

The Compaction Behaviour of Oxidised Silicon Powder

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Abstract

Milling silicon powder in aqueous media of high pH results in the deposition of thin surface layers of nanometre-dimension silicon dioxide particles. These layers cause strong agglomeration between the dried silicon particles, which in turn leads to the development of microstructural inhomogeneities in compacted powders. Silicon powder milled in propan-2-ol shows none of these undesirable features.

Das mahlen von Silizium-Pulver in wässrigen Medien mit hohem pH-Wert führt zur Abscheidung einer dünnen Oberflächenschicht auf Siliziumdioxid-Partikeln, deren Größenordnung im Nanometerbereich liegt. Diese Schichten verursachen eine starke Agglomeration der getrockneten Silizium-Partikel, wodurch es in verdichteten Pulvern zur Entwicklung mikrostruktureller Inhomogenitäten kommt. Silizium-Pulver, welches in Propan-2-ol gemahlen wird, zeigt keine der genannten unerwünschten Eigenschaften.

Le broyage d'une poudre de silicium en milieu aqueux à pH élevé conduit au dépôt de fines couches superficielles de particules nanométriques de dioxyde de silicium. Ces couches provoquent une agglomération forte des particules de silicium séchées, qui favorise à son tour le développement d'inhomogénéités microstructurales dans les compacts de poudre. La poudre broyée dans l'isopropanol ne présente aucune de ces caractéristiques indésirables.

1 Introduction

Silicon reacts with water to form silicon dioxide and hydrogen.^{1–6} The reaction of micrometre-

dimension silicon powder during milling in aqueous media is slow for pH values of less than 6, but becomes very fast as the hydrogen ion content is decreased. Simultaneously the milling efficiency is decreased slightly.⁶ The use of a non-ionic surfactant gassing suppressant retards oxidation and milling can then be carried out at higher pH values. The authors have continued an earlier study with an examination of the behaviour of dry silicon powders produced using different wet milling conditions. It has become clear that the products of any surface oxidation reaction can have an important bearing on the subsequent surface properties of the particles, which in turn have a strong influence on the compaction behaviour of the powder. The authors report here the results of this investigation, which show that compacted material with quite different characteristics can be obtained from one silicon powder treated under marginally differing milling conditions.

2 Experimental

The starting silicon powder was that used previously (KemaNord, Ljungaverk, Sweden, Sicomill 2C), and had a median particle size of $7.8 \mu\text{m}$ measured on powder dispersed in water with 300 g m^{-3} of a non-ionic surfactant gassing suppressant (Nonidet P42, an octylphenol ethylene oxide condensate; BDH Chemicals, Poole, Dorset, UK) using standard equipment (Micromeritics Sedigraph 5000ET). Silicon powder was milled gently by vibration at a fixed frequency, at 22°C , in a polypropene flask containing 25 g of powder and 450 g of cylindrical stabilised zirconia media, in 75 cm^3 of one of three fluids: deionised water, the hydrogen ion content of which was adjusted to give pH values of 5 and 10

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using aqueous hydrochloric acid or ammonia, and propan-2-ol (IPA, derived from the former name isopropylalcohol) (BDH Chemicals, Poole, Dorset, UK). Hydrogen evolved was collected over water and the volume corrected to STP. Batches of powder were milled for times up to 14 ks, and then dried quickly by rotary evaporation, under vacuum at 90°C for water, and under atmospheric pressure at 80°C for IPA. Possible further slight oxidation of the silicon during removal of the water was ignored because of previous observations that significant oxidation only occurred during milling or agitation at freshly exposed silicon surfaces.⁶

Dried silicon powders were examined in a number of ways. Specific surface area (a_s) was measured using a standard single-point nitrogen adsorption method (Perkin-Elmer 212D, Connecticut, USA) and the BET equation. Compaction behaviour was followed continuously using a 19 mm diameter steel die compressed in a standard testing machine (Instron 1185, High Wycombe, UK) at a cross-head speed of 1 mm min⁻¹; data were corrected to allow for systematic machine errors and die strain. Discs of ~3 mm thickness and ~18 mm diameter were produced by uniaxial pressing and iso-pressing under pressures up to 250 MPa. Disc density was determined by mensuration. Strengths of compacted powders were measured by a standard disc flexure method using concentric rings of balls, of 16 and 8 mm diameter, and a cross-head speed of 0.05 mm min⁻¹. Strength values (S) were calculated using the expression⁷ (Ref. 7 contains a typographical error in this expression)

$$S = \frac{3W}{\pi t^2} \left\{ (1 + \nu) \ln(r_s/r_L) + (1 - \nu) \frac{(r_s^2 - r_L^2)}{2r_D^2} \right\} \quad (1)$$

where W = load at failure; t = disc thickness; ν = Poisson's ratio of the disc material; and r_L , r_s and r_D = radii of the load multiball ring, support ball ring and the disc, respectively.

Fracture surfaces of broken discs were examined after gold coating by scanning electron microscopy (SEM).

Individual silicon particles were examined by transmission electron microscopy (TEM). A small quantity of powder was dispersed in acetone, and a drop evaporated on a standard copper grid which had previously been carbon coated to support the particles and ensure good electrical conductivity. Powders were also pressed into KBr discs at a concentration of ~0.34% for Fourier transform infrared spectroscopy (FTIR), using a wavenumber range of 450 to 4000 cm⁻¹.

3 Results

In agreement with earlier findings, the evolution of hydrogen during milling of silicon powder in water was strongly pH dependent. Figure 1 shows the volumes of hydrogen produced during standard milling treatments with water of pH 5 and 10. Gas

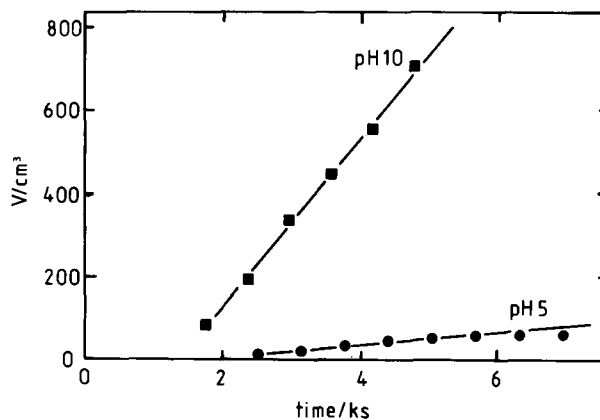


Fig. 1. Volume of hydrogen evolved (V) as a function of time for pH 5 and 10.

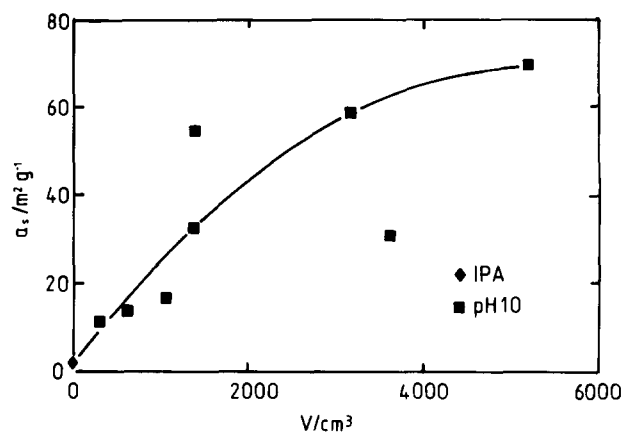


Fig. 2. Specific surface area (a_s) as a function of volume of hydrogen evolved (V) for silicon milled in IPA and in water of pH 10 for times up to 23.5 ks.

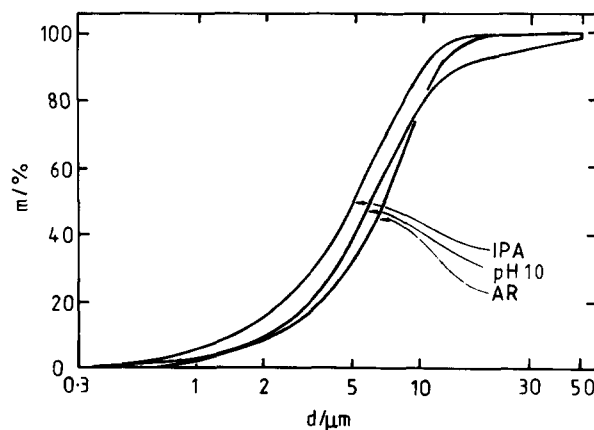


Fig. 3. Particle size distributions for as-received silicon powder (AR) milled for 14 ks in IPA (IPA) and milled for 14 ks in water of pH 10 (pH 10), dried and redispersed. Cumulative mass (m) % as a function of equivalent spherical diameter (d).

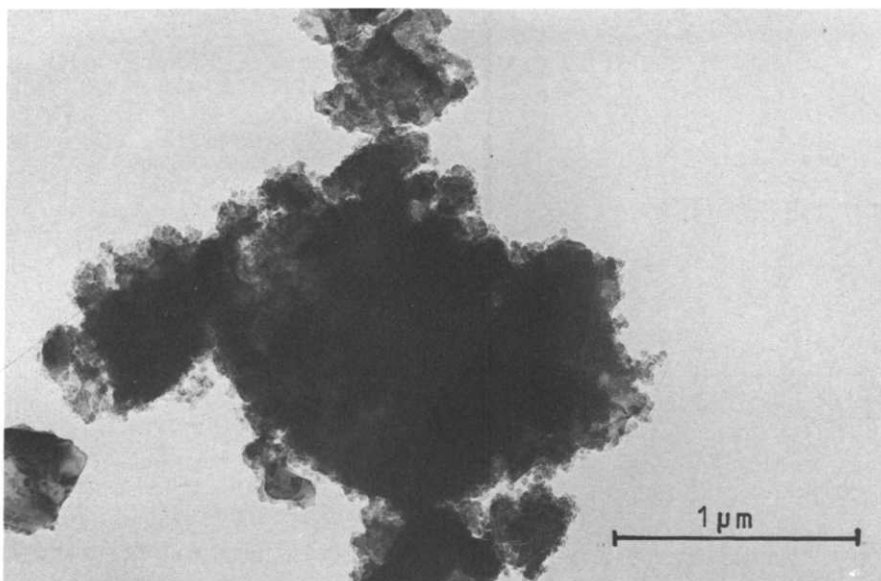


Fig. 4. TEM micrograph of silicon particles milled for 14 ks in water of pH 10.

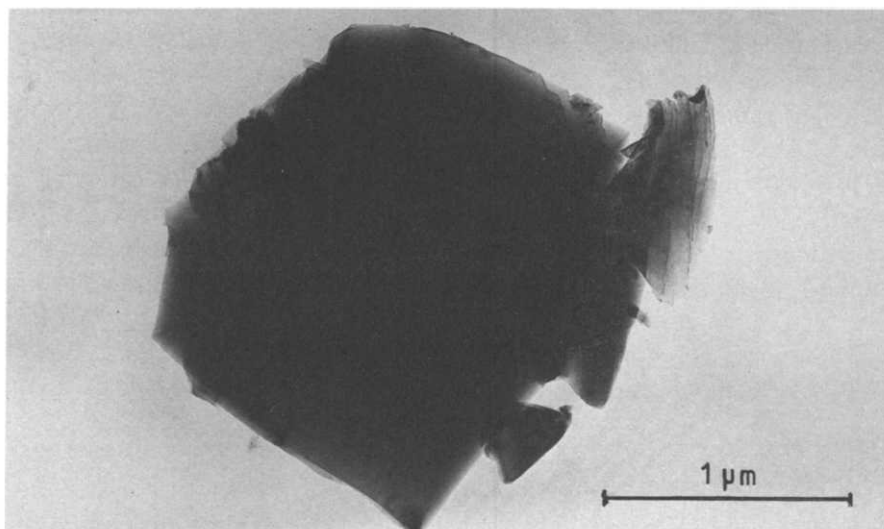


Fig. 5. TEM micrograph of silicon particles milled for 14 ks in IPA.

evolution during milling under propan-2-ol was negligible. The specific surface area (a_s) of the silicon powder depended on the milling treatment, and was related to the volume of hydrogen released. Figure 2 shows this relationship for batches of powder milled at pH 10 for times up to 23.5 ks. The increase in a_s was not due to simple fracture of silicon particles, because the Stokes' sedimentation of the powder indicated no decrease in median particle size; sedimentation data for redispersed dried powder are shown in Fig. 3. Instead it was evident that the increased powder surface area was that of the silicon dioxide oxidation product. The silicon dioxide is shown unambiguously by TEM examination to be located largely as small (50 nm) nodules on the silicon particle surfaces. Figure 4 shows TEM images for randomly selected silicon particles after milling for 14 ks at pH 10 and with a_s $50 \text{ m}^2 \text{ g}^{-1}$. In contrast, silicon milled in IPA showed no increase in a_s , and particles retained sharp surface features (Fig.

5). FTIR spectroscopy plots for silicon powder milled in IPA and in water of pH 5, 8, 9 and 10 for 7 ks are shown in Fig. 6. The height of the peak at 1120 cm^{-1} , corresponding to the SiO stretching

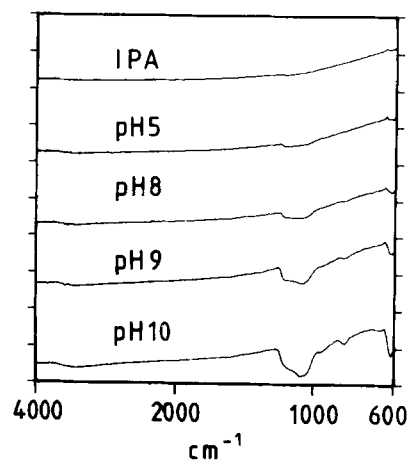


Fig. 6. FTIR data for silicon powder milled in IPA and water of pH 5, 8, 9 and 10 for 7 ks.

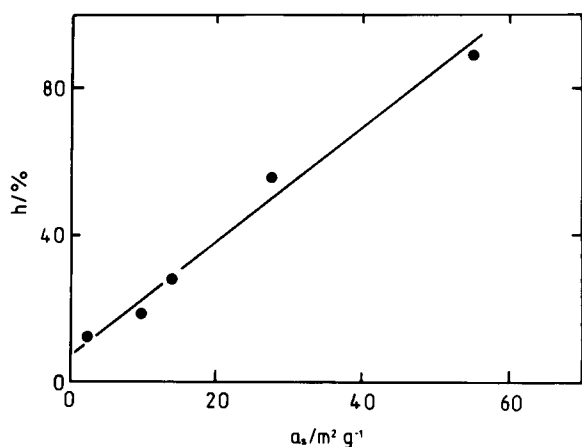


Fig. 7. FTIR 1120 cm^{-1} peak height (h expressed as a percentage of the highest peak) as a function of specific surface area (a_s).

absorption, is shown as a function of specific surface area in Fig. 7.

The compaction behaviour of silicon powders obtained by milling in water at pH 5 and 10, and in IPA, indicated significant differences in powder property. Plots of relative density as a function of (\log_{10}) compaction pressure for pH 5, pH 10 and IPA milled powders are shown in Fig. 8. Silicon milled in water of pH 10 shows an initially lower green density, but a significantly greater degree of compactibility, than pH 5 and IPA milled powders.

Table 1. Disc flexure strengths for compacted silicon powder milled in different fluids, and of a range of specific surface areas

Milling fluid	Mean strength (MPa)	a_s ($m^2 g^{-1}$)
IPA	1.6	1.9
Water pH 5	1.7	5.0
Water pH 10	4.8	82.0

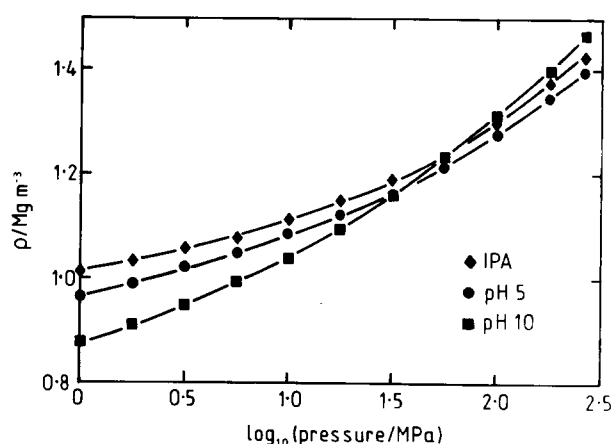


Fig. 8. Continuous compaction behaviour of silicon powder milled for 14 ks in IPA, and in water at pH 5 and 10.

Measurement of disc flexure strength showed that the compacted water-milled powders had considerably greater strength than IPA milled powder when pressing pressures were adjusted to ensure equal void fractions, with the greatest strengths being obtained for the pH 10 material. Values for the three materials are given in Table 1. Each value is the mean of four determinations made on discs of relative density 0.59 ± 0.02 , and thickness 2.9 ± 0.3 mm. Values for a_s for each batch of powder are also given.

Typical disc fracture faces are shown in Fig. 9 for IPA, and in Fig. 10(a) and (b) for pH 10 milled powders, after pressing at 400 MPa.

4 Discussion

The final result of the oxidation of silicon powder during milling in the aqueous media is the formation of a thin layer of particulate, amorphous, silicon

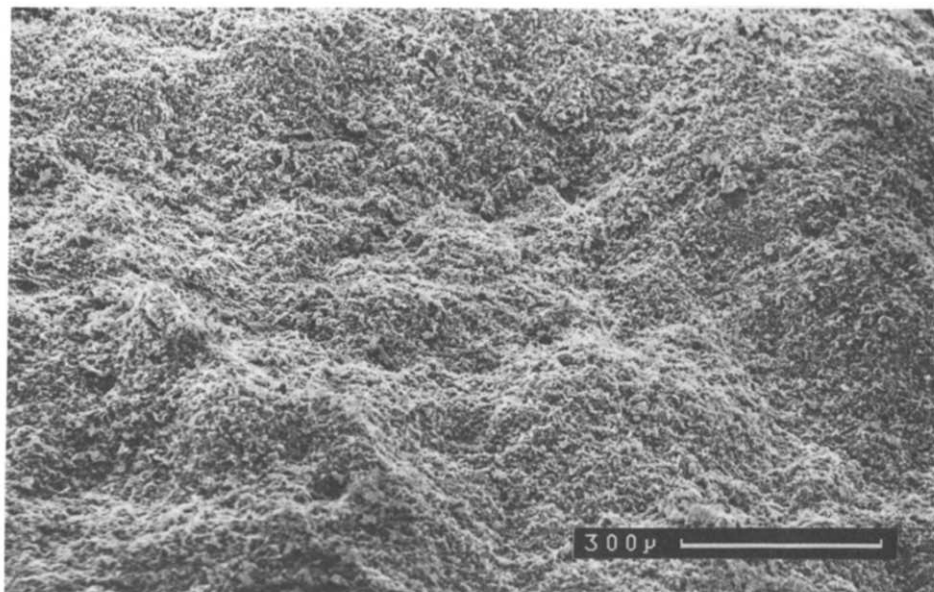
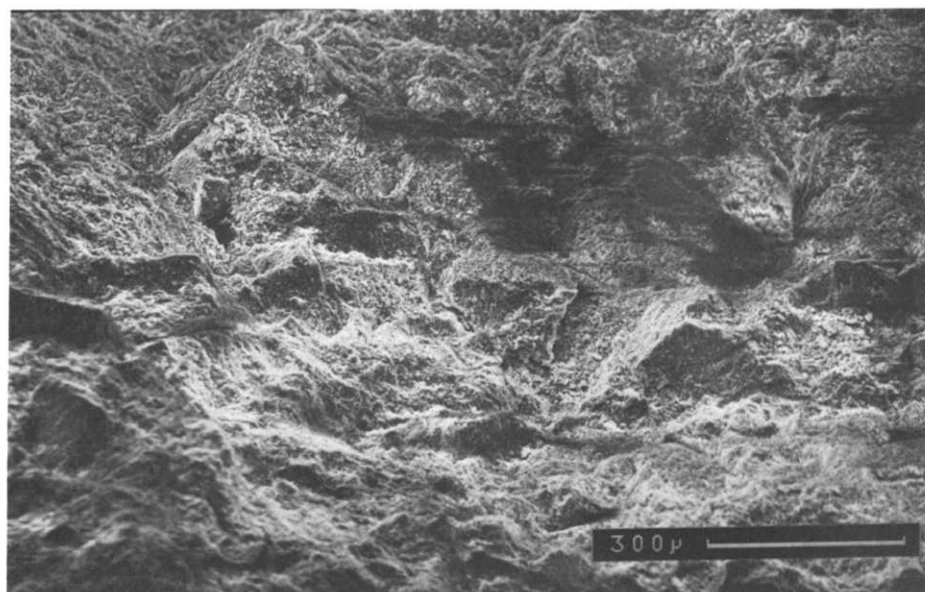
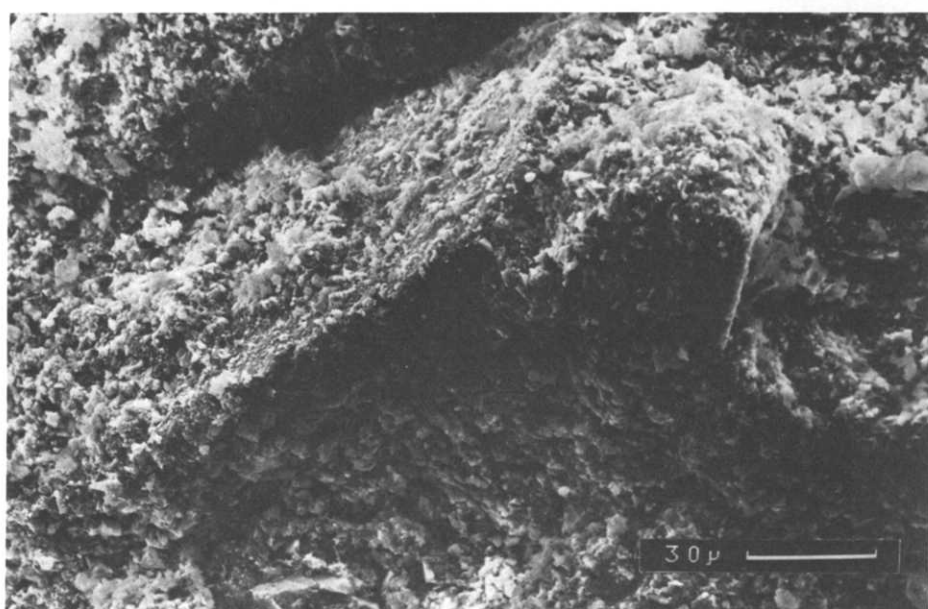


Fig. 9. Fracture face of a disc pressed from silicon powder milled for 14 ks in IPA.



(a)



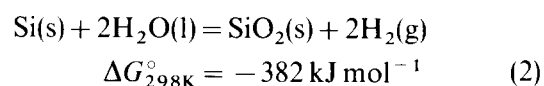
(b)

Fig. 10. (a) and (b) Fracture face of a disc pressed from silicon powder milled for 14 ks in water of pH 10.

dioxide on each silicon particle. Confirmation of the existence of the silicon dioxide is provided by the FTIR analyses, which show the expected correlation with extent of specific surface area. It is most likely that the silicon dioxide layer is deposited during the drying stage from a colloidal suspension of hydrated silicon dioxide, although its nucleation and growth on the silicon particle surfaces during milling cannot be ruled out. The nodular particles constituting this layer on powder milled in water at pH 10 medium appeared, from TEM observations, to be approximately 50 nm in dimension. Simple calculation shows that such a powder should have a specific surface area of $\sim 50 \text{ m}^2 \text{ g}^{-1}$. This matches approximately the measured a_s value, but the actual yield of silicon dioxide, on the basis of the volumes of

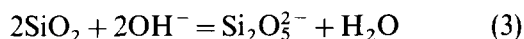
hydrogen evolved, corresponds to as much as 16% of the mass of starting silicon powder. The silicon dioxide actual specific surface area must therefore be closer to $500 \text{ m}^2 \text{ g}^{-1}$, corresponding to a 5 nm primary particle dimension on the basis of an assumed density for amorphous silicon dioxide of 2.2 mg m^{-3} . Such agglomeration in an essentially 'chemically prepared' powder would not be unusual.⁸

Because of the enhanced rate of oxidation of silicon powder under alkaline conditions



it was assumed earlier⁶ that silicon dioxide dissolution as $\text{Si}_2\text{O}_5^{2-}$ occurred to prevent the develop-

ment of a protective layer on each silicon particle. Under the conditions used this would have amounted to the production of a dilute solution of ammonium silicate. However, the amount of NH_4OH present in the milling solution of pH 10 ($\sim 100 \mu\text{mol}$) is insufficient to dissolve as silicate anion the large amount of silicon dioxide being formed by reactions such as



Solutions of pH 10 were achieved with virtually complete ionisation of the added NH_4OH and the possibility of a buffered solution effect was discounted. It seems more likely, therefore, that the function of the hydroxide ion is either to act as a deflocculant stabilising a colloidal suspension of hydrated silicon dioxide, and preventing its agglomeration at this stage on the silicon particle surfaces to form a protective film, or to catalyse the surface oxidation process.

The Stokes' sedimentation data indicate clearly the importance of the nanometre-dimension silicon dioxide particles for the behaviour of the silicon powder. Once the water-milled powder had been allowed to dry, the surface silicon dioxide particles acted to form strong silicon particle agglomerates, and it proved to be very difficult to achieve complete redispersion. The lower packing densities obtained at low compaction pressures with the water-milled, oxidised powders appears to reflect the low density of the silicon dioxide surface film, which is sufficient to compensate for an expected higher overall density arising from the wider particle size distribution of the strongly agglomerated powder. The silicon dioxide coating is itself weaker and more compressible than the silicon powder particles; increasing compaction pressure ultimately achieves higher densities than those obtained with the IPA-milled powder, for example (in view of the similar densities of silicon and amorphous silicon dioxide, 2.32 and 2.20 Mg m^{-3} , corrections to the measured compacted densities, to allow for the presence of the oxide layer, were not felt to be justified). The continued existence of agglomeration in the oxidised silicon powder after isostatic compaction at 400 MPa is shown by the nature of the compact fracture surfaces (Figs 9 and 10), which are markedly rougher for the pH 10-milled powder. Thus even at this pressure complete crushing of the agglomerates, and microstructural homogenisation, is not achieved.

A very similar mechanism for the development of agglomerates during the wet milling of high surface area alumina has been proposed by Niesz & Bennett.⁹ In this case the slow release of surface Al^{3+}

ions during milling into the water leads to the precipitation on drying of an aluminium hydroxide gel. With continued drying the gel partially dehydrates to form an aluminium oxide monohydrate of surface area $\sim 500 \text{ m}^2 \text{ g}^{-1}$, and able to act as a bond for agglomerates in the dried powder.

This study thus demonstrates that the packing behaviour of silicon powder, and compacted powder homogeneity, can be markedly influenced by a surface coating of nanometre-dimension silicon dioxide, which is able to bond the silicon particles strongly together into agglomerates. This is shown in the difficulty experienced in redispersing silicon powder after drying, in the retention of large agglomerates after extended periods of ultrasonic treatment, and most clearly in the strength of compacted powder discs. A further direct consequence of the agglomeration is the microstructural inhomogeneity of the compacted silicon powder, shown by the roughness of the pH 10 milled silicon disc fracture faces, compared to those of the IPA-milled powder.

Because extreme conditions of aqueous milling, using a high pH giving fast oxidation rates, were used for this study, the effects of the milling process on subsequent powder property were also extreme, and the consequences of which were thus readily detected and measured. Powder milled under more 'normal' conditions with water of pH nearer to 7 will oxidise to a lesser extent, and will therefore show a much less marked influence of surface coatings of silicon dioxide. On the other hand, it is clear that if maximum microstructural homogeneity of the compacted silicon powder (and hence reaction-bonded silicon nitride) is to be achieved, close attention must be paid to the chemical nature of the silicon particle surfaces and to the conditions existing during milling treatment applied to the silicon powder.

On the basis of the evidence obtained so far, milling under nonaqueous conditions, and using a gassing suppressant, would appear to be the most desirable. This should provide silicon powder of maximum powder packing density with lower compaction pressures, and maximum homogeneity of particle packing, and thus yield a narrow distribution of void sizes in the final fully nitrated reaction-bonded silicon nitride.

5 Conclusions

Milling silicon powders in aqueous media results in oxidation and the development after drying of

coatings of finely particulate silicon dioxide on the silicon particles. Oxidation rate is a function of medium pH; alkaline conditions favour oxidation. The effect of this nanometre-dimension silicon dioxide coating on the dried powder is to provide strong inter-particle bonding leading to the formation of hard agglomerates and to high green strengths in compacted powder. Agglomeration is detrimental to microstructural homogeneity. While in this study extreme conditions were used to facilitate analysis of the results of surface oxidation, it is clear that even slight oxidation of silicon powders during preparation stages is to be avoided if compacted silicon powder of optimum microstructural homogeneity and of minimum width of void size distribution is to be obtained.

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