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Oxidation of Silicon by Water

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Abstract

Silicon is oxidised in an aqueous environment with evolution of hydrogen. Relationships between the volumes of hydrogen evolved, hydrogen ion concentration, and particle size reductions, over times up to 7 ks have been examined. Milling at high hydrogen ion concentration (low pH) is found to be most effective, giving less gassing and greater efficiency of particle size reduction. At pH 8 the use of a commercial non-ionic surfactant was found to be effective both in controlling gas evolution and in giving improved particle reduction.

Silizium wird in wässeriger Umgebung unter Wasserstoffentwicklung oxidiert. Es wurden daher die Zusammenhänge zwischen dem Volumen des gebildeten Wasserstoffs, der Wasserstoffionenkonzentration und der Reduzierung der Teilchengrößen über Zeiten bis zu 7 ks untersucht. Es wurde herausgefunden, daß Mahlen bei hohen Wasserstoffionenkonzentrationen (niedriger pH-Wert) am effektivsten ist, wobei die Gasentwicklung geringer und der Wirkungsgrad der Teilchenreduzierung am größten ist. Bei pH 8 ist die Wirkung einer kommerziellen, nichtionischen, oberflächenaktiven Substanz geeignet, sowohl zur Kontrolle der Gasentwicklung als auch in Hinblick auf die Reduzierung der Teilchengrößen.

Le silicium est oxydé en milieu aqueux avec dégagement d'hydrogène. Les relations entre le volume d'hydrogène dégagé, la concentration en ions hydrogène et la réduction de la granulométrie ont été étudiées pour des durées allant jusqu'à 7 ks. On a trouvé que le broyage effectué à haute concentration en ions hydrogène (faible pH) est le plus efficace, provoquant moins de dégazage et une meilleure réduction de la granulométrie. A pH 8, on a trouvé que l'utilisation d'un tensioactif non-ionique du commerce était efficace tant pour le contrôle du dégazage que pour la réduction de la granulométrie.

1 Introduction

Silicon powder is the starting material for reaction-bonded silicon nitride. The reaction between silicon and water is of interest because water is a convenient medium for milling silicon powder, and because water-based casting slips are used to give microstructural control to compacted silicon powder,[1] which can then be nitrided to give high quality reaction-bonded silicon nitride.[2,3] Unfortunately, silicon oxidises in the presence of water, forming silicon dioxide and releasing hydrogen according to the equation

$$Si_{(s)} + 2H_2O_{(l)} = SiO_{2(s)} + 2H_{2(g)} \qquad (1)$$
$$\Delta G^\circ_{298} = -382\,\mathrm{kJ\,mol^{-1}}$$

Fine silicon powder vibro-milled in water for $\sim$1–7 ks has been found to react completely to yield silicon dioxide.[4] In fact, patents have been granted for the production of silicon dioxide by this route.[5,6] The exact oxidation mechanism is believed to be complex but is thought to involve as reaction intermediates either the formation and decomposition of silanone ($H_2Si = 0$) and hydroxysilylene (HSiOH where silicon is divalent)[7,8] or the formation and hydrolysis of silane (SiH_4).[9]

Because of the hydrogen formation reaction, aqueous silicon slips are normally aged[1–3,9,10] to allow the build-up of a silicon dioxide layer on each silicon particle, giving stable zeta potentials and allowing completion of foaming. The reaction also makes silicon difficult to wet-mill in aqueous media, a subject less well documented. The variation of rate

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of silicon reaction as a function of temperature is known,[4] but there appear to be no data for the influence of other factors such as hydrogen ion concentration. Kleebe and Zeigler[11] have measured particle size distributions for wet-milled silicon, but their work involved powders milled only in propan-2-ol.

2 Experimental Procedure

The starting silicon powder (KemaNord Sicomill 2C, see Table 1) had a median particle size of 7·8 μm, measured using a standard sedimentation technique ('SediGraph 5000 ET', Micromeritics) (Fig. 1). Silicon powder was milled by vibration at 22°C in a polypropene flask containing 450 g of commercial yttria stabilised zirconia media and 25 g of powder dispersed in 75 cm^3 of deionised water. The pH was adjusted in the range 3–11 by using hydrochloric acid and aqueous ammonia, and measured using a commercial glass electrode pH meter (Janway 3060). Gas evolved during milling was collected over water and the volume corrected to STP.

Table 1. Chemical analysis of silicon powder

Element	*Mass%*
Fe	0·41
Al	0·24
Ca	0·03
C	0·06

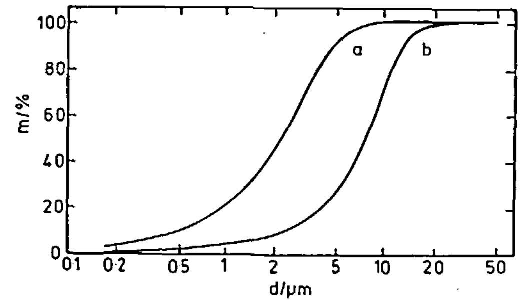

Fig. 1. Particle size distributions for (a) silicon powder milled for 32 ks at pH 4 with 300 g m^{-3} of gassing suppressant, and (b) starting silicon powder. Cumulative mass% as a function of equivalent spherical diameter.

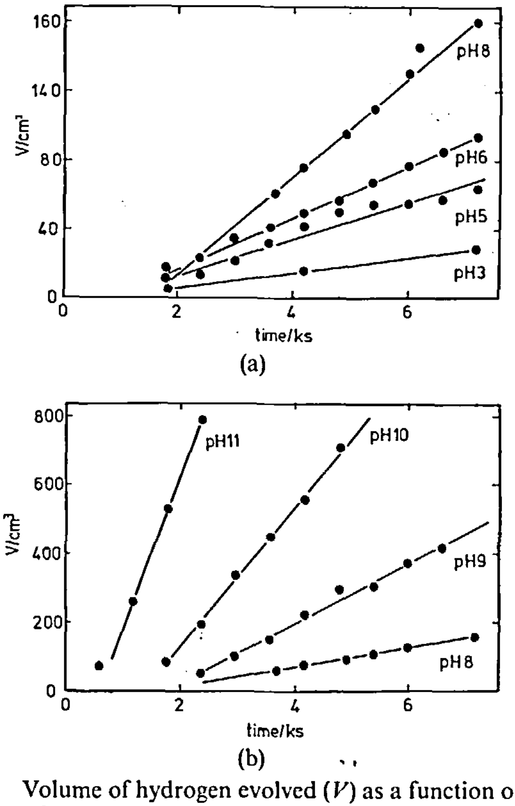

Fig. 2. Volume of hydrogen evolved (V) as a function of time for pH in the ranges (a) 3–8 and (b) 8–11.

Batches of powder were milled for times up to 7 ks, and gas evolution readings were made at intervals. Particle size analyses were carried out on powders obtained after milling for varying lengths of time. The effectiveness of a commercially available non-ionic surfactant gassing suppressant ('Nonidet P42', an octylphenol ethylene oxide condensate; BDH Chemicals, Poole, Dorset, UK) was also tested, using amounts of 100, 300 and 600 g m^{-3} in deionised water, adjusted to pH 10 with aqueous ammonia.

Extended milling using 350 g of silicon nitride grinding media and 50 g of silicon powder in 75 cm^3 of deionised water was carried out at pH 8 and pH 4, with 300 g m^{-3} of gassing suppressant. Samples were taken from the mill at intervals up to ~1 Ms for particle size analysis.

3 Results

The silicon powder evolved hydrogen when milled at all pH values in the range 3–11. Silicon powder left undisturbed in water of pH 10 (giving fast gas evolution during milling) did not evolve detectable amounts of gas. The largest rates of hydrogen evolution were at higher pHs, as shown in Fig. 2(a)

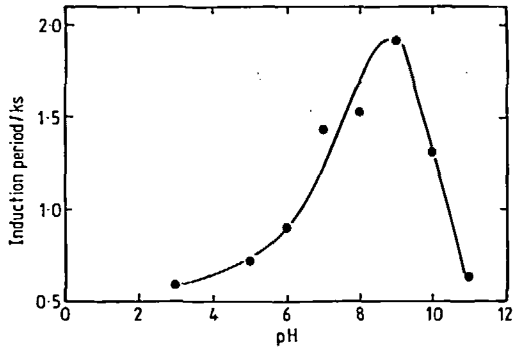

Fig. 3. Oxidation induction period (ks) as a function of pH.

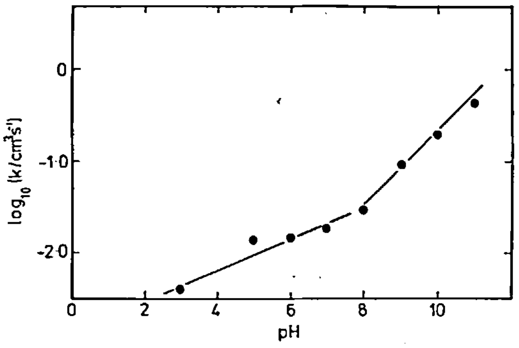

Fig. 4. Log_{10} (k/cm^3 s^{-1}) as a function of pH.

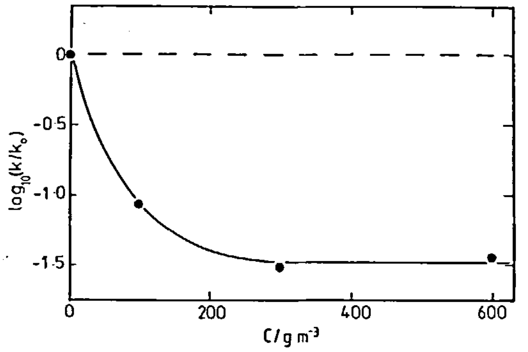

Fig. 5. $\text{Log}_{10}(k/k_0)$ as a function of surfactant concentration (C) at pH 10.

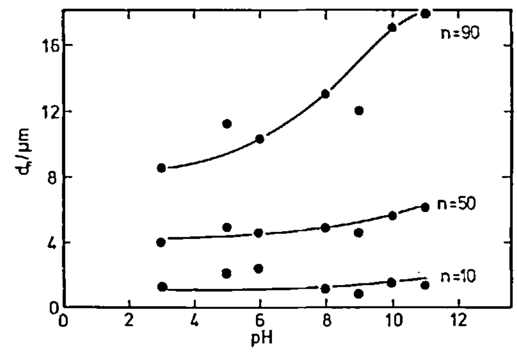

Fig. 6. Equivalent spherical diameter, d_n (μm), as a function of pH for silicon powder milled for 7 ks. The curves for three values of percentage undersize, n, are shown.

and (b). These plots are linear with a short induction period, during which little or no gas was evolved. The induction period was shortest at high and low pHs, and was at a maximum between pH 8 and 9 (Fig. 3). When reaction rates measured from Fig. 2 are plotted as a function of pH, linear behaviour is dominant in the pH range 3–8 and very fast reaction occurs beyond pH 8. A plot of the logarithm of the linear rate constant as a function of pH (Fig. 4) highlights this behaviour and shows a slope of ~0·2 for low pH and of 0·4 for pH ≥ 8.

The commercial gassing suppressant proved effectively to suppress the oxidation reaction at high pH. Standardised rate constants for increasing surfactant concentrations, shown in Fig. 5, indicate a large decrease in the reaction rate up to the addition of 300 g m^{-3} compared with that for milling without surfactant.

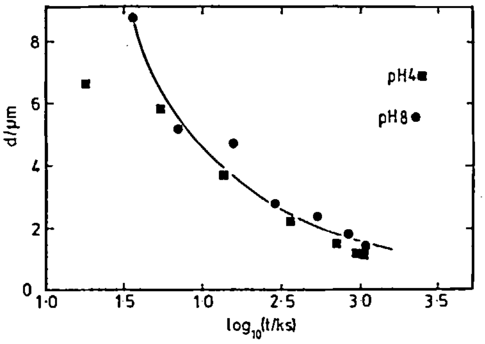

Fig. 7. Equivalent spherical diameter, d (μm), for $n = 50$, as a function of $\log_{10}$ (t/ks) for powder milled at pH 4 and 8.

Particle size analysis of the powders produced after ~7 ks milling over the pH range 3–11 (Fig. 6) showed that milling was most effective at low pH. The use of extended milling times, with 300 g m^{-3} of surfactant (Fig. 7), showed slightly higher efficiency at pH 4 than at pH 8 at short times but little change after ~60 ks under similar conditions.

4 Discussion

The silicon oxidation reaction, with hydrogen evolution, is clearly controlled by the H^+ or OH^- ion concentrations. At higher OH^- concentrations gas evolution is fast and creates a practical problem for milling and for slip stabilisation. Simple calculations show, however, that in terms of silicon dioxide formation the reaction rate is relatively slow, and even after 5 ks at pH 10 the mean thickness of silicon oxidised is only ~25 nm.

The existence of two reaction regimes, corresponding broadly to acid, and to alkaline, conditions is evident in the gas evolution rate (Fig. 4) and in the induction period (Fig. 3). At short oxidation times the apparent mean silicon dioxide film thickness becomes unrealistically thin and it is more likely that initially localised reaction is occurring at a limited number of surface nuclei. The absence of a marked reaction when silicon powder suspended in an alkaline medium is not milled shows that reactive nuclei formation, and their development, occurs only at freshly cleaved silicon surfaces.

Figure 3 suggests that nucleation is favoured by acidic conditions, but that nuclei growth, with silicon dioxide formation and hydrogen release, is favoured by alkaline conditions. The latter is as would be expected, because the development of a potentially protective silicon dioxide film at the developing nuclei will be prevented by solution in the higher pH media to give silicate ions:

$$2SiO_{2(s)} + 2OH^-_{(aq)} = Si_2O^{2-}_{5(aq)} + H_2O_{(l)} \qquad (2)$$

Catalysis by H^+ or OH^- seems not to be applicable because a slow drift of pH with time occurs, indicating irreversible reactions of these ions.

Silicon particle cleavage is favoured by conditions also suppressing silicon oxidation. A possible explanation is that hydrogen gas bubbles evolving on freshly exposed surface cushion the silicon particles against collision, and absorb the kinetic energy which would otherwise be transmitted to the particles to induce fracture.

5 Conclusions

Substantial evolution of hydrogen occurs when silicon powder is oxidised during milling of silicon in water of pH > 8. Milling is readily possible when a non-ionic surfactant is used in concentrations greater than ~300 g m^{-3}. Milling in low pH media without a surfactant is more effective than at high pH. At high pHs with surfactant good long-term milling behaviour is obtained.

Acknowledgements

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