



Stabilization of Silicon Carbide (SiC) micro- and nanoparticle dispersions in the presence of concentrated electrolyte



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ABSTRACT

Achieving a stable and robust dispersion of ultrafine particles in concentrated electrolytes is challenging due to the shielding of electrostatic repulsion. Stable dispersion of ultrafine particles in concentrated electrolytes is critical for several applications, including electro-codeposition of ceramic particles in protective metal coatings. We achieved the steric stabilization of SiC micro- and nano-particles in highly concentrated electroplating Watts solutions using their controlled coating with linear and branched polyethyleneimines (PEI) as dispersants. Branched polyethyleneimine of 60,000 MW effectively disperses both microparticles and nanoparticles at a concentration of 1000 ppm. However, lower polymer dosages and smaller polymers fail to disperse, presumably due to insufficient coverage and bridging flocculation. Dispersion stability correlates well with the adsorption density of PEI on microparticles. We discuss the results in the framework of DLVO theory and suggest possible dispersion mechanisms. However, though the dispersion is enhanced with extended adsorption time, the residual PEI in solution adversely affects electroplating. We overcome this drawback by pre-coating the particles with the polymer and resuspending them in Watts solution. With this novel approach, we obtained robust dispersions. These results offer new possibilities to control dispersion at high electrolyte concentration, as well as bring new insights into the dispersion phenomenon.

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1. Introduction

In many practical applications, it is critical to have stable dispersions and to prevent particle aggregation, such as for the processing of paints, pigments, paper and pulp, high performance ceramics, minerals, electronics and pharmaceutical and personal care products. Dispersion stability is especially critical for electro-codeposition of particles.

Recent approaches for producing wear-resistant coatings include codeposition of ultrafine sized particles into metal matrix, such as nickel films [1–3]. In case of electrocodeposition, particles dispersed in a plating bath are attracted towards the electrode and embedded into the growing metal film. Such polycomposite coatings can have improved material properties and mechanical resistance [4–6].

In electroplating applications, it is critical to have stable dispersions, to prevent particle aggregation and uneven particle incorpo-

ration. The incorporation of particles is dependent on the particle concentration [7] and size, stirring speed and particle aggregation [1], surface hydrophobicity [8–12] and surface charge [13].

Synergy between surfactants and polymers can be beneficially used for dispersion. Palla and Shah [14] used surfactant and polymer mixtures to stabilize slurries, but with low ionic strength, when compared with plating applications. Combination of a copolymer (Acrylic Acid-2-Acrylamido-2-Methylpropane Sulfonic Acid Copolymer) and polyvinylpyrrolidone has been shown to produce a synergistic effect on the rheology and the stability of SiC dispersions in deionized water [15]. Fluorosurfactants have also been reported to stabilize nanoparticle dispersions of SiC and SiN [16].

However, most of these studies were performed in deionized water or at much lower ionic concentrations than required for electroplating. Only a few studies have been focused on stabilization under plating conditions; cetyltrimethylammonium bromide [17,18], azo-cationic polymer [6] and carbon modification [8] were used to disperse and to support incorporation of ceramic particles during electroplating. In the case of nickel electroplating investigated here, the medium in which the particles are dispersed is extremely concentrated, with an ionic strength of around 2 moles, which makes conventional electrostatic stabilization of particles difficult [19].

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In the case of electro-codeposition of ceramic particles with Ni(II), the positive charge of the particles can improve their incorporation and, therefore cationic dispersive agents can be expected to be beneficial. Among such dispersants is PEI, a cationic polymer (Scheme 1). PEI has been tested as a dispersant for various ceramic particles, but under low ionic strength conditions [20–22]. The stability of the dispersions is determined by the adsorption density and surface saturation of PEI [21,23], pH [23] and electrolyte concentration [22]. A strong concentration dependence of flocculation has also been reported for kaolin suspensions stabilized with PEI [24] and silica suspensions with polyacrylic acid–polyethylene comb polymer [25]. Linear and branched PEIs of different molecular weight were tested by Kakui et al. [26] for the dispersion of alumina in ethanol.

Since most of the stabilization studies of PEI were done at a low ionic strength those results are not applicable to Watts solutions at extremely high electrolyte content. Therefore the dispersion of ceramic particles by PEI in Watts solution is studied in this work.

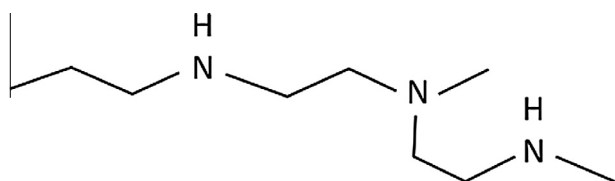
Herein, we address the dispersion properties of PEI in Watts bath, with a perspective of its possible application as a dispersant in highly concentrating plating solutions.

2. Materials and methods

2.1. Materials

Silicon carbide particles of two sizes were obtained from Alfa Aesar, both β -phase SiC, 99.8% (metal basis). The larger particles were of 1 μm average size and are called microparticles henceforth, while the smaller particles were of 45–55 nm size and are referred to as nanoparticles. Both particle types were characterized using TEM, XPS and Raman microscopy. TEM was performed on a Jeol JEM 100CX Transmission Electron Microscope operated in the bright field mode at 100 KeV. X-ray diffractograms were recorded using a Scintag Model X2 X-ray powder diffractometer. A Cu $K\alpha$ (= 0.154 nm) radiation source operated at 45 kV and 35 mA was used. The scan step size was 0.05 deg.

XPS spectra were collected with a Perkin Elmer 5400 instrument using monochromatic Al $K\alpha$ X-rays (1486.6 eV) with pass energies of 17.6 eV at a take-off angle of 45° at pressures of less than 4×10^{-9} Torr, calibrated using the Au(4f_{7/2}) peak at 84.0 eV. Regional XPS scans were collected at 0.1 eV steps. The atomic concentration ratios were evaluated using the PHI atomic sensitivity factors. The Shirley function was used to subtract the background. The XPS samples of initial particles were prepared by spreading a thin layer of their thick slurries on a UHV metallic holder followed by air-drying. Before measurements, particles were washed with water (two cycles of resuspension–centrifugation). Raman spectra were measured using a LabRam Aramis microscope (Horiba) equipped with a 532-nm laser. The zeta potential of SiC microparticles was estimated measuring electrophoretic mobilities of the particles in 0.01 M NaCl at a pH of 3.5 with Zeta-Meter 3.0+ (Zeta-Meter Inc.). Particles were dispersed in Watts plating solution of the following composition: 300 g/L NiSO₄·6H₂O, 35 g/L NiCl₂·6H₂O, 40 g/L H₃BO₃.



Scheme 1. Molecular structure of polyethyleneimine.

Branched polyethyleneimine of 60,000 average molecular weight was purchased from Acros Organics and is later referred to as PEI 60. Linear polyethyleneimine of a lower 1200 molecular weight (PEI 1.2) was purchased from Sigma Aldrich. Both polyethyleneimine samples were obtained as 50% aqueous solutions.

2.2. Dispersion preparation

All particulate dispersions were prepared at 20 g/L SiC content in Watts solution at pH 3.5. Specifically, the dry powders were added to a Watts solution containing polyethyleneimine and were stirred at 700 rpm for one hour. The dispersions were sonicated for 30 min after stirring to maximize dispersion. In order to study the effect of dissolved polymer in Watts solution on dispersion, the particles were first precoated with PEI and then redispersed in Watts bath. The precoating protocol involves (1) dispersion preparation step mentioned above, (2) centrifugation and supernatant decantation and (3) redispersion of solids in Watts solution without PEI. This method keeps the solid content constant but eliminates the presence and interference of polymer in the solution. To resuspend the particles, sonication was applied for additional 30 min.

2.3. Settling test

Settling tests were performed and evaluated according to [14] for 120 min and the settling was documented at discrete time intervals. The tests were performed right after sonication at laboratory temperature of 23 °C. The dispersion stability is expressed as dispersed volume (=100% – settled volume %).

2.4. Adsorption test

The total organic carbon (TOC) technique was employed to determine the amount of adsorbed PEI. Suspensions of SiC in deionized water and in 0.1 M NaCl solutions with PEI 60 were prepared, stirred at 700 rpm for one hour, sonicated for 30 min and centrifuged. The amount of total organic carbon in the supernatant was measured with a TOC-5000 A Shimadzu. Due to the limitations of this method, the Watts solution cannot be used and the adsorption was estimated for deionized water and 0.1 M NaCl solution. The adsorbed amount of PEI was estimated after 1, 2, 3, 5 and 7 days of adsorption time.

3. Results

The effect of polyethyleneimine on the stability of SiC dispersions in plating solution is first discussed and then, the quantification of the polymer adsorption and DLVO calculations are employed to explain the phenomena of particulate stabilization at high ionic strength.

3.1. Particle characterization

Morphology and size of the SiC micro- and nanoparticles were characterized using TEM. The microparticles are cubes of about 1 μm size (Fig. 1a), while nanoparticles have spherical shape with size of about 50 nm (Fig. 1b). The surface areas of particles specified by the supplier were 11.5 m²/g and 70–90 m²/g for microparticles and nanoparticles respectively.

Raman spectroscopic analysis shows that the SiC phase of both the particles is a zinc-blende 3C (β) phase. This phase is characterized by a peak at 780–800 cm⁻¹ (Fig. 2). In addition, the Raman spectra display peaks at ~1350 and ~1590 cm⁻¹ due to polycrystalline graphite [27]. The relative intensities of the graphite peaks

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