

Separation and Recovery of SiC Particles Discharged from Silicon Wafer Production Process

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Abstract: In the slicing process of silicon wafer from silicon single crystal, it has been the general way to cut silicon by wire saws with the lubricant mixture of silicon carbide, as SiC, particles and wrapping oil. After slicing the silicon single crystal, the waste liquor containing SiC and silicon powders is discharged from the process. The particle sizes of SiC and Si are about 10 μ m and 1 μ m, respectively and the weight ratio is about 9:1. The particles discharged from slicing waste liquor become the mixture of SiC and SiO₂, when the waste liquor is burned after treating the lubricant oil by a filter press. In terms of the minimization of wastes and environment, it is preferable to separate and recover the valuable SiC from SiO₂.

In order to solve the problem mentioned above, flotation method can be applied to accomplish the separation of SiC from SiO₂. The cationic surfactants of dodecyl-tri-methyl-ammonium chloride (abbreviated as DTMAC hereafter) and tri-methyl-octyl-ammonium chloride (abbreviated as TMOAC hereafter) were used in this study. The adsorption amount of surfactants on SiC and SiO₂ particles was measured. The flotation behaviors of SiC and SiO₂ were investigated by changing pH, gas flow rate and flotation time in the presence of DTMAC. The purity and yield of SiC were also discussed in the flotation process comprising of roughing, cleaning and scavenging steps. A series of flotation process for SiC gave the purity and yield of 99.7% and 96.7%, respectively.

Keywords: Flotation, SiC, SiO₂, silicon wafer slicing waste, TMOAC, DTMAC.

1. INTRODUCTION

Silicon carbide is used as grinding and cutting materials, refractory and semiconductor. It has a fire-resistant property and is stable up to 1873 K in air. The hardness is in the order of diamond > Boron carbide > SiC > alumina.

It has been the general way to cut silicon by wire saws with the lubricant mixture of SiC particles and wrapping oil in the slicing process of silicon single crystal ingot. Since the slurry contains SiC particles in the slicing process, it has been an environmental issue to treat the discharged waste liquor containing SiC (particle size; about 10 μ m) and Si (particle size; about 1 μ m) with weight ratio of 9:1.

The powders in the slicing waste liquor become the mixture of SiC and SiO₂ when the waste mixture is burned after treating the lubricant oil by a filter press. It is necessary to establish the process for separating valuable SiC from the waste liquor in terms of the minimization of wastes and environment. Specific gravity separation is not suitable for the separation of SiC and SiO₂, since the specific gravity of both particles is very close. It is also difficult to separate SiC and SiO₂ by using any cyclone, since both particles

have very small sizes. On the contrary, flotation is a preferable method which does not require the difference in specific gravity and particle size. Flotation takes place only by the surface property as a driving force for the separation [1-4]. Kusaka *et al.* reported the similarity of flotation behavior among Si, SiO₂ and SiC particles having average particle size under 1 μ m by using DTMAC. They also investigated the effect of copper ion on the SiC flotation behavior [5, 6].

In this study, the separation and recovery of SiC discharged in the slicing process of silicon wafer from silicon single crystal were carried out by a flotation method. Cationic surfactants were employed and the adsorption amounts of surfactants on SiC and SiO₂ particles were measured. The flotation behavior of SiC and SiO₂ was investigated by changing pH, gas flow rate and flotation time in the presence of cationic surfactant. The purity and yield of SiC were also discussed in the flotation process comprising of roughing, cleaning and scavenging steps.

2. EXPERIMENTAL

2.1. Reagent

Silicon carbide used in this study was provided from Showa Denko K.K. The color is green and median particle size is 22 μ m. Silicon dioxide was provided from Taki Chemical Co., Ltd. whose color is white and median particle size is 9.3 μ m. Since both particles

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were prepared for this study, these particle sizes are larger than the actual particle sizes discharged from the slicing waste liquor. It is necessary to take account of the particle size effect in the flotation behavior, but in this case they will be enough size to carry out the flotation test.

For the measurements of the particle sizes and zeta potential, laser scattering particle size analyzer, LA910 (Horiba, Ltd.) and Zetasizer Nano Z (Malvern Instruments Ltd.) were used, respectively. Autosorb 1MP-LP2 (Quantachrome Instrument Co., Ltd.) was used to measure the specific surface areas of SiC and SiO₂. The contact angles of SiC and SiO₂ were measured by a contact angle meter Type Q1 (Kyowa Kaimenkagaku Co., Ltd.) after treating by a tablet shaping machine. Table 1 shows the physical properties of SiC and SiO₂.

Table 1: Physical Properties of SiC and SiO₂

	SiC	SiO ₂
Median diameter [μm]	22.2	9.3
Surface area [m ² /g]	0.4	121
Contact angle [degree]	37	84

As cationic surfactants, TMOAC (Tokyo Chemical Industry, Co., Ltd.) and DTMAC (Tokyo Chemical Industry, Co.) were used in this study. Table 2 shows the chemical structure of TMOAC and DTMAC.

2.2. Method

As adsorption tests of surfactants on SiC and SiO₂, several slurries were prepared with different solid contents and surfactant concentrations. The slurries were adjusted to be at the fixed pH and stirred for 15 minutes. After the configuration of the slurry samples, the concentrations of surfactants in the supernatant were determined by the Orange II method [7] and calculated the adsorbed amount of surfactants by the mass balance.

Table 2: Cationic Surfactants Used in this Study

	Trimethyloctylammonium Chloride (TMOAC)	Dodecyltrimethylammonium Chloride (DTMAC)
Molecular weight	208	264
Structural formula	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3(\text{CH}_2)_7 - \text{N} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array} \right]^+ \cdot \text{Cl}^-$	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3(\text{CH}_2)_{11} - \text{N} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array} \right]^+ \cdot \text{Cl}^-$

The flotation tests of SiC and SiO₂ were carried out in the following manner. The flotation apparatus was made of PVC, and the column diameter and height were φ100 mm and 160 mm, respectively. After preparing the slurries containing each particle and surfactant at a fixed pH, the slurries were stirred for 15 minutes. Then, the slurries were transferred to the experimental apparatus and flotation tests were carried out by introducing N₂ gas from the bottom through the glass filter and stirring at 300 rpm. In the flotation tests, pine oil of 20 ppm was used as a frother. The recoveries of SiC and SiO₂ were determined by the gravimetry method after the particles recovered in the froth were filtered, rinsed and dried up.

3. RESULTS AND DISCUSSION

3.1. Adsorption of Cationic Surfactant for SiC and SiO₂

Figure 1 shows the zeta potential of SiC and SiO₂ particles. The P.Z.C.s of SiC and SiO₂ are located at the extremely acidic pH of 2.3 and 3.5, respectively. Based on the zeta potential of these particles, TMOAC and DTMAC were employed as surfactants. The relationship between the adsorption amounts of cationic surfactants on SiC and pH is shown in Figure 2. When the pH is over P.Z.C., the adsorption amount of surfactant increases with an increase in pH and the adsorption amount reaches a constant value over pH 6.0. The dissociation of these surfactants produces positive ionic species in the solution. The zeta potential measurement shows that SiC particles are positively charged in the lower pH range, while in the higher pH range SiC particles are negatively charged. Additionally, it is considered that in the pH range over P.Z.C., the occurrence of strong electrostatic attractive force between SiC surface and cationic surfactant species results in the increase in the adsorption amount. The broken line in Figure 2 indicates the saturated monolayer adsorption (1.1×10^{-5} mol/m²) of DTMAC obtained by Langmuir plot based on the relationship between the adsorption amount and

DTMAC concentration. It is considered from Figure 2 that the saturated monolayer adsorption of TMOAC is almost equal to that of DTMAC and also the adsorption amounts of both surfactants exceed the monolayer adsorption over pH 6.0. The adsorption isotherm of the surfactants for SiC at pH 8.5 is shown in Figure 3. The adsorption amounts of both cationic surfactants increase with an increase in their concentrations. The adsorption isotherms of TMOAC and DTMAC exhibit the same results; the saturated monolayer adsorption of cationic surfactants is obtained at the equilibrium concentration of $9.0 \times 10^{-4} \text{ mol/dm}^3$.

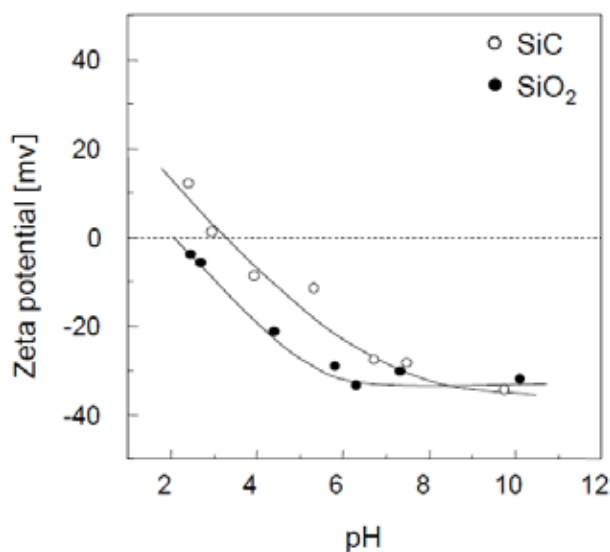


Figure 1: Zeta potential of SiC and SiO₂ as a function of pH.

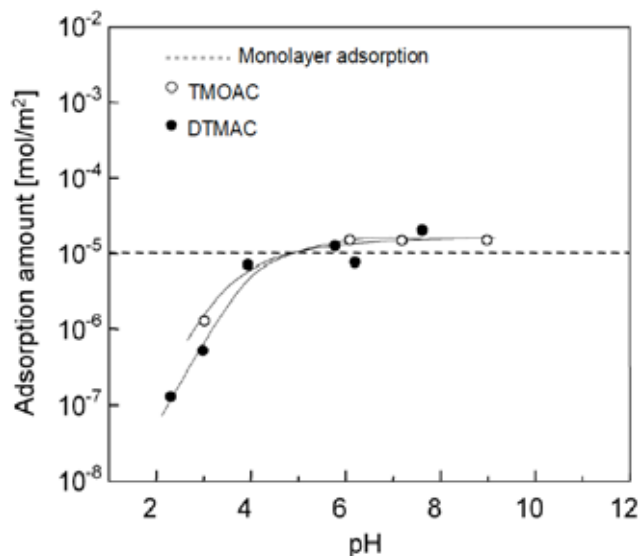


Figure 2: Adsorption amount of cationic surfactants on SiC as a function of pH.

(Solid content : 0.3wt%
Surfactant concn.: $9 \times 10^{-4} \text{ mol/dm}^3$)

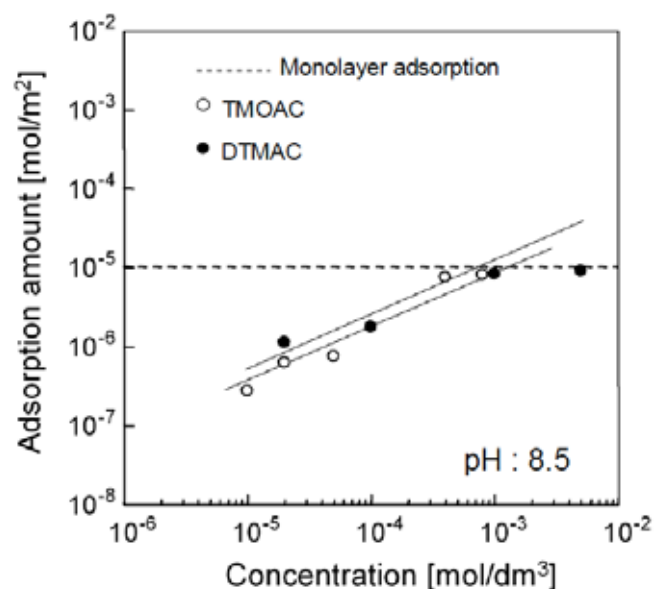


Figure 3: Adsorption isotherm of cationic surfactants on SiC. (Solid content: 0.3wt%).

Figure 4 shows the relationship between the adsorption amount of cationic surfactants for SiO₂ and pH. Both surfactants give the small adsorption on SiO₂ in the lower pH range, while the adsorption increases with increasing pH. In any pH range, the adsorption amounts of TMOAC and DTMAC for SiO₂ are less than the saturated monolayer adsorption. The broken line in the Figure 4 indicates the saturated monolayer adsorption ($3.7 \times 10^{-6} \text{ mol/m}^2$) of DTMAC obtained by

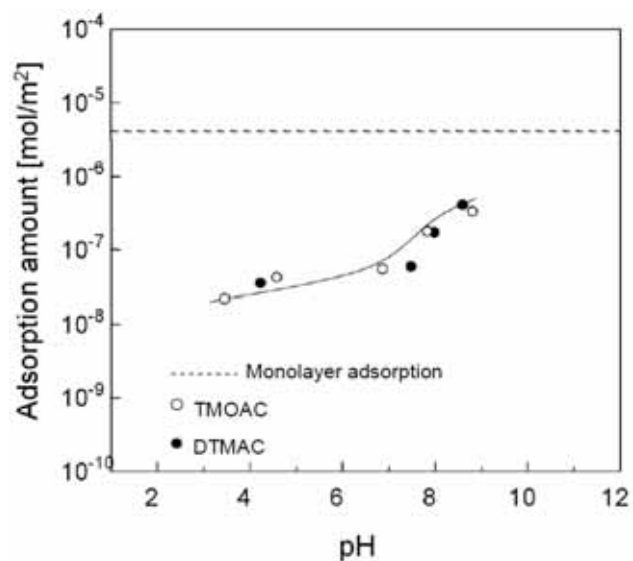


Figure 4: Adsorption amount of cationic surfactants on SiO₂ as a function of pH.

(Solid content : 0.3wt %
TMOAC : 10^{-4} mol/dm^3
DTMAC : $9 \times 10^{-4} \text{ mol/dm}^3$)

Langmuir plot. The saturated monolayer adsorption of TMOAC is almost the same as that of DTMAC. Figure 5 shows the adsorption isotherms of DTMAC and TMOAC for SiO₂ at pH 8.5. The adsorption amounts of both surfactants increase with increasing their concentrations. When the equilibrium concentration is 9.0×10^{-4} mol/dm³, the adsorption amount becomes to be 1.7×10^{-7} mol/m². If the surface coverage is assumed to be unity at the saturated monolayer adsorption and this value is converted into the surface coverage, it would be a very small value; 1.7×10^{-7} [mol/m²] / 3.7×10^{-6} [mol/m²] = 0.046. TMOAC and DTMAC exhibit very similar adsorption isotherms for SiO₂. The reason for the similarity of adsorption isotherms is considered to be based on the fact that TMOAC and DTMAC are quaternary ammonium salts and they have similar molecular structures with only different hydrophobic group.

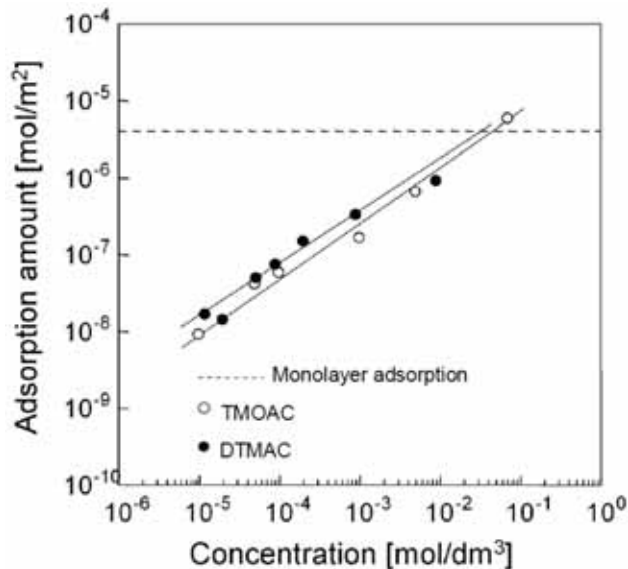


Figure 5: Adsorption isotherm of cationic surfactants on SiO₂.

(Solid content: 0.3wt%, pH : 8.5).

3.2. Flotation Separation of SiC and SiO₂ with Cationic Surfactants

The flotation tests were carried out for SiC and SiO₂ independently with cationic surfactants. Figure 6 shows the flotation results with DTMAC. When TMOAC was employed for the flotation of SiC alone, the recovery percentages were 27% at pH 2.3 and 38% at pH 9.0. It is found that the flotation recovery of SiC with DTMAC is 30% at pH 3.1 and the recovery increases with increasing pH. When the pH value is 6.0, the 78% recovery of SiC is obtained, while over pH 6.0 the flotation recovery of SiC becomes almost constant.

This pH value agrees with the pH where the adsorption amount of surfactant for SiC becomes constant. The recovery difference occurred in these tests is based on the fact that DTMAC gives stronger hydrophobic property on SiC surface than TMOAC, because DTMAC has a longer alkyl carbon chain as a hydrophobic group than TMOAC.

When TMOAC is used as the surfactant, the recovery of SiO₂ alone is less than 5% in any pH range. It follows from Figure 6 that in the case of DTMAC, the flotation recovery of SiO₂ alone increases with an increase in pH, e.g. 6.0% and 30% at pH 3.5 and 8.5, respectively. DTMAC brings the largest differences of flotation recovery of SiC and SiO₂ at pH 6.0, where the recoveries of SiC and SiO₂ are 78% and 15%, respectively. In the case of the flotation of SiC from SiO₂, it is preferable to employ DTMAC as a surfactant.

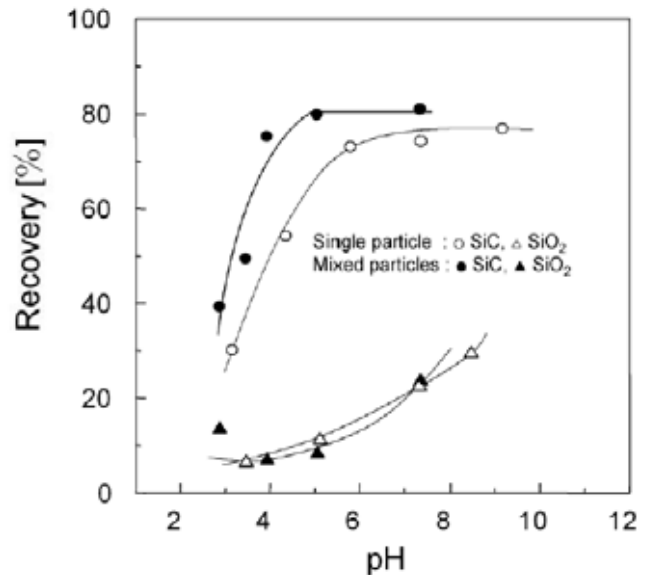


Figure 6: Flotation recovery of single and mixed particles with dodecyltrimethylammonium chloride as a function of pH.

(Solid content : 0.3wt % (SiC : SiO₂ = 9 : 1)
DTMAC concn. : 9×10^{-4} mol / dm³
Flotation time : 1.5min)

The reason why the flotation recovery of SiO₂ is smaller than that of SiC is possibly related to the surface coverage of the surfactant although the adsorption amount of surfactant on SiO₂ is larger than that on SiC. As mentioned above, if the surface coverage is assumed to be unity when the adsorption is saturated in monolayer state, the coverage for SiO₂ is 0.046. Since the specific surface area of SiO₂ is larger than that of SiC, the small coverage of SiO₂ is

understandable even if the adsorption amount of surfactant on SiO_2 is larger than that on SiC. In this case, the surfactant coverage for SiC is unity or more than unity. From the comparison of the contact angles between SiO_2 and SiC particles shown in Table 2, SiC surface has stronger hydrophobic property than SiO_2 surface. Thus, it is considered that the difference of flotation recovery between SiC and SiO_2 is related to the adsorption of surfactant and properties of the particles.

The flotation test for SiC and SiO_2 mixture was carried out with DTMAC. Figure 6 also shows the relationship between the flotation recovery of SiC and SiO_2 from the mixture, and pH. The recovery of SiC is 40% at pH 3.0, while SiO_2 particles are recovered by 6% at the same pH. The SiC recovery increases with increasing pH and 80% of SiC is recovered at pH 6.0. Over pH 6.0, the recovery of SiC goes to constant. SiO_2 particles are recovered with 6% at pH 3.0. Concerning SiO_2 , the recovery increases with increasing pH and 22% of SiO_2 is recovered at pH 7.3. When pH value is 6.0, there is the largest recovery difference between SiC and SiO_2 , where the recoveries are 80% and 10%, respectively. Therefore, the preferable pH is 6.0 if SiC is separated from SiO_2 using DTMAC by flotation.

Figure 7 shows the relationship between N_2 gas flow rate and flotation recovery. From the viewpoint of separation, pH was fixed at 6.0 in this test. The constant SiC recovery of 80% was obtained regardless of gas flow rate, whereas SiO_2 recovery depends on the gas flow rate. The SiO_2 recovery increases with an increase in the gas flow rate and the recovery becomes about 8% at the gas flow rate of $200 \text{ cm}^3/\text{min}$. When the N_2 gas flow rate is $200 \text{ cm}^3/\text{min}$, there is the largest recovery difference between SiC and SiO_2 . Figure 8 shows the relationship between the flotation time and recovery. When the flotation time is 5 minutes, SiC is recovered at 43%. Thus, the recovery depends on the flotation time. Flotation more than 15 minutes results in the constant SiC recovery of 78%. SiO_2 recovery also depends on the flotation time, namely 8% for 0.5 minutes and 19% for 3 minutes, respectively. When the flotation time is 1.5 minutes, there is the largest recovery difference between SiC and SiO_2 . From these results, the preferable flotation operation conditions for the mixture of SiC and SiO_2 are as follows; the N_2 gas flow rate of $200 \text{ cm}^3/\text{min}$ and flotation time of 1.5 minutes.

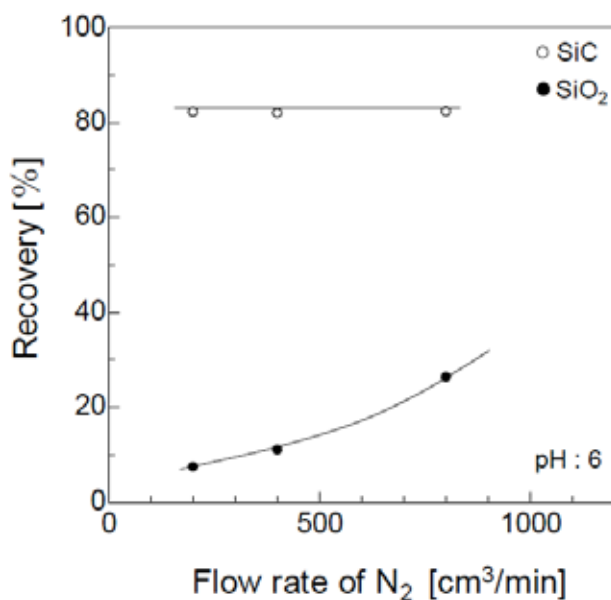


Figure 7: Relationship between flotation recovery and flow rate of N_2 in case of dodecyltrimethylammonium chloride.

(Solid content : 0.3wt % (SiC : SiO_2 = 9 : 1)
DTMAC concn.ion : $9 \times 10^{-4} \text{ mol} / \text{dm}^3$
Flotation time : 1.5min

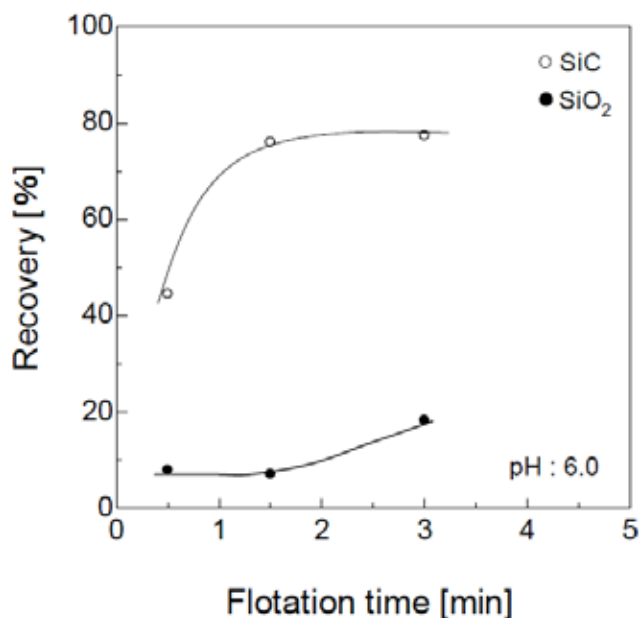


Figure 8: Relationship between flotation recovery and flotation time in case of dodecyltrimethylammonium chloride.

(Solid content : 0.3wt % (SiC : SiO_2 = 9 : 1)
DTMAC concn.: $9 \times 10^{-4} \text{ mol} / \text{dm}^3$
Flow rate of N_2 : $200 \text{ cm}^3 / \text{min}$

The flotation of SiC and SiO_2 with DTMAC was carried out to clarify the dependency of the mixing ratio of SiC and SiO_2 , which may work efficiently for the

separation of SiC and SiO₂. In the mixing ratio of SiC and SiO₂ of 10:1, 4:1 and 1:1, each flotation recovery increases with increasing pH and the recovery of SiC reaches the constant of 80% at pH 6.0. On the other hand, the recovery of SiO₂ is less than 30% in any pH range even though the SiO₂ recovery increases with an increase in pH. Therefore, the flotation with DTMC at pH 6.0 makes it possible to separate SiC from SiO₂.

The effect of DTMAC concentration on the flotation of SiC and SiO₂ was investigated. When the DTMAC concentrations are 4.0×10^{-4} mol/dm³ and 1.6×10^{-3} mol/dm³, 80% of SiC is recovered over pH 6.0 as well as the concentration of 9.0×10^{-4} mol/dm³. Under all the pH range, SiO₂ recovery is less than 30%. The decrease in the recovery of SiO₂ is due to the fact that the low concentration of DTMAC like 9.0×10^{-5} mol/dm³ gives the low surface coverage of the surfactant and this causes the weak adherence of N₂ bubbles on particle surface. The effect of solid/liquid ratio for SiC and SiO₂ mixture on flotation was investigated. It was found that the solid concentration less than 10% gives

the 80% SiC recovery at any solid concentration, whereas the recovery of SiO₂ is less than 10%. Therefore, this is the preferable flotation condition.

3.3. Flotation Separation Process for SiC

A series of investigations with cationic surfactants clarified that the flotation with DTMAC makes it possible to separate SiC from SiO₂. Figure 9 shows the flotation separation process of SiC from the mixture of SiC and SiO₂ with DTMAC. The separation process is composed of the following steps. The float and the sink are separated after flotation of the mixture of SiC and SiO₂ in the roughing step. The float is sent to the cleaning step where the float is recovered as SiC with high purity. The sink generated in the roughing and cleaning steps is conveyed to the scavenging step, where the float is circulated to the roughing step with feed particles and the sink is recovered as SiO₂. In the proposed flotation process, any step is carried out at pH 6.0 which shows good separation of SiC from SiO₂. Table 3 shows the flotation results in the each flotation

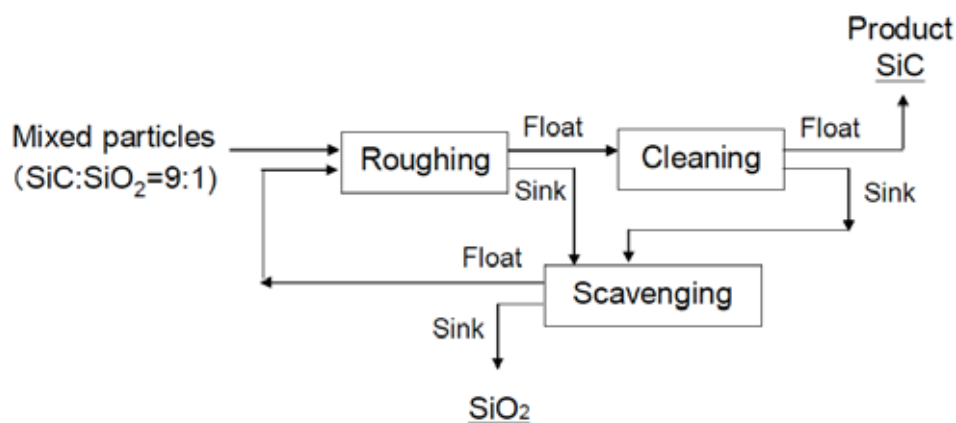


Figure 9: Separation process of SiC and SiO₂.

Table 3: Flotation Recovery of SiC and SiO₂ in Roughing, Cleaning and Scavenging Steps

Step		SiC [g]	SiO ₂ [g]	Purity of SiC [%]	Yield of SiC [%]
Roughing	Feed	90	10	90.0	-
	Float	77.5	1.0	98.7	86.1
	Sink	12.5	9.0	58.1	-
Cleaning	Feed	77.5	1.0	98.7	-
	Float	67.2	0.2	99.7	86.7
	Sink	10.3	0.8	92.8	-
Scavenging	Feed	22.8	9.8	69.9	-
	Float	19.8	0.9	95.7	86.8
	Sink	3.0	8.9	25.2	-

Solid content: 10wt%, DTMAC concn.: 4.0×10^{-3} mol/dm³.
Flow rate of N₂: 200 cm³/min, Flotation time: 1.5 min, pH : 6.0.

step when the solid concentration is 10wt%. The purity and the recovery of SiC in the roughing step are 98.7% and 86.1%, respectively. In the cleaning step, SiC can be obtained as the float with high purity and recovery, e.g. the purity and recovery are 99.7% and 86.7%, respectively. Concerning the sink in the scavenging step, the purity and recovery of SiO₂ are 78.4% and 90.8%, respectively. The combination of roughing, cleaning and scavenging steps allows recovering SiC with 99.7% purity and 96.7% recovery.

4. CONCLUSION

It was clarified that SiC can be separated from SiC and SiO₂ mixture by flotation if added surfactants strengthen the hydrophobic property of SiC surface. When DTMAC is used as a surfactant, high separation takes place between SiC and SiO₂. Since DTMAC has a longer hydrophobic group among water soluble cationic surfactants, DTMAC can give hydrophobic property by adsorbing on the SiC particles. As the flotation results for SiC and SiO₂ mixture using DTMAC, the recoveries of SiC and SiO₂ were 80% and 10% at pH 6.0, respectively, where the highest separation percentage can be obtained in the single batch test. It was confirmed that the combination of roughing, cleaning and scavenging steps permits to

recover SiC with 99.7% purity and 96.7% recovery from the investigation of flotation process. In the scavenging step, SiO₂ can be obtained as sink with 74.8% purity and 90.8% recovery.

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