Effect of polymeric surfactant on particulate structure in nickel-terpineol suspensions

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Price of noble metals (e.g., platinum, palladium, etc.) has risen rapidly over the years, so using base metals (e.g., nickel) as the interconnection material for microelectronic hybrid thick-film components has received much attention recently [1–4]. Taking the fabrication of a multilayer ceramic capacitor as an example, a stabilized nickel (Ni) slurry with a high solids concentration and an appropriate colloidal rheology is necessary for the production of defect-free, internal electrode layers. By tailoring the interparticle potentials in the slurry [5], a stable ink with a desired particulate structure may be attainable. Sánchez-Herencia *et al*. [6] recently prepared aqueous Ni colloids, in which nickel powders of 27% volume were mixed uniformly with κ-carrageenan in water to form "flowable" suspensions. The Ni colloids were then transformed into compacts with a sufficient "green" strength before being subjected to sintering at elevated temperatures. Bhattacharya *et al*. [7] examined rheological behaviors of nickel laterite suspensions at various temperatures, concentrations, particle sizes, and pH values. When solids concentration of the laterite slurries reached 20 wt%, a Bingham plastic flow behavior was observed. The present authors [8, 9] also investigated rheological behaviors of Ni suspensions when different polymeric surfactants and liquid solvents were used in the suspension formulation. Minor addition of appropriate organic surfactant was found effective in reducing the suspension viscosity, hence leading to an increased maximum solids concentration allowable for powdered suspensions.

Even though the addition of organic surfactant to the rheology of Ni slurries has been studied rather extensively [6–9], a report that addresses the change of suspension *structure* when the surfactant is introduced into the powdered mixtures is limited [8]. In this study, we intend to compare the structural change of a model Ni-terpineol suspension when a propylene glycol was used as a surfactant. Submicrometer Ni powders (210 H, Inco Co., USA) with particle size in a range of 0.2–0.5 μm, and a specific surface area 4–8 m^2/g (vendor specification) were used as the raw material. The Ni particles were extensively agglomerated, as shown in Fig. 1, from the scanning electron microscopy (SEM, JSM-6335F, Jeol, Japan). A commercially available polymeric dispersant (KD-6, ICI Surfactant, USA) consisting of propylene glycol as its major composition was uniformly mixed with reagent-grade α-terpineol (90%, Aldrich Chemical Co., USA) before addition of the powders to form ink slurries. All the powdered slurries were ball-mixed in polyethylene bottles for a period of 24 hr before their viscosity (η_s) being determined by a strain-controlled concentric viscometer (VT550, Gebruder HAAKE Gmbh, Germany) equipped with a sensor system (MV-DIN 53019, HAAKE, Germany) of a cone-cup geometry operated at a constant temperature (25 °C). The viscosity measurement was performed with a steady increment of shear rate ($\dot{\gamma}$) over a range of 1–1000 s^{-1}. An SEM observation revealed that the Ni particles remained almost spherical in shape after the high-shear ball mixing. This indicated that the impact force involved in the mixing process did not deform the powders into flake forms that might substantially hinder the flow behavior of the suspensions.

The suspensions all showed a shear-thinning flow character over the shear-rate range examined. This indicated that the suspensions were flocculated in structure and the Ni aggregates remained existing in the carrier liquid, even with the addition of propylene glycol. The extent of the powder aggregation appeared to be dependent on the shear rate applied, namely, the floc reduced in size as the shear rate increased, as revealed from the shear-thinning flow behavior of the suspensions.

Yield stress (τ_y) of the suspensions can be estimated from the Casson model [10]:

$$\tau^{1/2} = \tau_y^{1/2} + (\eta_s \cdot \dot{\gamma})^{1/2} \qquad (1)$$

As shown in Fig. 2, the (shear stress, τ)$^{1/2}$ appeared to follow a satisfactory linear dependence with the (shear rate, $\dot{\gamma}$)$^{1/2}$ over the shear rates and solids concentrations examined. The τ_y values were then determined from extrapolations of the curve-fitted, linear lines to $\dot{\gamma}^{1/2} \to 0$, and were tabulated in Table I. The yield values with 2 wt% propylene glycol are apparently lower than those of the suspensions without the glycol surfactant.

The flocculated nature of the suspensions examined allowed us to analyze the suspension *structure* using the fractal geometry [11–13]. The Ni particles in the terpineol liquid were expected to attach to one another to form porous aggregate structures, due mainly to the van der Waals attraction involved in the interparticle potentials. Shih *et al*. [11] recently suggested a model which enables a quantitative evaluation of flocculated powder suspensions by means of the fractal dimension (D_f). The model correlated the suspension τ_y with solids concentration (ϕ) in a form

$$\tau_y \sim (1 - 1.5\alpha\zeta^2)\left(A/24s_o^{3/2}\right)(1/R^{d-3/2})\phi^m, \qquad (2)$$
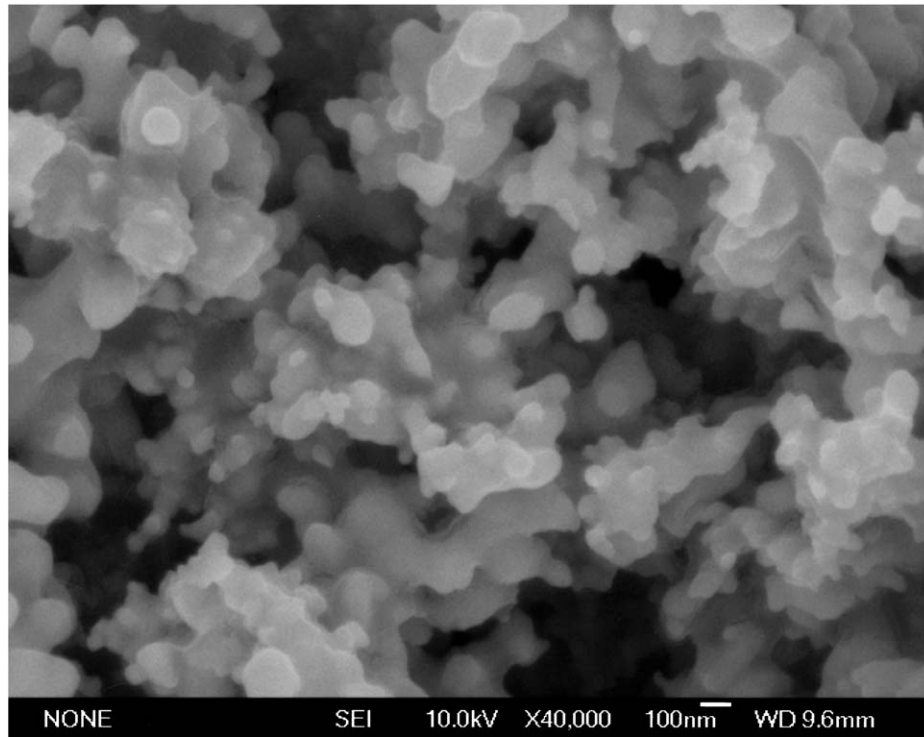
Figure 1 Micrograph of Ni particles used in the study.
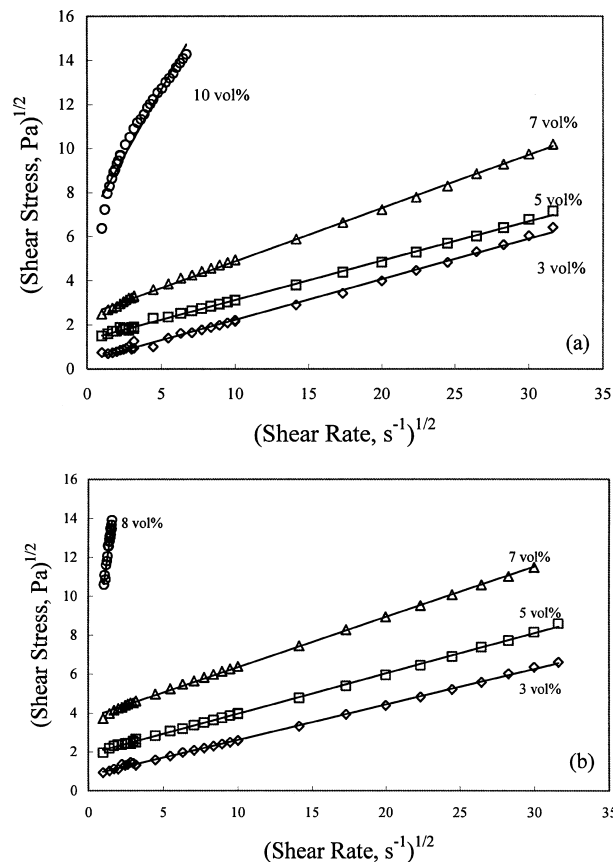

Figure 2 The $\tau^{1/2}$–$\dot{\gamma}^{1/2}$ dependence for determining the suspension yield stress (τ_y) following the Casson model: (a) with the propylene-glycol surfactant and (b) without the propylene-glycol surfactant.

where α is a constant related to the Debye thickness (κ^{-1}) and the surface separation (s_o) between particles; ζ is the zeta potential; A is the Hamaker constant; R is the particle radius; d is the Euclidean dimension;

TABLE I Yield stresses of the Ni slurries estimated from the Casson equation

Solids concentration (vol%)	Yield stress (Pa)	
	With 2 wt% propylene glycol	Without propylene glycol
3	0.15	0.64
5	1.79	3.58
7	6.07	14.13
8	N.A.	19.30
10	44.01	N.A.

N.A.: Not applicable.

$m = (d + X)/(d - D_f)$ with D_f and X the fractal dimension of the clusters and the backbone of the clusters, respectively. The Euclidean dimension $d = 3$ when considering structures in three dimensions, and the backbone of the cluster $X \approx 1$ under most situations [11]. D_f is then related to the rheological properties (i.e., τ_y and ϕ) of the suspensions and can hence be determined once m becomes available.

As shown in Fig. 3, the experimental τ_y–ϕ relationships were fitted by power-law equations to determine the exponent m value. The broken line and solid line represent the power-law fits of the Ni-terpineol suspensions with and without the propylene glycol, respectively. The m exponents were then estimated as 4.61 ($R^2 = 0.996$) and 3.56 ($R^2 = 0.997$). These yielded fractal dimensions of $D_f = 2.1$ and 1.9 for the Ni suspensions with and without the propylene glycol, respectively.

Two distinct regimes in the fractal geometry of flocculated powder suspensions have been identified [12]. A diffusion-limited cluster–cluster aggregation (DLCA) is expected to occur when there is a negligible
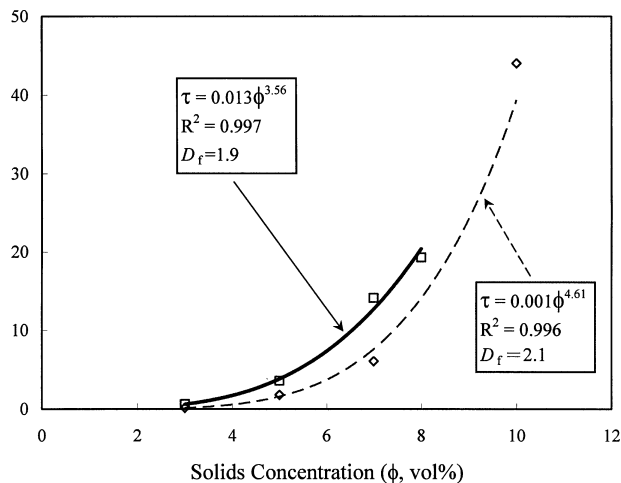
Figure 3 The τ_y–ϕ relationship for the determination of fractal dimensions.

repulsive force existing between the colloidal particles in liquid. Single particles can stick to other particles or clusters with a "sticking" probability being one to form large fractal aggregates via random walks. The aggregation rate is sorely limited by the time taken for the clusters to encounter one another by a diffusion process. The scale-invariant fractal dimension of DLCA is determined as $D_f \approx 1.78$ [13]. Additionally, a reaction-limited cluster–cluster aggregation (RLCA) occurs when there is a substantial, but not insurmountable, repulsive force existing between particle surfaces in liquid [12, 13]. In this case, more than one collision is then needed before a particle sticks to another particle or a cluster to form aggregates. The fractal dimension D_f of RLCA is about 2.0 in three dimensions [13]. D_f can be increased to 2.2 if particle rearrangement was allowed to occur, hence leading to a denser packing configuration.

In our flocculated suspensions, D_f equals 2.1 when the surfactant was involved in the suspensions. The particle structure is hence probably belonged to the RLCA model as the propylene glycol was introduced into the Ni suspensions, whilst, for the flocculated suspensions without the surfactant, $D_f = 1.9$, the suspension structure is then somewhere between the DLCA and the RLCA models. Addition of the glycol surfactant appeared to have altered the particulate structure

of the model Ni suspensions. This accordingly changed the macroscopic flow behavior of the suspensions. In a separate study [15], we have found that the glycol molecules would adsorb preferentially on the Ni particle surface in a Langmuir-type adsorption. This adsorption would increase the interparticle seperations between the neighboring particles in the terpineol liquid, and hence provide steric hindrance to an undetermined extent so that the interparticle attractions were reduced.

Acknowledgments

References
1. Y. SAKABE, *Amer. Ceram. Soc. Bull.* **66**(8) (1987) 1338.
2. H. SHOJI, Y. NAKANO, H. MATSUSHITA, A. ONOE, H. KANAI and Y. YAMASHITA, *J. Mater. Synth. Process.* **6**(6) (1998) 415.
3. I. HOTOBY, J. HURAN, L. SPIESS, S. HASCIK and V. REHACEK, *Sensors Actuators* B **52** (1999) 147.
4. S. T. ARUNA, M. MUTHURAMAN and K. C. PATIL, *Solid State Ion.* **111** (1998) 45.
5. J. A. LEWIS, *J. Amer. Ceram. Soc.* **83**(10) (2000) 2341.
6. A. J. SANCHEZ-HERENICA, A. J. MILLAN, M. I. NIETO and R. MORENO, *Acta Mater.* **49** (2001) 645.
7. I. N. BHATTACHARYA, D. PANDA and P. BANDOPADHYAY, *Int. J. Miner. Process.* **53** (1998) 251.
8. W. J. TSENG and C.-N. CHEN, *Mater. Sci. Eng.* A **347** (2003) 145.
9. W. J. TSENG and S. Y. LIN, *ibid.* **362** (2003) 165.
10. N. CASSON, "Rheology of Dispersed System" (Pergamon Press, New York, 1959) p. 84.
11. W. Y. SHIH, W.-H. SHIH and I. A. AKSAY, *J. Amer. Ceram. Soc.* **82**(3) (1999) 616.
12. M. Y. LIN, H. M. LINDSAY, D. A. WEITZ, R. C. BALLI, R. KLEIN and P. MEAKIN, *Nature* **339** (1989) 360.
13. R. J. PUGH and L. BERGSTROM, "Surface and Colloid Chemistry in Advanced Ceramics Processing" (Marcel Dekker, New York, 1994) p. 206.
14. C.-N. CHEN, Master Thesis, The Chinese Culture University, 2002.