

Electrokinetic Properties of Nanosized SiC Particles in Highly Concentrated Electrolyte Solutions

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In this research, the electrokinetic behavior and stability of nanosized SiC particles suspended in various electroplating solutions were studied. Analyses were performed using electrophoretic mobility photometry and streaming current (SC) techniques. The electrolytes included NiCl₂, Ni(SO₃NH₂)₂, and Na₃Co(NO₂)₆, which are currently used in composite plating solutions with concentrations as high as 0.5M. The results showed that the adsorption of dissolved Ni²⁺ ions onto the surface of the SiC in the pH range 4–8 changed the sign and magnitude of the surface potential. Moreover, trivalent complex species Co(NO₂)₆³⁻ replaced nickel species on the SiC surface and decreased the surface charge of SiC to between pH 3 and pH 5. Even in a highly concentrated electrolyte solution, the SiC particles still maintained a positive charge in a Ni(SO₃NH₂)₂ suspension with nickel coplating on the cathode. The difference between the SC reading and the zeta potential, as well as the surface adsorption of various species onto the SiC, are discussed here.

I. Introduction

COLLOIDAL processing of nanosized SiC powder (particle size <100 nm) recently has received increasing attention because it provides various advantages, such as low-temperature sintering, mechanical-property improvement, and high-temperature superplasticity.^{1–3} When nanosized SiC particles are dispersed in a metallic matrix prepared by composite plating, the wear resistance of the SiC/nickel composite improves ~50 times over that of a pure nickel sample after heat treatment at 400°C.⁴ However, agglomeration often occurs in these ultrafine powders with high specific surface areas during powder processing, leading to various defects in the green and sintered ceramics. These defects are the major reasons for inhomogeneous microstructures, low density, and poor mechanical properties.

In an aqueous or nonaqueous colloidal system, dispersion of these ultrafine powders is one of the key steps toward achieving optimal mechanical properties for composites prepared by slip casting, electrophoretic deposition, or composite electroplating. The stability of nanoparticles in suspension is controlled by the colloidal properties, e.g., the thickness of the double layer and the zeta potential of the fine particles. According to the Deryagin, Landau, Verwey, and Overbeek (DLVO) theory,⁵ the van der Waals attractive force and the electrostatic repulsive force are two important interaction forces dominating in an aqueous suspension

system. If the surface charge of the powders is sufficiently high, a well-dispersed suspension is obtained.

Wang and Wei⁶ showed that the addition of polyethylenimine (PEI) could disperse submicrometer SiC powder in an aqueous or alcoholic solution. PEI increased the pH of the suspension, and the adsorption of PEI onto SiC reversed the surface charge of the SiC from negative to positive. Therefore, the isoelectric point (IEP) of the SiC powders shifted from pH 3.2 to pH 10.1 in the solution with dissolved PEI. A similar attempt was made by Iskra,⁷ who used various ionic compounds to float coarse SiC powder with particle sizes of 75–150 μm. Iskra found that cationic dodecylammonium chloride could be adsorbed onto the surfaces of the SiC particles, leading to an IEP change from pH 2.8 to pH 10.

The IEPs of SiC reported in the literature range from pH 2 to pH 3, similar to that of SiO₂.⁸ A possible explanation for this similarity may be the presence of a thin SiO₂ layer on SiC. If the free SiO₂ layer is leached by HF, the IEP of pure SiC particles increases to pH 6, and the stability of the SiC suspension decreases, because of the presence of a native hydrophobic layer.⁹ An increase in the stability of the SiC suspension, caused by the increase in the thickness of the hydrophilic amorphous SiO₂ layer by heat treating at 650°C, also is documented.

Streaming current (SC) is one of the techniques used for measuring the electrokinetic properties of particles in solution.^{10,11} The SC method is capable of monitoring electrokinetic properties of the particles on line in a highly concentrated electrolyte and/or a high-solids-content solution. In a previous investigation,¹² we measured the SC of ZrO₂ suspensions with different solids contents or electrolytes. Those results showed that the SC reading and zeta potential of a ZrO₂ suspension fit a linear correlation. Therefore, the SC method can replace electrophoretic mobility photometry (EMP) for measuring the electrokinetic properties of a ceramic suspension.

To produce a well-dispersed composite layer during the composite plating of ultrafine ceramic particles with metal, the particles in the plating suspension must have a positive surface charge and must not agglomerate. In this study, we investigated the surface charging and dispersive behaviors of ultrafine SiC in solutions that contained nickel sulfamate (Ni(SO₃NH₂)₂), nickel chloride (NiCl₂), and other chemical species. Because of the high ionic strength and solids loadings of the SiC suspensions used in the electroplating, the surface properties of the plating suspensions were beyond the measurement capabilities of EMP. Therefore, the SC technique was chosen in the present study to investigate various SiC suspensions.

II. Experimental Procedure

A plasma-synthesized SiC powder (PJ-PL-SiC, PlasmaChem GmbH, Mainz, Germany) of ultrafine particle size was used in this study. The particle size was measured by a particle-size analyzer, based on the laser light-scattering technique (Mastersizer 2000, Malvern Instruments, Ltd., Malvern, U.K.), and transmission electron microscopy (TEM; Model 100CXII, JEOL, Tokyo, Japan). For the analysis of particle size, a suspension containing 2 vol% of PEI (Scientific Polymer Products, Inc., Ontario, NY) was ultrasonicated for 30 min, to decrease agglomeration. The chemical formula and mean molecular weight (M_w) of the PEI were (CH₂CH₂NH)_n and ~5000 g/mol, respectively.

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Diluted suspensions with deionized water ($\Omega > 15$ Mohm-cm) were prepared with various solids loadings. The pH of the suspensions was adjusted by a reagent-grade 0.1M HCl or NaOH solution. The electrolytes $\text{Ni}(\text{SO}_3\text{NH}_2)_2$ (Phibrochem, Inc., Fort Lee, NJ), NiCl_2 (EP grade, Showa Denko, K.K., Tokyo, Japan) or sodium hexanitrocobaltate ($(\text{Na}_3\text{Co}(\text{NO}_2)_6)$, Jassen Chimica, Beerse, Belgium) were used. Suspensions with these electrolytes were exposed to an ultrasonic probe (Model RK103, Sonorex, Taiwan, R.O.C.) at 35 kHz and 150 W, for 10 min, and the pH values before and after electrokinetic measurement were recorded, for studying reactions within the suspension. The temperature of all of the suspensions was kept constant at $25^\circ \pm 1^\circ\text{C}$. Unless specified in the text, 0.01M NaCl (reagent grade, Nacalai Tesque, Inc., Kyoto, Japan) was added to the suspensions, to maintain the same ionic strength as before addition of the powders.

The microstructures and phases of the powders were observed by TEM, high-resolution TEM (HRTEM; Model 400FX, JEOL) and X-ray diffractometry (XRD; Model PW1792, Philips Research Laboratories, Eindhoven, The Netherlands). An electrophoretic mobility meter (Laser Zee 501, Pen Ken, Inc., Bedford Hills, NY) and an electrokinetics charge analyzer (Model ECA2000, Chemtrac Systems, Inc., Norcross, GA) were used to measure the zeta potential and SC, respectively. During measurement of the electrophoretic mobility, larger particles ($\geq 0.1 \mu\text{m}$) were easier to observe than small particles (~ 20 nm) by optical microscopy. Thus, the assumptions made for the Smoluchowski equation were effective for estimating the zeta potential of the larger SiC particles, but a 5%–20% variation of the surface potential was possible for the smaller particles.

III. Results and Discussion

(1) Characterization of the SiC Powder

The morphology of the ultrafine SiC powder observed by TEM is shown in Fig. 1(a). The SiC was angular in shape for nanosized particles and nearly triangular for some submicrometer-sized particles. The particle-size distribution was close to a Gaussian distribution, as shown in Fig. 1(b). The mean particle size of the as-received powder was 62 nm. HRTEM study of the surface revealed that the SiC was surrounded by a thin, amorphous SiO_2 layer 2–5 nm thick. According to thermogravimetric (TGA) analysis, the SiC powder did not oxidize before 350°C .

(2) Streaming Current and Zeta Potential of the SiC

The SC reading and zeta potential of the SiC particles in the 0.01M NaCl electrolyte are shown in Fig. 2. These two curves show a similar trend, but the points of zero value (either potential or current) measured by the two methods are different. The IEP and isocurrent point (ICP) of the SiC are pH 2.6 and pH 3.0, respectively. These results are very close to the IEP value of SiO_2 reported previously.⁸

From the result of Fig. 2, the relationship between the SC reading (I) and the zeta potential (ζ) is plotted in Fig. 3. As the curves depict, these data points can be fitted as either a linear function or a polynomial function of the second order. A shift from the zero point occurs. Zero potential is found at a streaming current of 0.18 mA.

The offset is a result of the positive charge on the surface of the capillary passage in the SC detector. The surface charge of the SiC particles was nearly neutral when the suspension was strongly acidic (pH 2.5–3.5). With no electric repulsive force, the van der Waals force between the particles dominated the surface forces, and the particles tended to aggregate. As shown in Fig. 4, the SC reading of the polytetrafluoroethylene (PTFE) was 0.3 mA at pH 2.6. The PTFE detector contributed a positive charge to the SC reading.

(3) Influence of the Electrolyte

NiCl_2 is added to a sulfamate plating solution to decrease polarization of the anode during electroplating. Figure 5 shows the zeta potential and SC readings of dilute SiC suspensions (0.01 vol%) with NiCl_2 as the electrolyte. The zeta potential of the SiC surfaces changed polarity from negative to positive at pH

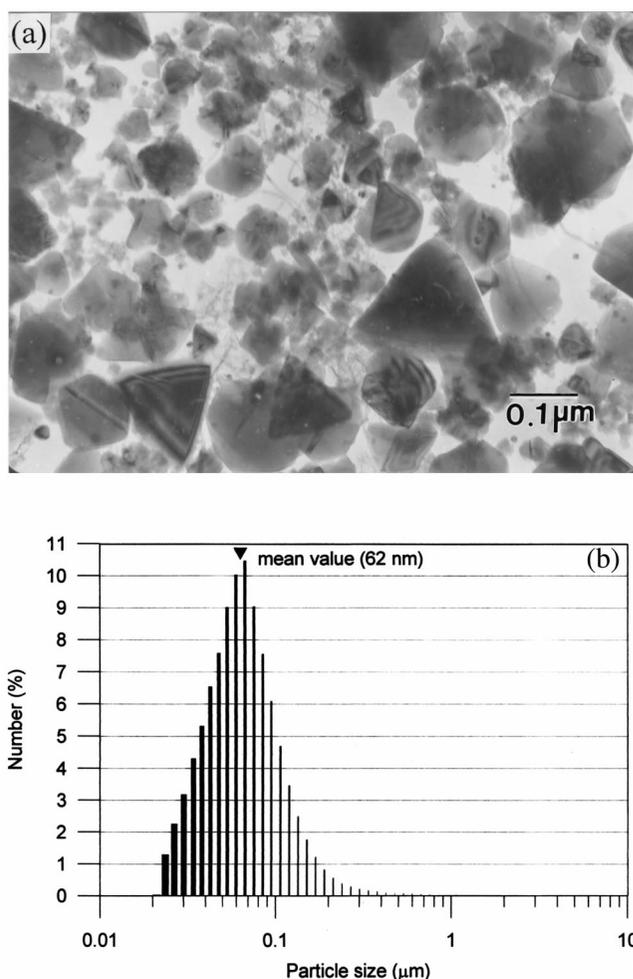


Fig. 1. (a) Transmission electron micrograph of nanosized SiC and (b) particle-size distribution of SiC; mean particle size is 62 nm, and 2 vol% of PEI dispersant was added.

values >4 and reached a maximum at pH 7. When the pH value was >7 , the Ni^{2+} ions tended to form a hydrate $\text{Ni}(\text{OH})_2$ precipitate, and the zeta potential of the SiC decreased (Fig. 5(a)). The trend of zeta potential change in the suspensions was similar at various concentrations of NiCl_2 . Even a trace amount, 10^{-6}M ,

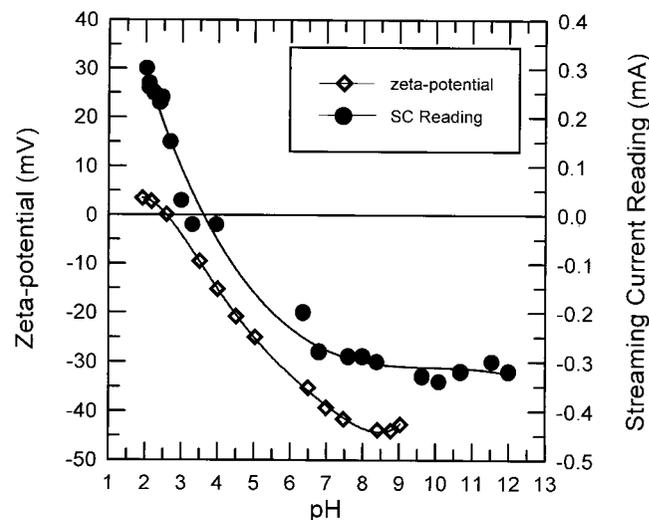


Fig. 2. Variation of zeta potential and SC readings of SiC with pH in diluted suspension (0.01 vol% particle loading).

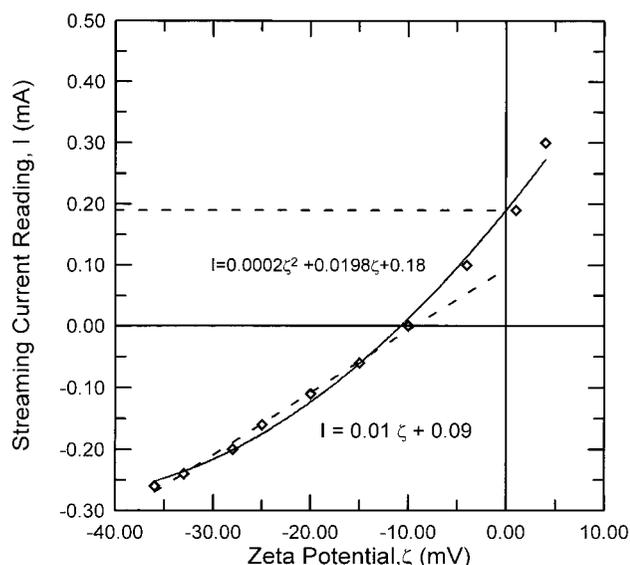
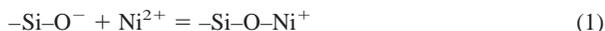


Fig. 3. Zeta potential plotted versus SC reading for SiC powder. Zero value of zeta potential equals the SC reading at 0.18 mA for the suspension with 0.01 vol% particle content.

of NiCl_2 changed the surface potential. In the same way, the SC readings (Fig. 5(b)) show a trend parallel with that for the zeta potential. However, the values of the SC reading decreased somewhat when the concentration of NiCl_2 was 0.023M.

The surface charge changed from negative to positive in the pH range 4–6 when NiCl_2 was added. This result suggests that adsorption of the divalent ion Ni^{2+} onto the particle surface is possible. The adsorption equilibrium can be written as follows:



The solubility product (K_{sp}) of $\text{Ni}(\text{OH})_2$ at 25°C is 3×10^{-16} .¹³ When the concentration of Ni^{2+} is 0.023M and the pH value is >7.1 , $\text{Ni}(\text{OH})_{2(s)}$ is oversaturated and begins to precipitate. When $\text{Ni}(\text{OH})_2$ precipitation occurs on the heterogeneous SiC surface, the Ni^{2+} charge on the surface of the SiC is neutralized, thus reducing the surface charge. Consequently, some SiC agglomerates form in the weakly basic solution. In similar cases, Mg^{2+} or

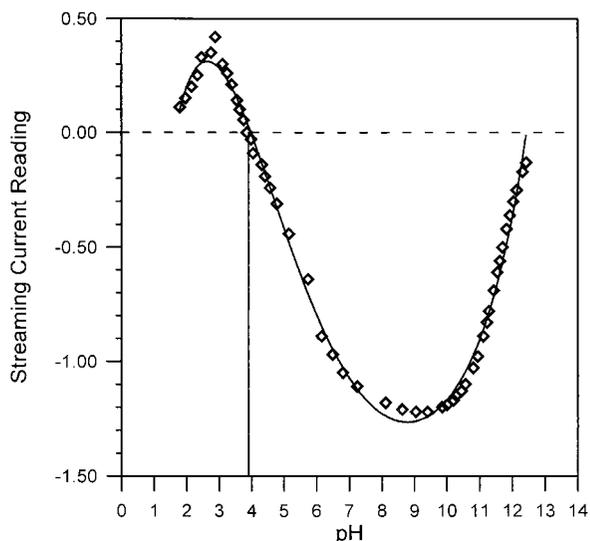


Fig. 4. Variation of SC of the SC detector made by PTFE plotted versus pH. Solution contains 0.01M NaCl as the electrolyte and no added SiC particles.

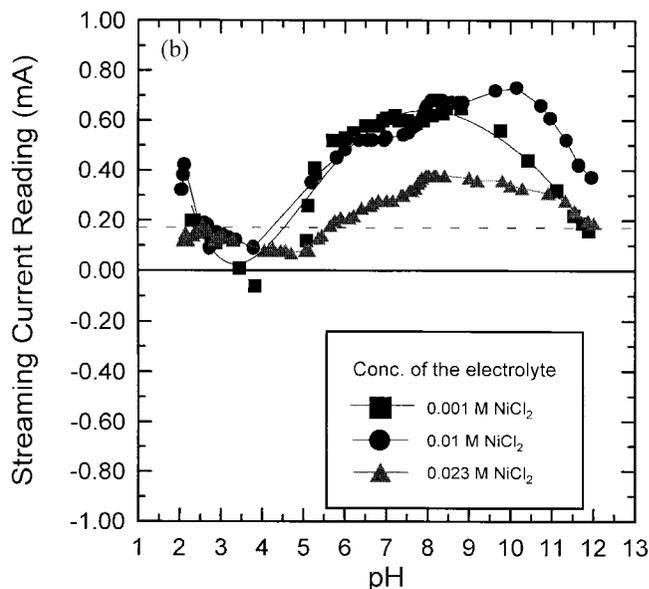
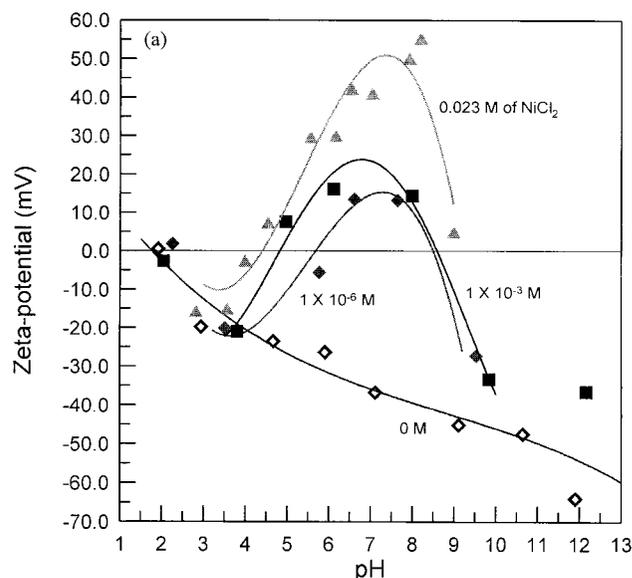


Fig. 5. (a) Zeta potential and (b) SC reading of SiC suspensions, as a function of different concentrations of NiCl_2 .

$\text{Mg}(\text{OH})^+$ adsorbed onto the SiC particle surface have been reported,¹⁴ depending on the pH range. In a high pH range, $\text{Mg}(\text{OH})_{2(s)}$ also precipitates onto the surface of the particles.

$\text{Ni}(\text{SO}_3\text{NH}_2)_2$ is the other important electrolyte for nickel electroplating. Similarly to NiCl_2 , $\text{Ni}(\text{SO}_3\text{NH}_2)_2$ dissolves in an aqueous solution and contributes Ni^{2+} ions to the solution. Figure 6 shows that the zeta potential of SiC in the $\text{Ni}(\text{SO}_3\text{NH}_2)_2$ electrolyte behaved similarly to that in the NiCl_2 solution. When the pH value of the suspension was in the range 2–3, the SiC particles had almost no surface potential. However, the potential increased, then decreased, as the pH of suspension changed from 4 to 8.

(4) Adsorption of Aliovalent Ions

$\text{Na}_3\text{Co}(\text{NO}_2)_6$ is one type of surfactant used in composite plating to modify the SiC solids content in the electroplated nickel layer.⁴ When 2 vol% of $\text{Na}_3\text{Co}(\text{NO}_2)_6$ is added to SiC suspensions containing $\text{Ni}(\text{SO}_3\text{NH}_2)_2$ as an electrolyte, the zeta potential of SiC gradually becomes negatively charged, for $\text{pH} \geq 4$, as indicated by the broken lines in Fig. 6. $\text{Na}_3\text{Co}(\text{NO}_2)_6$ readily dissolves in water. The cation Na^+ and the anion $\text{Co}(\text{NO}_2)_6^{3-}$ form in the solution, similarly to the case for $\text{Ni}(\text{SO}_3\text{NH}_2)_2$. However, Ni^{2+} ions are likely to interact with water molecules to form a complex ion,

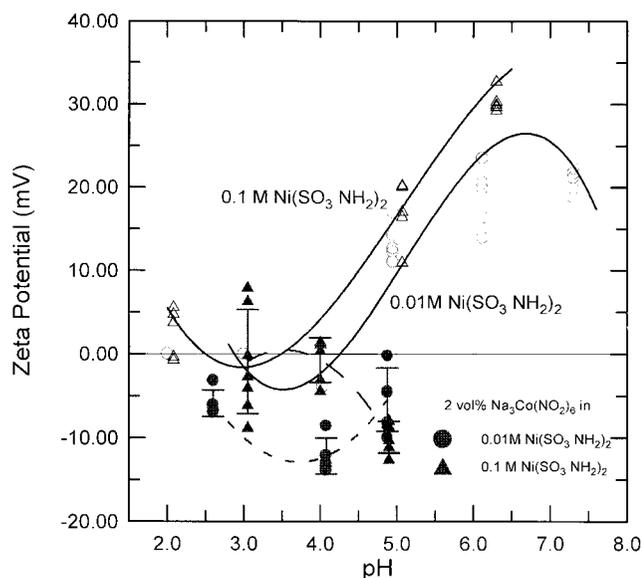


Fig. 6. Zeta potential of dilute SiC suspensions containing $\text{Ni}(\text{SO}_3\text{NH}_2)_2$ as the electrolyte (open symbols) and 2 vol% of $\text{Na}_3\text{Co}(\text{NO}_2)_6$ (filled symbols).

$\text{Ni}(\text{H}_2\text{O})_6^{2+}$, in an aqueous solution. Two types of situation may occur: the negative anion $\text{Co}(\text{NO}_2)_6^{3-}$ may adsorb on top of the Ni^{2+} cations and neutralize the particle charge, or the adsorption of $(\text{Co}(\text{NO}_2)_6^{3-}$ or $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ onto SiC may be competitive. The $\text{Co}(\text{NO}_2)_6^{3-}$ ion has a stronger change intensity, defined as the ratio of valence to size of an ion, than that of $\text{Ni}(\text{H}_2\text{O})_6^{2+}$. Therefore, the decrease of the zeta potential of SiC can result from the adsorption of the anion $\text{Co}(\text{NO}_2)_6^{3-}$, which replaces the adsorbed $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ and neutralizes the positive surface of the SiC. Moreover, the $\text{Co}(\text{NO}_2)_6^{3-}$ in $\text{pH} > 4$ may reverse the surface charge of the SiC from positive to negative. That reverse makes the coplating of SiC with nickel ineffective. In the practical exercise of composite plating, the solution contains 1 vol% of SiC particles; 0.28M $\text{Ni}(\text{SO}_3\text{NH}_2)_2$, as a source of Ni^{2+} ions; 0.023M NiCl_2 ; and 0.48M H_3BO_3 , as a buffer to keep the solution acidic, at pH 4.

(5) Electroplating of SiC with Nickel

The SC readings of SiC in a series of suspensions with different concentrations of $\text{Ni}(\text{SO}_3\text{NH}_2)_2$ solutions are shown in Fig. 7. All

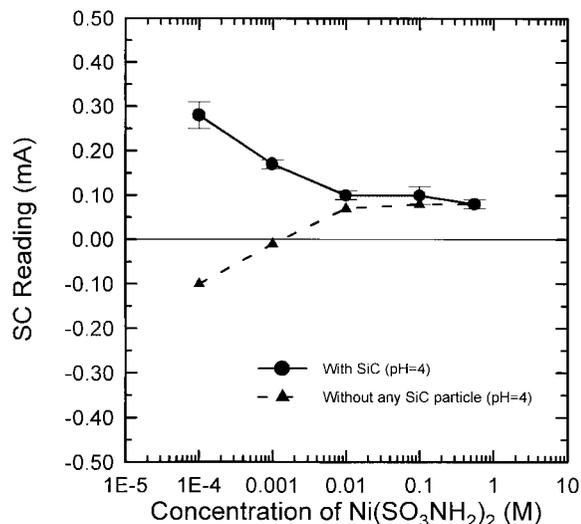


Fig. 7. SC readings of the electroplating solution with and without SiC particles, at various concentrations of $\text{Ni}(\text{SO}_3\text{NH}_2)_2$.

of the $\text{Ni}(\text{SO}_3\text{NH}_2)_2/\text{SiC}$ suspensions had 0.48M H_3BO_3 and 0.023M NiCl_2 added. The results consist of two sets of data. The set without SiC, used as the control, reveals that the SC readings changed gently from -0.1 to 0.8 mA as the Ni^{2+} ion strength increased. When 1.0 vol% of SiC was suspended in highly ionic solutions, the double-layer thickness of SiC was compressed, and the particles began to agglomerate. The contribution of SiC to the SC reading was insignificant, and the PTFE material of the capillary wall of the detector dominated the SC results.

In the high-concentration electrolyte solutions, the SC reading of the PTFE changed from negative in a dilute electrolyte to positive when the $\text{Ni}(\text{SO}_3\text{NH}_2)_2$ concentration was $>0.001\text{M}$. Those results illustrate that the PTFE surface also adsorbed $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ ions. However, the net SC values ($\Delta\text{SC} = \text{SC}_{\text{SiC}} - \text{SC}_{\text{PTFE}}$) of the SiC suspensions were still positive for the concentration of $\text{Ni}(\text{SO}_3\text{NH}_2)_2 < 0.5\text{M}$. These results imply that positive SiC particles can move to the cathode during composite electroplating.

IV. Conclusions

The electrokinetic properties of nanosized SiC particles were measured by EMS and SC techniques, the latter of which are capable of operating in a suspension with a broader range of electrolyte concentrations and powder loadings. The IEP of the SiC suspension obtained by EMS was pH 2.6, but the ICP for the SC technique was pH 3.0. A 0.18 mA offset of the SC reading when the zeta potential was zero is attributed to the effect of the surface charge of the PTFE material on the SC detector at pH 2–3.

In an aqueous solution containing Ni^{2+} ions, divalent ions are adsorbed onto the surface of the ultrafine SiC particles and change the polarity of the SiC from negative to positive, in the pH range 4–8. This phenomenon was found in the suspensions containing NiCl_2 and/or $\text{Ni}(\text{SO}_3\text{NH}_2)_2$ as electrolytes. However, $\text{Ni}(\text{OH})_2$ formed and precipitated in a basic solution when the pH values were >7 . When trivalent ions, $\text{Co}(\text{NO}_2)_6^{3-}$, were added to the suspensions, the complex ions adsorbed onto the positive surface of the SiC and neutralized the surface charge, ultimately reversing the surface polarity of the SiC.

The surface-potential analysis results indicate that SiC particles can be suspended in a highly concentrated nickel electroplating solution. The surface charge of the SiC can adsorb Ni^{2+} ions and show a positively charged surface. A slightly positive surface charge is maintained as the concentration of $\text{Ni}(\text{SO}_3\text{NH}_2)_2$ is increased to as high as 0.5M.

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