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Effects of Surfactants and Surface Treatment on Aqueous Dispersion of Silicon Carbide

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The effects of the addition of surfactants and of the surface treatment upon the aqueous dispersion of silicon carbide were examined. In the case of β-SiC, the addition of nonionic surfactants having relatively longer lengths of hydrocarbon and oxyethylene chain to the β-SiC treated with a silane coupling agent enhanced the dispersion stability. On the other hand, the lack of a difference for the dispersion stability was observed between a silane coupling treated α-SiC and an untreated one by the addition of surfactants. These differences in the surface property of two kinds of SiC were confirmed by measuring the zeta potential and the heat of immersion in water.

In recent years particle-reinforced composites have become attractive for many fields because of their excellent properties. Particularly, interest in electrodeposited composite coatings has increased rapidly. The purposes for composite plating are improved abrasion resistance, friction resistance, corrosion resistance, functional plating and so on. The detailed properties and applications of such plating have been reported.[1-5] From many studies, it has been confirmed[6,7] that agitation and current density are two major factors that affect the rate of entrapment of electrodeposite composite plating.

Besides, it is important to disperse the component particles in the plating solution in order to obtain a homogeneous surface of composite plating. The dispersion of solid particles in an aqueous solution is often considerably influenced by the addition of a small amount of water-soluble substances. The dispersion effect by nonionic ethoxylated surfactants[8-10] is dependent on their chemical structure and on the kind of particles to be dispersed. Since nonionic ethoxylated surfactants have both hydrophilic and hydrophobic parts, it is expected that their adsorption behavior will be affected not only by their affinity to solids, but also by the affinity to the medium in the suspensions. It is also suggested that the adsorption of nonionic surfactants is strong when either the particle or medium is polar and the other is nonpolar.

In this study, interactions between treated silicon carbide with a silane coupling agent or an untreated one and nonionic surfactants in an aqueous solution of high concentration of electrolytes were investigated by measuring the zeta-potential, the particle size, the turbidity and the heat of immersion from the standpoint of basic electrodeposited composite plating.

Experimental

Materials. α-SiC was provided from Showa Denkou Co., Ltd., and β-SiC from Ibiden Co., Ltd.

The physical properties of silicon carbides are as follows: a density of 3.2 g cm^{-3} and a specific surface area of 9.5 m^2 g^{-1} for α-SiC and 3.2, 17.0 for β-SiC,

The nonionic surfactants were obtained from Nikko Chemical Co., Ltd.; their types and structural formula are

$C_{16}H_{33}$-O-$(CH_2CH_2O)_nH$ (BC-*n*),
$C_{22}H_{45}$-O-$(CH_2CH_2O)_nH$ (BB-*n*),
$C_{18}H_{35}$-O-$(CH_2CH_2O)_nH$ (BO-*n*), and
$C_{18}H_{37}$-CO-O-$(CH_2CH_2O)_nH$ (MYS-*n*),

where *n* indicates the mole number of oxyethylene units included in the surfactant.

Sodium dodecyl sulfate was provided from Wako Pure Chemical Industrial Ltd. and purified by recrystallization from ethanol.

Sodium chloride, calcium chloride and aluminum chloride were of commercial high pure grade reagents.

A nickel sulfamate aqueous solution was used as the plating solution. It was provided by the Electroplating Engineers of Japan Ltd.

The treatment of silicon carbide was carried out with a 5 w% solution of trimethylchlorosilane (TMCS), provided by Chisso Co., Ltd., in isopropyl alcohol by stirring for 2 h. After the treatment, the silicon carbide was washed five times with pure isopropyl alcohol. Then, the treated powder was dried for 2 h at 140 °C.

The water used in all experiments was purified by passing it through an ion-exchanged column followed by filtration in a Milli-Q Water Purification System.

Apparatus and Procedure. 0.5 g of silicon carbide was added to a nonionic surfactant solution (1 L) with a high electrolyte concentration and agitated with an ultrasonic bath for 10 min. Then, after shaking for 1 h at 25 °C, the absorbance of the suspension was recorded every 5 min during 1 h at 500 nm by means of a Hitachi 220-A-type double-beam spectrophotometer using 0.2-cm cells at 25 °C.

The stability of the suspension can be expressed as

$$[\mathrm{O.D}]_t/[\mathrm{O.D}]_5,$$

where $[\mathrm{O.D}]_5$ is the absorbance after 5 min and $[\mathrm{O.D}]_t$ is the absorbance after *t* minutes.

The heat of immersion in water for these samples was measured using a calorimeter (Tokyo Rikou Co., Ltd.) at 25 °C: after silicon carbide was placed into a glass ample tube and evacuated at 1×10^{-2} Torr for 1 h, the glass ample tube was sealed and set in a calorimeter with water, until it reached thermal equilibrium at 25 °C. Then, the glass ample tube was broken and the silicon carbide was immersed in water. The liberated heat was recorded and calibrated by the normal procedure.

The zeta-potential of silicon carbide was measured by an electrophoresis apparatus Laser Zee TM Model 500 (PEN KEM, Inc.). The mean particle size was measured by a particle sizer (Malvern Co., Ltd.).

The pH of the silicon carbide suspension was measured using a pH meter 130 (Corning Co., Ltd.).

The surface of silicon carbide was measured by FTIR-ATR (Japan Spectroscopic Co. Ltd.).

Results and Discussion

1. Dispersion of Silicon Carbide in Aqueous Solution. Variations in the zeta-potential of α-SiC and β-SiC as a function of pH are given in Fig. 1. The silicon carbide particles had a positive charge at a low pH; their charges became negative with an increase in the pH. The isoelectric point of α-SiC was found to be in the vicinity of pH 2.3, and of β-SiC in the vicinity of pH 5. The pH of dispersion (0.5 g L^{-1}) of α-SiC and β-SiC in pure water was 5.6, at which the zeta potential of α-SiC was about −30 mV, and of β-SiC was about −7 mV, and their mean particle sizes were about 470 and 7300 nm, respectively.

Variations in the zeta-potential of silicon carbide with the concentration of each electrolyte solution are given in Fig. 2. The zeta-potential of silicon carbide in aqueous solution was altered from negative to zero by the addition of an electrolyte. By a further addition of the electrolyte, the charge of the particles became positive. In the case of aluminum chloride, upon a further addition, the charge of the particles again became zero.

On the other hand, the zeta-potential became high with the valency of cationic ions. Accordingly, the isoelectric point (i.e.p.) of silicon carbide was remarkably shifted to the low concentration with an increase in the valency of cationic ions.

It was found that both α-SiC and β-SiC had the highest positive charge by the addition of 1×10^{-4} M[†] $AlCl_3$. At this concentration, the absorbance of dispersion of α-SiC was initially 0.73, but greatly decreased to 0.01 after 24 h, while that of β-SiC gradually decreased from 1.45 to 0.85.

Variations in the zeta-potential of α-SiC and β-SiC

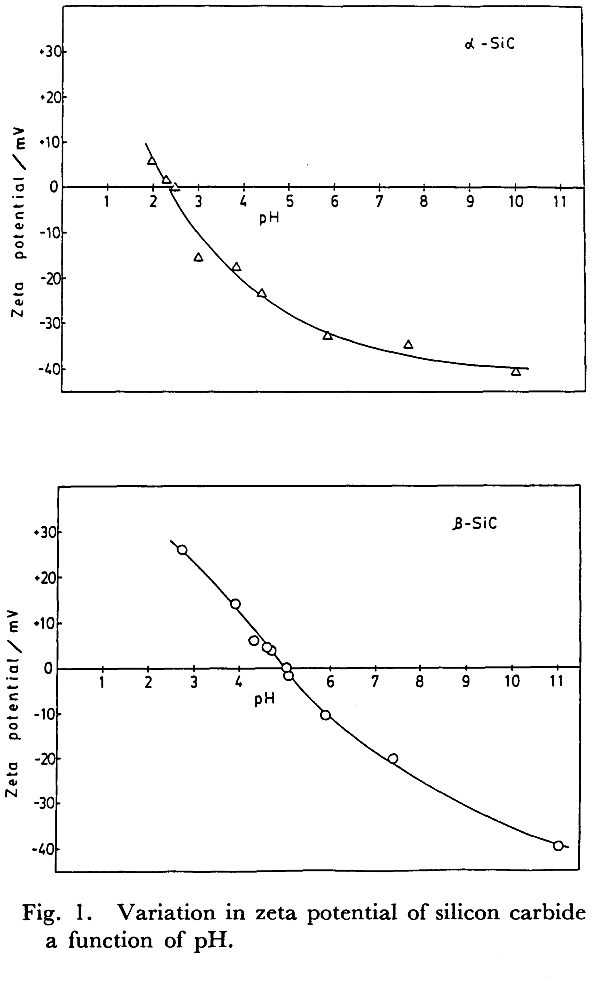

Fig. 1. Variation in zeta potential of silicon carbide as a function of pH.

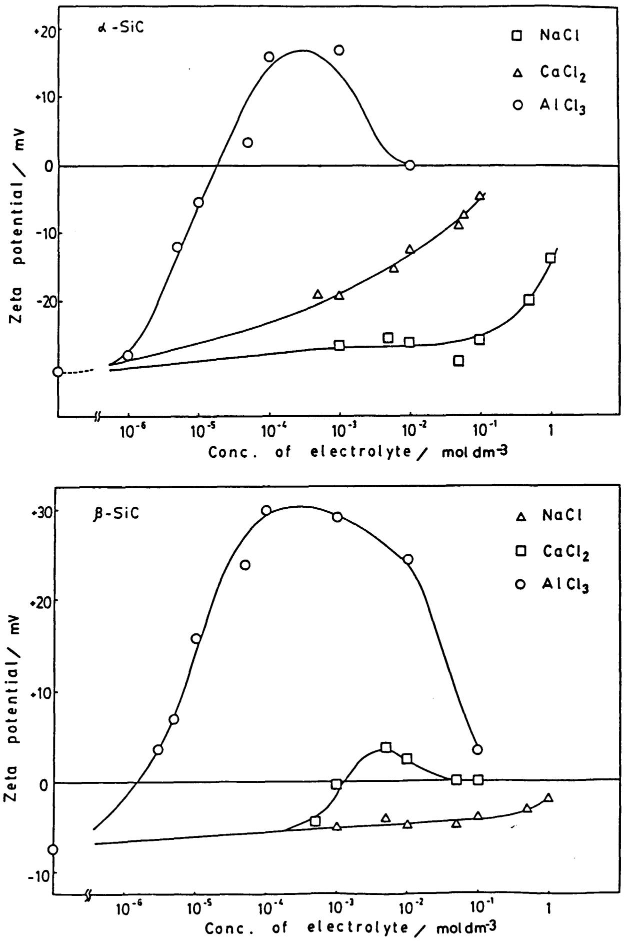

Fig. 2. Variation in zeta potential of silicon carbide with concentration of electrolyte.

[†] 1 M=1 mol dm^{-3}.

having a positive charge in a 1×10^{-4} M $AlCl_3$ aqueous solution with the concentration of an anionic surfactant (SDS) are given in Fig. 3. Particles of α-SiC and β-SiC had a positive charge during the initial state, and the mean particle sizes of α-SiC and β-SiC were about 800 and 300 nm, respectively. These positive charges of α-SiC and β-SiC decreased to zero upon the addition of a small amount of SDS whose concentrations were 2×10^{-4} and 5×10^{-4} M, respectively. Then, the SiC flocculated and the mean particle sizes of those flocculate were about 4000 and 5000 nm, respectively. Upon a further addition of SDS, α-SiC and β-SiC became negatively charged, and the flocs redispersed again. This resulted in a mean particle sizes of about 600 and 250 nm, respectively.

From these results, the processes of flocculation and redispersion of silicon carbide were observed by the addition of SDS. The stability of the dispersion of silicon carbide by the addition of 1×10^{-2} M SDS was altered as follows: The absorbance of the α-SiC suspension was initially 0.86 but decreased to 0.46 after 24 h, while that of β-SiC suspension gradually decreased from 1.44 to 1.00.

The absorbance at 500 nm for a suspension of α-SiC and β-SiC, which had flocculated by addition of SDS, changed with the concentration of added nonionic surfactant (BB-*n*). The results given in Fig. 4 show

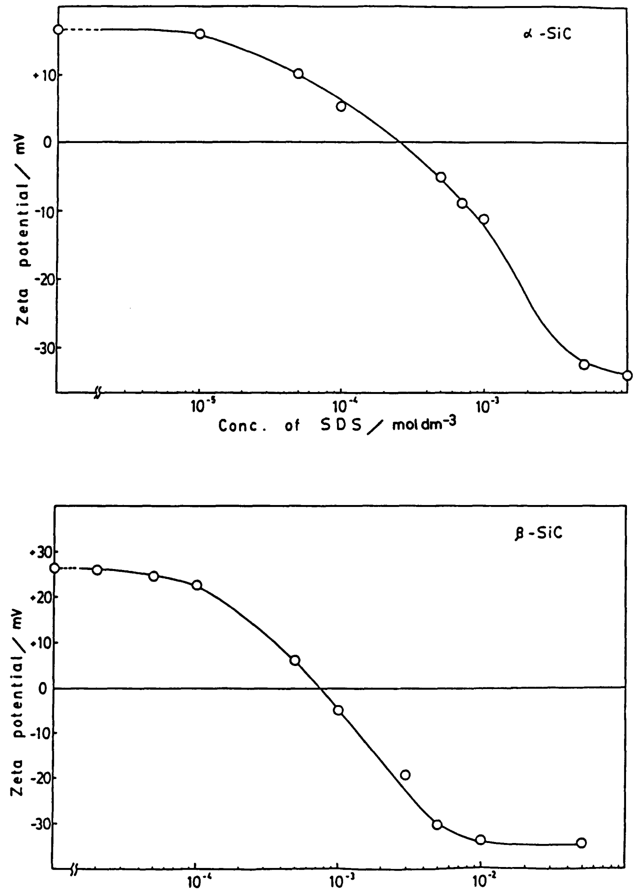

Fig. 3. Variation in zeta potential of silicon carbide in $AlCl_3$ solution(1×10^{-3} M) with a concentration of SDS.

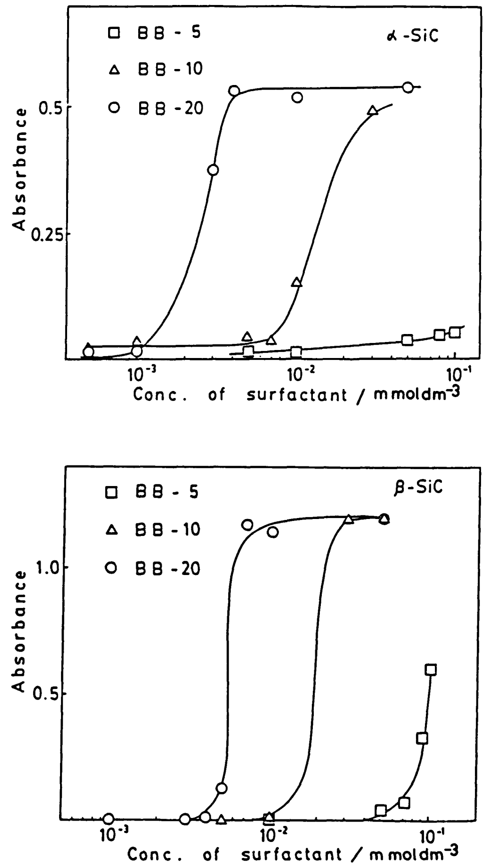

Fig. 4. Variation in absorbance for silicon carbide suspension, flocculated by addition of SDS, with addition of BB-5, BB-10, and BB-20.

Table 1. Dispersion Stability of Silicon Carbide

Sample	α-SiC		β-SiC	
	$[O.D]_0$	$[O.D]_{1d}{}^{a)}/[O.D]_0$	$[O.D]_0$	$[O.D]_{1d}{}^{a)}/[O.D]_0$
$AlCl_3$	0.73	0.01	1.45	0.59
$AlCl_3$+SDS	0.86	0.54	1.44	0.69
$AlCl_3$+SDS+BB-20	0.92	0.58	1.53	0.78

a) 1d indicates 1 day.

that the absorbance increases and becomes constant with the addition of BB-5, BB-10, and BB-20, indicating that a redispersion of α-SiC and β-SiC could be attained. A well redispersion was obtained by a smaller addition of a nonionic surfactant which had a longer oxyethylene chain, at which the mean particle sizes of α-SiC and β-SiC were about 800 and 310 nm, respectively. However, the addition of BB-5, scarcely gave a well redispersion.

The mechanisms of flocculation and redispersion can be explained in terms of a "two-fold adsorption layer," similar to that suggested earlier[11-14] That is, silicon carbide becomes positively charged in an aqueous aluminum chloride solution, providing a well dispersed state characterized by a minimum in the mean particle size and a maximum in the zeta-potential. By the addition of low concentrations of SDS, the particles are discharged and the size of flocculated particles increases. As the hydrocarbon chains of SDS are oriented outward, the particles become hydrophobic and flocculation takes place. On a further addition of SDS, the adsorption of this surfactant occurs by a chain interaction resulting in a two-fold layer with the ionized groups of the second layer oriented towards the solution. Accordingly, the particles become recharged and a redispersion is achieved due to the electric repulsion. A redispersion upon the addition of nonionic surfactants, on the other hand, is most likely due to a steric hindrance between the adsorbed nonionic surfactant molecules.

Table 1 shows the above results for the stability of dispersion. It is recognized that the positive charged particles flocculated by the addition of SDS are redispersed by the addition of a nonionic surfactant which has relatively longer lengths of the oxyethylene chain (BB-20); also, the stability of redispersion is remarkably enhanced.

2. Dispersion of Silicon Carbide in Aqueous Solution with High Concentration of Electrolyte. A well dispersion stability of silicon carbide treated with SDS and BB-20 was not obtained in a 0.1-M $AlCl_3$ aqueous solution since the zeta-potentials of α-SiC

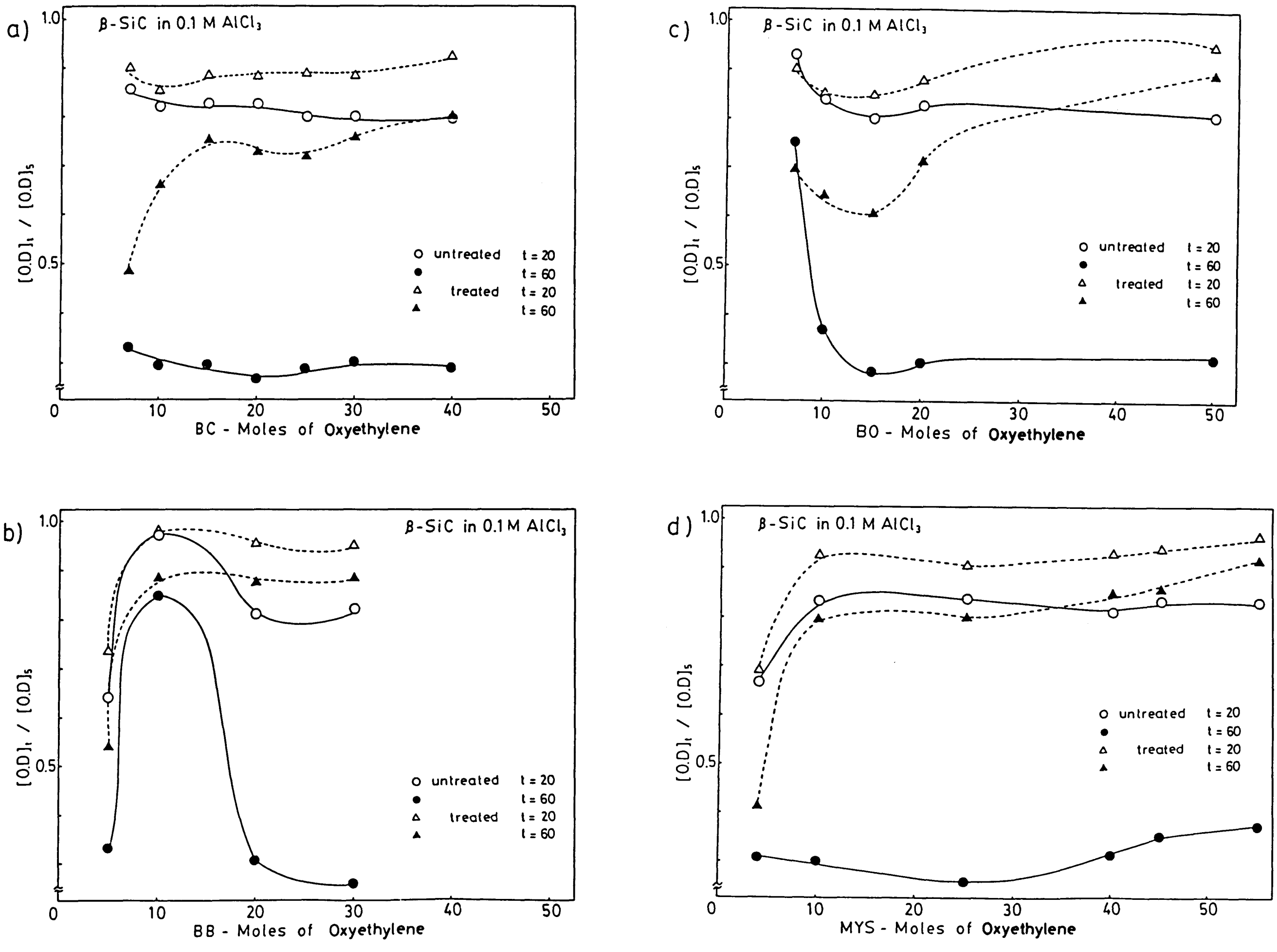

Fig. 5. Variation in $[O.D]_t/[O.D]_5$ of treated and untreated β-SiC with mole of oxyethylene included in nonionic surfactants in 0.1 M $AlCl_3$ aqueous solution.

and β-SiC are almost zero in a 0.1-M $AlCl_3$ aqueous solution or a 1-M $CaCl_2$ aqueous solution and the adsorption of SDS and BB-20 hardly occurred on the surface of silicon carbide. Therefore, a surface treatment of silicon carbide by a silane coupling agent was performed and the effect was examined. Variations in $[O.D]_t/[O.D]_5$ of TMCS-treated α-SiC and untreated α-SiC with the mole of oxyethylene included in each nonionic surfactants in a 0.1-M $AlCl_3$ aqueous solution were measured. Particularly, a well dispersion stability by the addition of BC-*n* or BB-*n* or MYS-*n* (n=10), and BO-*n* (n=7) was obtained. However, the effects of treatments with TMCS were not observed.

The results for TMCS-treated β-SiC and untreated β-SiC are given in Figs. 5 (a–d). In the case of β-SiC, the addition of nonionic surfactants, which had longer lengths of hydrocarbon and oxyethylene chains enhanced a dispersion stability of the treated sample significantly.

Similar results to that of α-SiC and β-SiC were also obtained in a 1.0-M $CaCl_2$ aqueous solution.

It was recognized through an FTIR–ATR measurement that silanol group exists on the surface of silicon carbide. Therefore, the reaction of trimethylchlorosilane with silanol would occur in the following manner[15–17]:

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-OH} + (\mathrm{CH_3})_3\mathrm{SiCl} \longrightarrow \mathrm{-SiOSi(CH_3)_3} + \mathrm{HCl}.$$

Table 2 shows the immersional heat into water of untreated α-SiC, TMCS-treated α-SiC, untreated β-SiC and TMCS-treated β-SiC. In the case of β-SiC, by the reaction with TMCS, the heat was reduced, indicating that the surface of silicon carbide becomes appreciably hydrophobic under the treatment. As for α-SiC, the lack of difference in the heat between untreated α-SiC and TMCS-treated α-SiC implies that the surface of silicon carbide is not covered with TMCS.

As a general rule, interactions at water-solid surfaces are due to the van der Waals force, hydrogen bonding of water to hydroxyl groups and an electrostatic force (proportional to the surface charge). The hydrophilicity of a solid surface is mainly due to the latter two forces. Therefore, the dispersion stability of silicon carbide in water can be improved by the addition of an electrolyte, an anionic surfactant and a nonionic surfactant.

Table 2. Heat of Immersion of Silicon Carbide in Water ($J\,m^{-2}$) at 25 °C

	α-SiC	β-SiC
Untreated	0.20	0.17
TMCS-treated	0.19	0.11

However, in an aqueous solution with a high electrolyte concentraiton, silicon carbide hardly disperses, because the forces for adsorption of surfactants are very weak when particles are discharged due to a depression of electric double layer.

On the other hand, with an increase in the amount of the combined trimethylsilyl group, the silicon carbide particles start to float on the water surface without surfactants, and obviously reveal the surface hydrophobicity. Therefore, the mechanisms of dispersion of TMCS-treated β-SiC is explained as follows: the hydrocarbon chain of nonionic surfactants is oriented to the hydrophobic surface of TMCS-treated β-SiC. The force of adsorption is stronger between the surface and the hydrocarbon chain when the surface of β-SiC becomes hydrophobic. Accordingly, a well dispersed state is obtained when the length of the oxyethylene chain of a nonionic surfactant is relatively longer, even in an aqueous solution with a high electrolyte concentration.

For an application of electrodeposition, the SiC dispersion in a nickel sulfamate aqueous solution (plating bath) was studied. The results were similar to those for a in 1.0-M $CaCl_2$ aqueous solution or a 0.1-M $AlCl_3$ aqueous solution. Furthermore, the proportion of co-deposit TMCS-treated β-SiC on the plating surface to the concentration of TMCS-treated β-SiC in a plating bath by the addition of BC-40 or without BC-40 is given in Fig. 6. From this result, it is apparent that the amount of co-deposit after treatment with TMCS increases twice that without the treatment. Thus, the above result demonstrates that the dispersion of SiC is an important factor for an electrodeposite composite.

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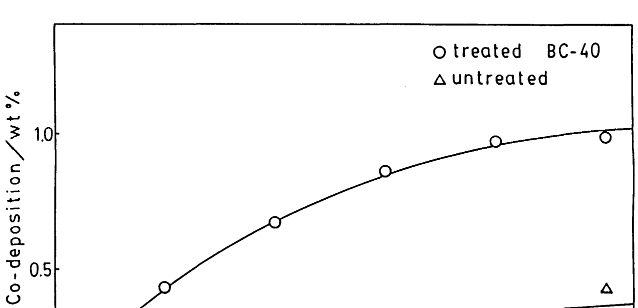

Fig. 6. Variation in amount of co-deposit of silicon carbide as a function of concentration of silicon carbide.

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