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Conversion of precipitated silica from geothermal water to silicon nitride

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Precipitated colloidal silica from geothermal discharge waters of Wairakei, New Zealand was used as the raw material to produce silicon nitride. Mixtures of α and β forms of silicon nitride in the ratio 90/10 to 95/5 were produced by carbothermal reduction and nitridation of this silica in the temperature range 1350 to 1440° C between 2 and 10 h. Three other commercial fine-grained silicas were also nitrided under the same conditions. The geothermal silica was found to be as good if not better than any of these silicas.

1. Introduction

The exploitation of geothermal resources for the production of electricity results in discharge waters containing appreciable concentrations of silica. Geothermal resources are widespread throughout the world and the potential exists for the recovery of this silica. Silica scale is deposited in pipes and drains, and also makes any further use of the hot water impracticable [1]. The total silica in discharge waters from Wairakei, New Zealand is $\sim 0.5\,\mathrm{kg\,t^{-1}}$ and can be precipitated in colloidal form [2]. Because the silica is reasonably pure it may be considered a potential source for the preparation of silicon nitride, a product with considerable added value.

Several workers have produced silicon nitride from different sources of silica by carbothermal reduction and nitridation in the temperature range 1350 to 1600° C [3–8]. According to Lee and Cutler [5] the reduction of silica (to SiO) and the nitridation takes place predominantly as a solid/gas reaction forming silicon nitride, the overall reaction being:

$$3SiO_2 + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO \qquad (1)$$

The stoichiometric ratio should therefore be $2C : 1SiO_2$ but the previous work [3, 5, 7] has shown that the C/SiO_2 molar ratio should be greater than this (4 to 20) to obtain pure silicon nitride. The excess carbon requirement is partly to counteract moisture in the silica [6] and also to maintain the partial pressure of oxygen at less than 10^{-20} atm which suppresses the formation of silicon oxynitride [5].

The types of silica used in previous work [6, 7] were mainly fume silica and precipitated silica; there is no work reported on the use of geothermal silica. Therefore, the present study was undertaken to compare the preparation of silicon nitride from geothermal silica with that formed from three other commercial fine-grained silicas. Having optimized the conditions for conversion of geothermal silica to silicon nitride, the other silicas were reacted under the same conditions to permit direct comparison.

2. Experiment procedure

2.1. Raw materials

Trace element analyses of all the silicas used in this study are presented in Table I, which shows them to be reasonably pure apart from a slightly higher sodium and iron content in the precipitated silica. During handling of the silicas it was noticed that all except the silica flour had a strong tendency to agglomerate. Therefore, the silicas were characterized with respect to their agglomeration and particle size. The morphology of the agglomerates of precipitated silica and geothermal silica is similar (Fig. 1): the silica flour does not agglomerate because it is coarser than the others (Figs 1 and 2); the individual particles of the silicas (except the silica flour) are spheroidal (Fig. 2a); the fume silica and precipitated silica are finer than the geothermal silica.

The particle characteristics of the silicas and the carbon lampblack are listed in Table II. The fume silica has a large volume compared to the other silicas and the carbon lampblack.

2.2. Preparation of mixes

Mixtures of carbon lampblack/silica powders in various molar ratios were stirred in acetone using a high-speed stirrer, dried and re-mixed in a mechanical agate mortar for 1 h. The difference in colour of the powders gave an indication of the mixing, geothermal silica taking only 10 min to reach a homogeneous mix compared to fume silica (requiring about 30 min) and the other silicas (20 min). A cylindrical pellet (10 mm diameter × 10 mm) pressed from the powder mixture at a pressure of 7 MPa was placed in an alumina boat on a bed of the same powder. A low pressure was used to compact the powder in order that nitrogen could flow freely inside the pellet and powder. The main aim was to nitride the pellet rather than the powder, the purpose of the latter being to prevent any contact with the alumina boat.

2.3. Nitridation and product characterization

The alumina boats containing the C/SiO_2 mixtures

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TABLE I Arc-spectrographic trace element analyses of silica source materials used for the preparation of silicon nitride

Code	Type of silica	Source	Fe (%)	Al (%)	Ti (%)	Ca (%)	Na (%)	Ba (%)	B (%)	Be (p.p.m.)	Mg (p.p.m.)	Mn (p.p.m.)	Ga (p.p.m.)	Pb (p.p.m.)
GS	Geothermal	Wairakei, NZ	< 0.06	0.3 ± 0.1	n.d.	0.07	0.3	n.d.	0.15 ± 0.05	20	50	25 ± 5	50	n.d.
FS	Fume	Degussa, W. Germany	0.2	0.025 ± 0.005	0.05 ± 0.04	< 0.01	n.d.	< 0.02	⩽0.0015	n.d.	⩽25	n.d.	n.d.	< 100
CS	Precipitated, Colloidal	BDH Ltd, England	0.4	0.08 ± 0.02	0.04 ± 0.01	0.06 ± 0.01	1.25 ± 0.25	⩽0.001	n.d.	n.d.	100 ± 50	n.d.	n.d.	n.d.
SF	Silica Flour	ACI Minerals, Australia	0.06	0.20 ± 0.05	0.018 ± 0.002	0.001 ± 0.005	n.d.	0.001	n.d.	n.d.	⩽50	⩽20	n.d.	n.d.

Other elements not detected (n.d.): Bi, Mo, Ni, Sn, V, W, Ge, Th, Tl, Cd, Sb, P, Hg, Te, Se, Cu, Sr, K, Zn, Co, Zr, Ag, Au, In, Y.

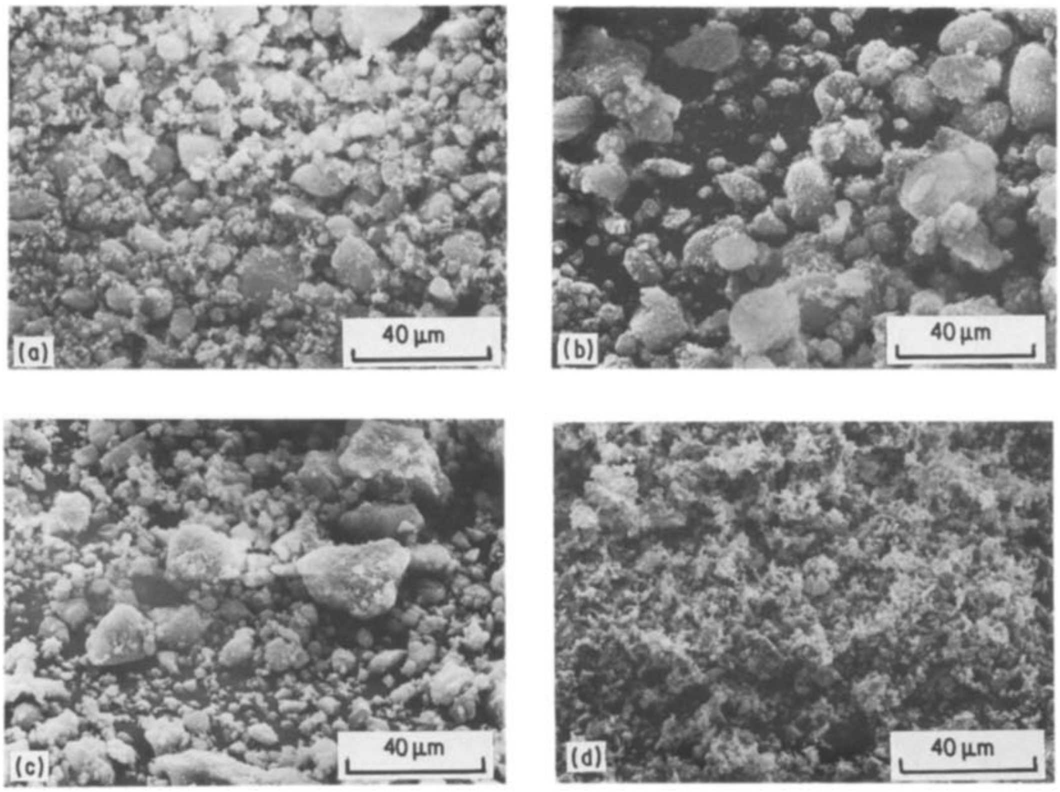

Figure 1 Scanning electron micrographs of silica agglomerates, (a) geothermal silica, (b) fume silica, (c) precipitated silica, (d) silica flour.

were placed in an electric tube furnace and fired at 1350 to 1440° C for 2 to 10 h in flowing oxygen-free nitrogen (10 p.p.m. oxygen) at 1 atm pressure. The products were characterized by X-ray diffraction (XRD) and weight change measurements. The ratio of α/β Si_3N_4 was estimated from peak heights of the α-(1 0 2) and β-(1 0 1) reflections according to Liddle and Thompson [9]. The ratios were rounded off to the nearest 5.

3. Results and discussion

The results for geothermal silica are summarized in Table III. Except for the $C/SiO_2 = 2$ run, silicon nitride (α and β) was the major phase, as found by Komeya and Inoue [3] for colloidal silica. The phase analyses of both the powder and the pellet were the same but the α/β ratios were slightly different. Residual carbon detected by XRD after the reaction disappeared when decarburized in air at 800° C for 4 h, but the X-ray pattern was otherwise unchanged. α-Si_3N_4 is the preferred starting material to produce dense β-Si_3N_4; however, the maximum ratio of α/β obtained in this work was 95:5. Szweda *et al.* [6] record the complete conversion of fume silica to α-Si_3N_4 at $C/SiO_2 = 2$ after 17 h at 1400° C, but in order to obtain silicon nitride free of impurities they had to fire at 1500° C using higher C/SiO_2 (ratios (4 : 1 and 15 : 1). Franchini [7] produced silicon nitride from colloidal silica at $C/SiO_2 = 20$ in 17 h at 1390° C and 20 h at 1350° C. Others [3, 5, 10] found a silicon carbide impurity formed above 1450° C. The optimum conditions for geothermal silica (as shown in Table III) are about 10 h at 1350° C, 6 h at 1400° C or 2 h at 1440° C. For comparison, the other silicas were reacted under these conditions and the results are listed in Table IV, which also includes comparable results for geothermal silica from Table III.

The fume silica and silica flour form phases additional to silicon nitride except at the higher temperature. Although fume silica has a small particle size, its

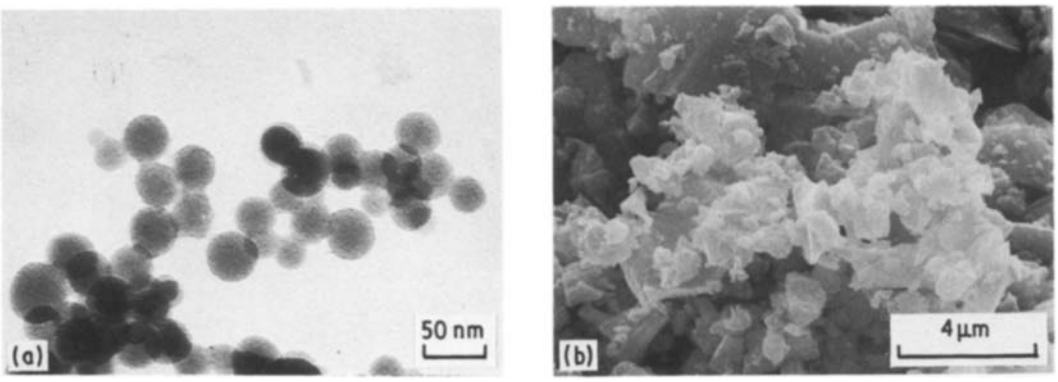

Figure 2 (a) Transmission electron micrograph of geothermal silica particles (after Owers [2]); (b) scanning electron micrograph of silica flour particles.

TABLE II Particle characteristics of silicas and carbon

	Silica*				Carbon[†]
	GS	FS	CS	SF	
Specific Surface Area ($m^2 g^{-1}$)[‡]	54	187	119	5.2	–
Mean particle size (μm)[§]	0.04	0.012	0.01	1.5[¶]	6.0
Mean agglomerate size (μm)[¶]	14	23	15	none	none
Specific bulk volume ($ml g^{-1}$)	3.2	20.0	10.7	1.8	3.0

*Code refers to Table I.

[†] Carbon lampblack: Baird and Tatlock Ltd, UK.

[‡] By nitrogen adsorption.

[§] By transmission electron microscopy.

[¶] By scanning electron microscopy.

TABLE III Results of carbothermal reduction and nitridation of geothermal silica

C/SiO_2 mol ratio	Time* (h)	Crystalline phases by XRD		Total wt. loss (%)[§]	Theoretical wt. loss (%)[¶]
		Major ($\alpha:\beta$)[†]	Minor[‡]		
15:0	6	95:5(br)	C	83.6	80.6
7.5	6	85:15	C	70.3	68.9
6.1	6	90:10	C	65.3	65.0
6.1	10[1]	85:15	C	65.0	65.0
5.5	2	95:5	S, C(tr)	64.1	63.1
5.5	6	95:5	C(tr), Cr(tr)	65.3	63.1
5.5	10	90:10	C, Cr	64.8	63.1
5.5	2[2]	90:10	C	64.1	63.1
5.0	6	90:10	Cr(tr)	61.9	61.1
2.0	6	S, Cr	α, β	41.0	44.5

*All runs fired at 1400° C except [1] 1350° C and [2] at 1440° C.

[†] Calculated from XRD peak heights from [9] (br: broad lines).

[‡] Minor is < 10%; C, carbon; S, silicon oxynitride; Cr, cristobalite; tr, trace.

[§] Total weight loss calculated from weight loss after decarburization.

[¶] Theoretical weight loss calculated from Reaction 1 assuming all the residual carbon is oxidized.

agglomerates are large and it also has a large bulk volume compared to the carbon lampblack (Table II). The difficulty in mixing results is having unreacted silica which is present as cristobalite. Silica flour has coarser particles, which contribute similarly to the formation of cristobalite.

Precipitated silica has overall more β-Si_3N_4. A vapour-phase reaction would favour α-Si_3N_4 [5] (Reaction 2 below), while the presence of any liquid phase or iron impurity favours β-Si_3N_4 [11, 12].

$$\left.\begin{array}{l} SiO_2 + C \rightarrow SiO(g) + CO(g) \\ 3SiO(g) + 2N_2(g) + 3C \rightarrow Si_3N_4 + 3CO(g) \end{array}\right\} \quad (2)$$

Precipitated silica would be expected to form more liquid phase because of the high sodium and iron content (iron forms iron silicide which is liquid at 1250° C). Siddiqi and Hendry [12] have concluded that silica should be free of iron for the production of α-Si_3N_4, as iron not only increases β-Si_3N_4, but also produces SiC. The amount of iron present in all silicas (< 1%) is insufficient to produce SiC below 1440° C. Geothermal silica with the lowest iron content produces the highest α/β ratio free of other phases at two different temperatures (Table IV).

The weight losses in most cases were slightly more than the theoretical, suggesting some volatilization of

TABLE IV Results of carbothermal reduction and nitridation of silicas

C/SiO_2 mol ratio	Type of silica	Temperature (° C)/ time (h)	Crystalline phases by XRD		Total wt. loss (%)*	Theoretical wt. loss (%)[†]
			Major ($\alpha:\beta$)	Minor (< 10%)		
6.1	GS	1350/10	85:15	C	65.0	65.0
6.1	GS	1400/6	90:10	C	65.3	65.0
5.5	GS	1440/2	90:10	C	64.1	63.1
6.1	FS	1350/10	90:10	C, Cr	63.7	65.0
6.1	FS	1400/6	90:10	C, Cr	64.5	65.0
5.5	FS	1440/2	80:20	C	63.8	63.1
6.1	CS	1350/10	80:20	C	66.5	65.0
6.1	CS	1400/6	75:25	C	66.0	65.0
5.5	CS	1440/2	70:30	C	66.8	63.1
6.1	SF	1350/10	80:20	C, Cr, S	64.1	65.0
6.1	SF	1400/6	85:15	C	64.8	65.0
5.5	SF	1440/2	90:10	C	64.5	63.1

C = carbon, Cr = cristobalite, S = silicon oxynitride.

*Total weight loss calculated from weight loss after decarburization.

[†] Theoretical weight loss calculated from Reaction 1 assuming all the residual carbon is oxidized.

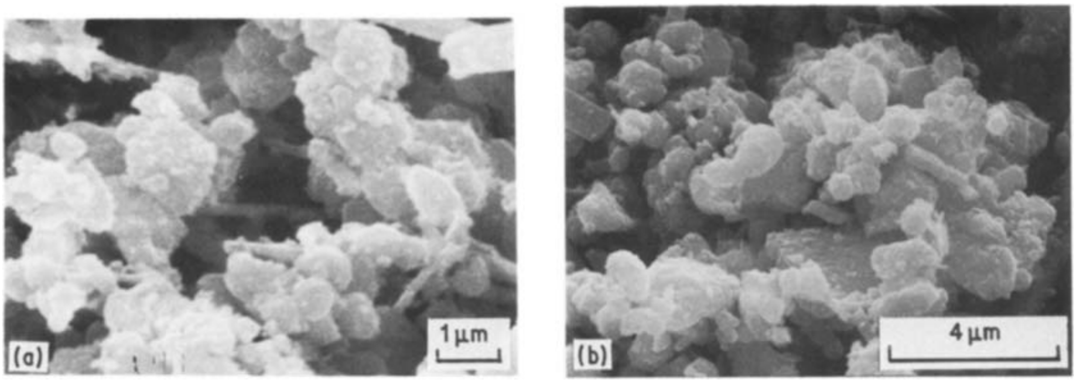

Figure 3 Scanning electron micrographs of α-Si_3N_4 crystals in samples of C/SiO_2 = 5.5 nitrided at 1440° C for 2 h: (a) geothermal silica, (b) fume silica.

silica as silicon monoxide. The silicas which formed cristobalite or silicon oxynitride had slightly lower weight losses as would be expected.

The α-Si_3N_4 crystals formed from geothermal silica are slightly smaller ($\sim 0.6\,\mu m$) and more fibrous than those from other silicas were also fibrous similar to geothermal silica but had larger crystals than fume silica (Fig. 3).

A fibrous morphology was also observed by other workers [3, 8] and the sizes of their α-Si_3N_4 crystals were about the same size as geothermal silica. A small particle size of α-Si_3N_4 is preferred if it is to be sintered to make dense β-Si_3N_4 [13]. This enhances the usefulness of α-Si_3N_4 made from geothermal silica.

4. Conclusions

Geothermal silica from Wairakei, New Zealand is a good source of silica for producing silicon nitride, being easy to mix with carbon lampblack and reasonably pure, with a low iron content. It can be converted to an economically valuable material containing up to 95/5 ratio of α-Si_3N_4 to β-Si_3N_4. Comparative nitriding experiments with three other commercially available fine-grained silicas show that under identical reaction conditions, geothermal silica is at least as good as, if not a better than, other raw materials for silicon nitride production.

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