, and aluminum oxide. Submicrometer and nanoparticles are able to modify the crystalline growth of the growing nickel films [2–4] and create dispersion hardening effects at low incorporation levels [2,12].

The potential benefits of such nanometer size particle reinforcement can only be realized if the particles are well dispersed in the nickel coating. This can be realized when codeposition is done from well-dispersed composite plating systems.

Recently, stabilization of alumina colloidal particles in EN solutions at room temperature was achieved with commercial comb-polyelectrolyte surfactants [13]. In the present work we extend this investigation to dispersion stability in EN under plating conditions (80–90 °C). Ni-P/alumina coatings codeposited from both stabilized and nonstabilized systems are compared.

2. Materials and methods

2.1. Materials

The nano- and submicrometer powders used in the current study were AluC (Evonik Degussa, Germany) and Taimicron TM-DAR (TaiMei, Japan), respectively. Specific surface area was measured with a Coulter SA 3100 BET apparatus. The AluC is a mixed phase δ/γ-alumina nanopowder with primary particle size of ∼14 nm and specific surface area of 98 m^2/g. The TM-DAR is α-alumina with an average primary particle size of ∼150 nm and surface area of 12.5 m^2/g. MelPers4343 and MelPers0030, commercial comb-polyelectrolyte surfactants, consisting of polyether side chains grafted onto a polycarboxylate backbone, and molecular weights in the 20,000 g/mol range were obtained from BASF, Germany. MelPers4343 and MelPers0030 have polyether side chains with molecular weights of 500 and 5800 g/mol, respectively. Polyelectrolytes were diluted to 7.5 wt% solids with DI water and acidified to pH 4 with HCl or H_2SO_4 before use. NiPlate600 and 500, medium and high phosphorus commercial EN plating solutions, respectively, were obtained from Micron s.r.l., Italy. Both EN solutions are supplied in two makeup parts (A and B) and an additional replenishing part (part C). Part A contains primar-

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ily $NiSO_4$ and parts B and C contain the reducing agent NaH_2PO_2 along with proprietary complexing agents. Urea, propylene glycol (PrG), cetyl trimethylammonium bromide (CTAB), sodium pyrophosphate, ammonium iodide, and sodium thiocyanate (>99%) were all purchased from Sigma Aldrich, Switzerland.

The concentrations of the polyelectrolytes, CTAB, and sodium pyrophosphate are given in weight percentage on a particle basis whereas the other additives are given on dispersion weight basis.

2.2. Preparation of dispersions and composite bath

The 10 wt% colloidal alumina dispersions in DI water were prepared by ball milling (90 rpm) with 0.5-mm ZrO_2 balls for 3 h. The dispersions were diluted and ultrasonicated after the addition of the preacidified surfactants. A low amount of PrG (∼1 wt%) was found necessary to increase dispersion stability in water beyond several days.

The composite plating was carried out in a magnetically stirred 2-L glass beaker. Mixing of the composite EN bath components was done in the following order: 1 L DI water, alumina dispersion, 120 ml NiPlate600 part A, and 180 ml of NiPlate600 part B. Finally, DI water was added to a total bath volume of 2 L. The initial bath contains 6 g/L nickel and 23 g/L NaH_2PO_2. The pH of the mixed bath is 4.5 ± 0.1. Additives (e.g., PrG) were added to comb-polyelectrolyte-stabilized baths. All mixing procedures are done at room temperature (RT). Alumina dispersions in Niplate tested for temperature stability were prepared in a similar manner.

2.3. Temperature stability and particle size distribution

Particle size distribution (PSD) was measured with a Beckman Coulter LS230 equipped with polarization intensity differential scattering (PIDS). The measurement medium was EN solution. Nano- and submicrometer alumina dispersions containing various types and amounts of comb-polyelectrolytes, additives, and/or coadditives were tested for their temperature stability. Partially evacuated capped polypropylene bottles containing 20 ml dispersions were placed in an oven at temperatures between 60 and 90 °C for periods of 0.5–48 h. PSD was remeasured after cooling of samples to RT. Dispersion stability is assessed by the variation of the PSD with time and temperature.

2.4. Zeta potential measurements

Zeta potential and pH measurements were made with a Zetaprobe analyzer (Colloidal Dynamics, USA). Alumina dispersions in EN solutions were measured before and after temperature stability tests. Each experimental point is corrected with a background measurement made with EN solution of matching conductivity. All measurements were done at RT.

2.5. Electroless composite plating

Disks (0.5 dm^2) made of construction steel (CS) or 100Cr6 steel were used as substrates for composite EN plating. Substrates were degreased, activated, and coated with a 0.2-μm electrodeposited nickel layer (100Cr6) or several micrometers of Ni-P layer (CS) before composite plating. The mixed composite bath was heated to plating temperatures of 80–88 °C. The pretreated samples having total surface of ∼100–200 cm^2 were placed in the bath immediately after pretreatment. The bath was mixed by a magnetic stirrer (100–200 rpm) and kept at temperature (±1 °C) with a controlled hot plate. Replenishing of the bath was done by stepwise addition of 10 ml of both part A and part C for each 0.5 g/L Ni consumed during plating. The pH was kept at 4.5 ± 0.1 by frequent additions of 20% ammonia solutions. Samples for PSD determination were collected at the end of the plating to confirm dispersion stability in the chemically varying plating bath. Since plating rate increases strongly with temperature, plating temperatures were selected as the maximum temperature where dispersion stability is guaranteed for the duration of the plating. This topic is discussed in detail in Section 3.1. Based on the stability criterion, plating temperatures of 85 and 80 °C were selected for the stabilized nanoalumina and submicrometer alumina systems, respectively. The nonstabilized dispersions were plated at 88 °C.

2.6. Characterization of nanocomposite coatings

Particle distribution and concentration in the Ni-P/alumina composite coatings were evaluated by SEM/EDS (LEO 1455/Oxford Instruments). For the examinations, cross sections of the disks were embedded in a conductive resin. The metallographic preparation followed a standard procedure. The last polishing step was 1 μm diamond. The SEM conditions for all measurements were working distance of 15–20 mm, acceleration voltage of 20 kV, and probe current 350–500 pA. The pictures were taken using a BSE detector. The EDS signal was calibrated with a cobalt standard before each series of measurements.

3. Results and discussion

3.1. Dispersion stability in EN solution under plating conditions

The dispersion stability of nano- and submicrometer aluminum oxide in EN solution at room temperature was investigated in an earlier work [13]. It was found that the nano- and submicrometer alumina can be stabilized with >7–11 and >2 wt% MelPers comb-polyelectrolytes, respectively. In the present work, dispersions that were stable at RT were further investigated in the vicinity of plating temperatures (80–90 °C).

Fig. 1a shows the PSD of 4 wt% alumina colloidal particles stabilized with 11 and 14 wt% of short-chain MelPers4343 comb-polyelectrolyte after 1 h at 80 °C. The MelPers sterically stabilized dispersions that showed no appreciable PSD change after several weeks at RT (reference curve 11%, RT in Fig. 1) flocculate within <1 h at 80 °C. This phenomenon is believed to be associated with the decreased solubility of the MelPers polyether side chains with increased temperature in the high ionic strength EN solution. Napper and co-workers introduced the concept of the critical flocculation temperature (CFT) [14,15]. Sterically stabilized aqueous dispersions flocculate at a temperature near the theta temperature of the steric component (e.g., polyether side chain). The CFT is highly dependent on the salt concentration and type in the dispersion. Increased salt concentration reduces the maximum temperature where side chains are soluble in aqueous dispersions. Due to the reduced side-chain solubility, the steric repulsive force decreases and becomes attractive above the CFT [14–16]. This may result from changes in the hydration sheath surrounding the side chain as well as changes in the hydrogen-bonded structure of the water [17]. Certain additives such as urea and propylene glycol (PrG) are found to increase the CFT of nonionic surfactant-stabilized emulsions and affect the conformation of proteins [18–20].

Indeed, stability of the MelPers4343 stabilized nanoalumina dispersions is established at 80 °C with additions of 2 wt% urea or 2–10 wt% PrG (Fig. 1b). This suggests that the CFT of the dispersions is raised above 80 °C with >2 wt% urea or PrG for MelPers4343 concentrations >11 wt%.

The CFT can be increased further to >85 °C with 4 wt% PrG as shown in Fig. 2. Certain other additives such as sodium pyrophosphate and CTAB appear to increase the stability of the alumina dispersions in EN solutions but not as effectively as PrG or urea.