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Synthesis of silicon and silicon nitride powders by vapour-phase reactions

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The Bureau of Mines is investigating vapour-phase reactions for syntheses of high-purity, nanometre-sized silicon and Si_3N_4 powders suitable for industrial applications. In this study, submicrometre-sized silicon powder was formed by a vapour-phase reaction of $SiCl_4$, NH_3, and magnesium vapor at temperatures ranging from 950–1050 °C. The silicon was subsequently nitrided to form Si_3N_4 at 1150 °C.

1. Introduction

Silicon nitride, because it possesses high hot-strength properties and hardness, good thermal shock resistance, high fatigue life, chemical inertness, and electrical resistance, has been used and is being considered as a substitute material for machine tools [1–3], engine parts [4], and bearings [5]. Metal components currently being used contain high percentages of strategic and critical metals such as tungsten, cobalt, chromium and nickel. The above properties make Si_3N_4 an excellent candidate for substituting these metal components.

The increasing demand for higher productivity and lower manufacturing costs of improved machine tools capable of operating at higher speeds is imposing a need for new processing development. High machine speeds generate higher stress and temperature than metal cutting tools are capable of and thus require use of more refractory ceramics in the machine-tool materials. Engine performance will also benefit from ceramic components that can operate at higher temperatures, thus saving fuel and increasing turbine efficiency. Si_3N_4 bearings have also been shown to have 10–50 times better fatigue life than the commercial high-quality steel bearing [5]. However, the limiting factors in greater widespread use of Si_3N_4 are the lack of high-quality and low-cost Si_3N_4 powder [3].

Methods for producing the Si_3N_4 powder have been reviewed by many authors [6–8]. The most important processes for synthesis of Si_3N_4 powder are listed in Table I. The processes can be divided generally into five categories: (a) solid-state reactions of silicon and nitrogen, and SiO_2, carbon and nitrogen, (b) combustion reaction of silicon and nitrogen, (c) vapour-phase reaction of $SiCl_4$ and NH_3, (d) liquid-phase reaction of $SiCl_4$ and NH_3 to form an imide followed by decomposition of the imide, and (e) vapour-phase reaction of SiH_4 and NH_3. The solid state reaction is kinetically very slow, requiring long reaction times and high reaction temperatures. The solid-state reaction processes produce coarse Si_3N_4 which has to be milled and purified. The combustion synthesis requires a nitrogen pressure over 700 atm to sustain the combustion [9]. The vapour-phase reaction of $SiCl_4$ and NH_3 produces a thin film of Si_3N_4, but this process is not suitable for mass production of the Si_3N_4 powder [10]. The decomposition of imide requires a temperature over 1600 °C and very often produces fibrous Si_3N_4 which is difficult to handle [11]. The vapour-phase reactions of $SiCl_4$ and NH_3, and SiH_4 and NH_3 rely on a laser [12] or a plasma [13] to promote the reaction. Commercial application of these processes would be very energy intensive.

In earlier Bureau of Mines research for the preparation of TiN powder as a substitute for imported tungsten used in metal cutting tools and wear-resistant applications, submicrometre TiN powder was produced by vapour-phase reactions of $TiCl_4$ with magnesium vapour in the presence of anhydrous NH_3 at 1000 °C [14, 15]. The vapour-phase reaction technique was also applied to produce titanium powder by other workers [16].

The calculated heats of reaction for the formation of Si_3N_4 by reaction of $SiCl_4$ and NH_3, for formation of silicon by reduction of $SiCl_4$ with magnesium vapour, for formation of Si_3N_4 by nitridation of silicon with NH_3, and for formation of Si_3N_4 by reaction of $SiCl_4$, magnesium vapour and NH_3, are shown in Fig. 1. The data show that the reaction of $SiCl_4$ and NH_3 is endothermic, while the reactions of $SiCl_4$ and magnesium, silicon and NH_3, and $SiCl_4$, magnesium vapour and NH_3 are exothermic. It appears that addition of magnesium to $SiCl_4$, and addition of magnesium to $SiCl_4$ and NH_3 reactions can energize the reactions to enhance formation of silicon and Si_3N_4 respectively. This approach of using magnesium addition instead of laser or plasma energy, was attempted in this study for syntheses of silicon and Si_3N_4 powders.

After considering the use of $SiCl_4$ or SiH_4 as a starting material, $SiCl_4$ was selected. $SiCl_4$ is an abundant resource, that can be obtained by chlorination of SiO_2 or as a by-product of zirconium manufactured by chlorination of zircon [17] and is easier to handle than SiH_4 which is flammable and explosive.

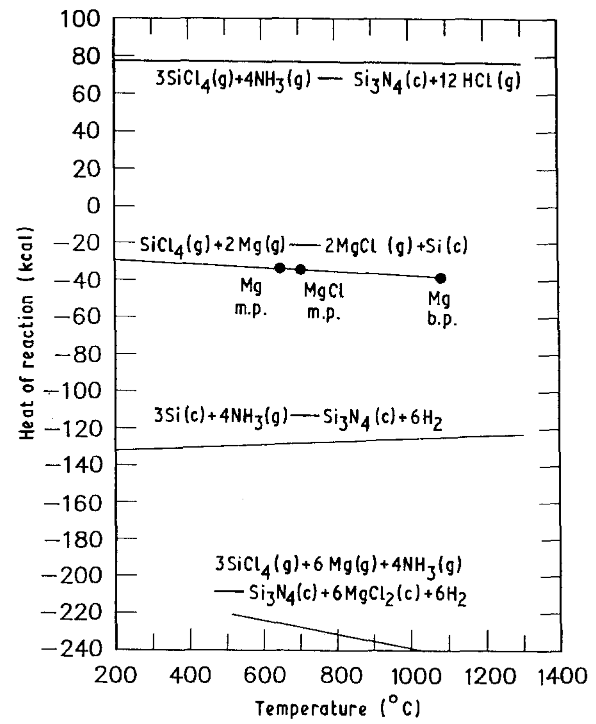

Figure 1 Heat of reaction for the reactions of $SiCl_4$ and NH_3, $SiCl_4$ and magnesium, silicon and NH_3, and $SiCl_4$, magnesium and NH_3.

TABLE I Various processes for synthesis of silicon nitride

Process	General reaction
Nitridation of silicon	$3Si + 2N_2 \xrightarrow[1200-1500\,^{\circ}C]{} Si_3N_4$
Carbothermic reduction of SiO_2 (new route with aqueous or organic sol–gel)	$3SiO_2 + 6C + 2N_2 \xrightarrow[1200-1700\,^{\circ}C]{} Si_3N_4 + 6CO$
Combustion synthesis	$3Si + 2N_2 \xrightarrow[700\ atm]{} Si_3N_4$
Vapour-phase reaction	$3SiCl_4 + 4NH_3 \xrightarrow[1100-1350\,^{\circ}C]{} Si_3N_4 + 12HCl$
Imide decomposition	$SiCl_4 + 6NH_3 \xrightarrow[-30\ to\ +70\,^{\circ}C]{} Si(NH)_2 + 4NH_4Cl$ $3Si(NH)_2 \xrightarrow[1600\,^{\circ}C]{} Si_3N_4 + 2NH_3$
Laser synthesis	$3SiH_4 + 4NH_3 \xrightarrow[CO_2\ laser]{} Si_3N_4 + 12H_2$
Plasma synthesis	$3SiH_4 + 4NH_3 \xrightarrow[plasma]{} Si_3N_4 + 12H_2$ $3SiCl_4 + 4NH_3 \xrightarrow[plasma]{} Si_3N_4 + 12HCl$

The initial objectives of this research were to determine the feasibility for formation of silicon and Si_3N_4 by vapour-phase reactions of $SiCl_4$ and magnesium vapour in the presence of NH_3. The final objective will be directed toward developing a low-cost continuous process for mass production of high-quality Si_3N_4 powder. This paper discusses initial test results for the feasibility study.

2. Experimental procedure

A schematic flow diagram for producing silicon powder is shown in Fig. 2. The principal laboratory apparatus was a vertical reactor made of type 310 stainless steel tubing, 7.6 cm diameter and 91.4 cm high, and an electrostatic precipitator (ESP). Details of the reactor are published elsewhere [14]. The ESP was used to collect the powder suspended in the exiting gas stream from the reactor and was maintained at 150–180 °C to prevent moisture and unreacted $SiCl_4$ vapour from reacting with silicon and $MgCl_2$ powders. Materials used were 99% pure $SiCl_4$ and 99.9% pure magnesium. Other materials, argon, NH_3 and nitrogen, were of 99.99% minimum purity.

2.1. Synthesis of silicon powder

Synthesis of silicon powder is represented by the following vapour reactions of $SiCl_4$ and magnesium vapour in the presence of NH_3:

$$SiCl_4\ (g) + 2Mg(g) \xrightarrow[950-1050\,^{\circ}C]{NH_3(g)} 2MgCl_2(g) + Si(c) \tag{1}$$

At 1030 °C, $\Delta H = -37.7$ kcal and $\Delta F = -79.6$ kcal [18].

The NH_3 gas was introduced into the reaction to test whether the produced silicon could react with NH_3 simultaneously to form Si_3N_4. The gas flow rates of $SiCl_4$ and NH_3 and the amount of magnesium needed for the reaction were obtained based on the formulated reaction

$$\begin{aligned} 3SiCl_4(g) + 4NH_3(g) + 6Mg(g) &\rightarrow Si_3N_4(c) \\ &+ 6MgCl_2(g) + 6H_2 \end{aligned} \tag{2}$$

Prior to starting a run, the reactor was evacuated using a mechanical pump then backfilled and purged with argon gas. After a satisfactory leak check of the reactor, argon was flowed through the reactor while it was heated to a desired temperature between 950 and 1050 °C, over a maximum 2 h period. The maximum operating temperature of the reactor was limited to 1100 °C by the reactor materials of construction and the furnace available.

Stoichiometric amounts of $SiCl_4$ and NH_3 together with an excess of the stoichiometric requirement of magnesium reductant were used as feed to the reactor. A total of 2980.5 ml min^{-1} gas were fed to the reactor and it was composed of 0.5 ml min^{-1} $SiCl_4$, 140 ml min^{-1} NH_3, 140 ml min^{-1} Ar to the magnesium pot for dispersion of magnesium vapor, and 2700 ml min^{-1} Ar to the $SiCl_4$ line to prevent plugging. This resulted in a gas residence time of about 1 min based on the total volume of the reactor and the total gas flow rate. Three concentric tubes extended downwards through one-third of the reactor. The $SiCl_4$ was pumped from a graduated cylinder through the inside tube at rate of 0.5 ml min^{-1} using a peristaltic pump and entered the reaction zone. Argon gas entered through the inside tube, and acted as a purge and carrier gas to keep the $SiCl_4$ discharge line free from blockage due to deposited products. Argon gas also entered through the outside tube and acted as a carrier gas to transport the magnesium vapour from the mag-

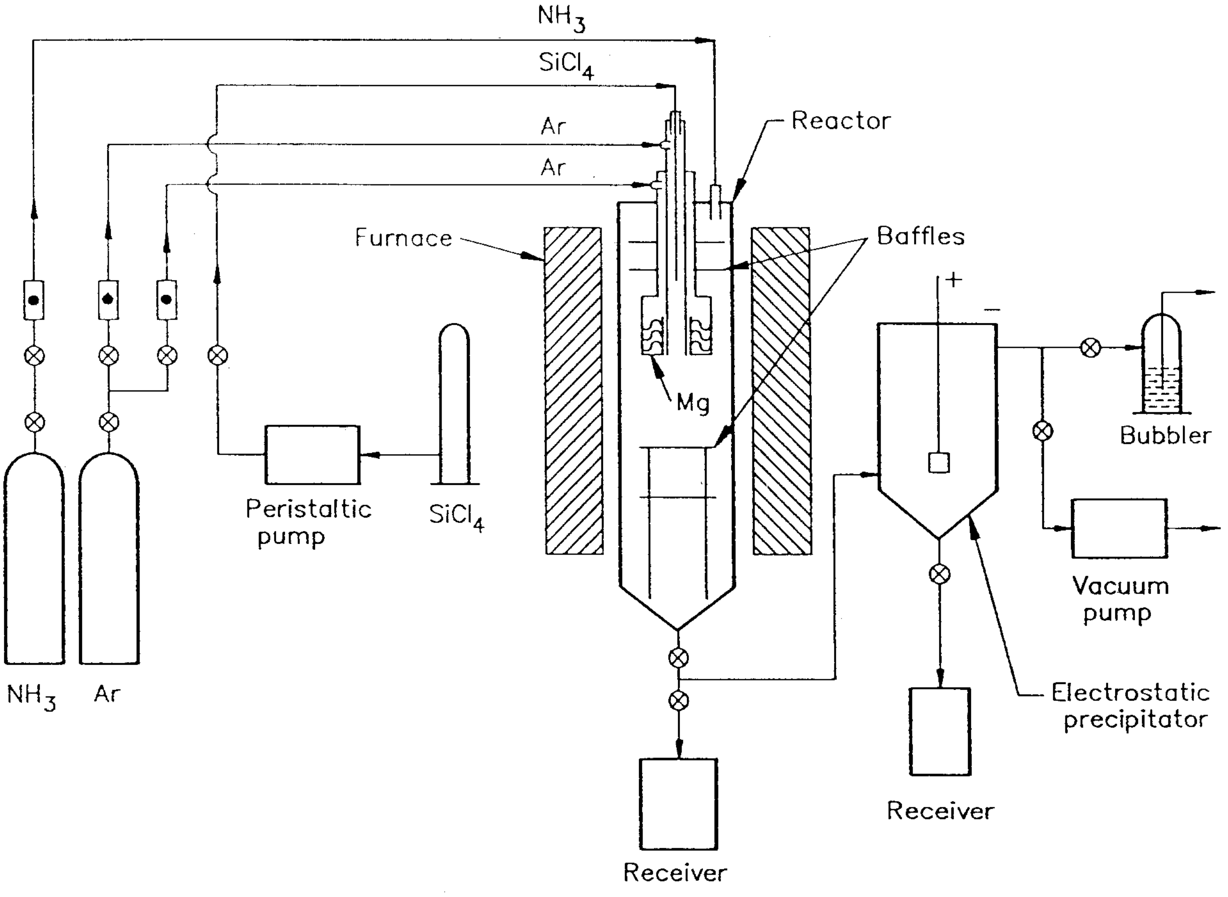

Figure 2 Schematic flow diagram of experimental apparatus for synthesis of silicon powder.

nesium pot to the reaction zone. Ammonia entered the reaction zone through a separate tube on the reactor's top plate.

Argon gas carrying suspended silicon powder exited from the reactor and passed into the ESP which was operated at 5–10 kV and 0.1 mA. The collected powder flowed by gravity into a receiver attached to the bottom of the ESP. Some powder was also recovered at the bottom of the reactor.

2.2. Purification of silicon powder

Powders obtained from the ESP and the bottom of reactor were mixed. The powder was purified by either acid leaching or vacuum distillation. The powder was leached with 23 wt % HCl solution at 15 wt% solids at 100 °C for 1 h. The leached powder was filtered and dried for sampling. Vacuum distillation was also used [15]. The retort was evacuated to an ultimate pressure of about 20 μm using a mechanical pump in combination with an oil diffusion pump. The crude powder was then gradually heated to 880 °C and held at that temperature for 2 h at a pressure between 30 and 50 μm. At 880 °C, the vapour pressures of magnesium, $MgCl_2$ and silicon obtained from the literature are, respectively, about 70 mm, 5 mm and zero, as shown in Fig. 3. At this temperature, only magnesium and $MgCl_2$ vaporize. At the end of the heating period, the retort was cooled to ambient temperature, backfilled with argon and the crucible with purified powder removed.

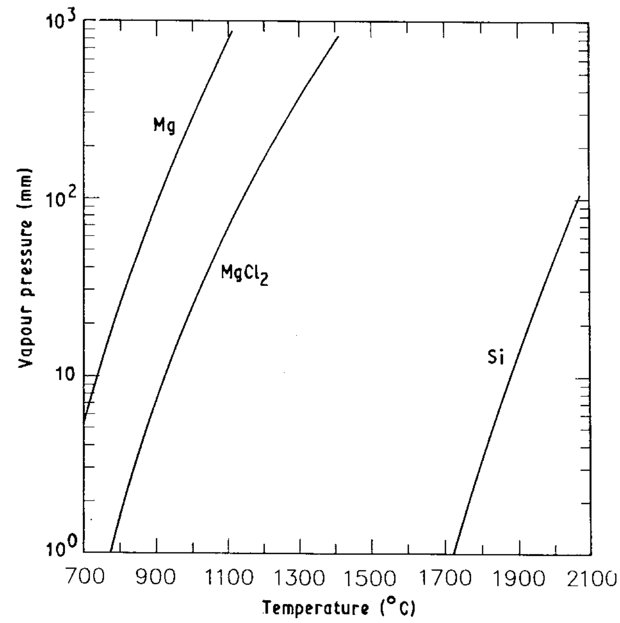

Figure 3 Vapour pressures of magnesium, $MgCl_2$ and silicon pertinent to vacuum distillation. Melting temperature Mg = 651 °C; $MgCl_2$ = 712 °C; Si = 1420 °C.

2.3. Synthesis of Si_3N_4 powder

A horizontal tubular alumina reactor, which could be operated up to 1300 °C, was used for nitridation of silicon. Both ends of the reactor were sealed for operating under a controlled atmosphere. After silicon powder was loaded into the reactor, the reactor was evacuated and purged with nitrogen. After a satisfactory leak check of the apparatus, the unit ran with a flow of 250 ml min^{-1} nitrogen and was heated up to 1000 °C. From 1000 °C to a final temperature of 1150 °C, an additional 250 ml min^{-1} NH_3 was flowed into the reactor. The reactor was held at that temperature for 15 min and then the furnace was shut off to let the reactor cool naturally to ambient temperature and a sample was then removed.

Powders produced by reactions of $SiCl_4$ and magnesium, by purification of silicon, and by nitridation of silicon were characterized by X-ray powder diffraction. Particle size and particle-size distribution of silicon and Si_3N_4 were analysed using a Horiba Motel 707 particle-size distribution analyser.

3. Results and discussion

Powders produced by reaction of $SiCl_4$ and magnesium vapour in the presence of NH_3 at 950 and 1050 °C, respectively, for 2 and 4 h were evaluated. Two or more runs were conducted at each temperature. About 10–20 g Si powder were produced from each run. Both powders contain a primary phase of $MgCl_2$, a minor phase of silicon and a trace of $MgCl_2 \cdot 2H_2O$. Based on the chemical reaction of Equation 1, the powder should contain 87.1 wt % $MgCl_2$ and 12.9 wt% Si. The amount of powder produced agree well with the theoretical result. The 1050° C powder contained a barely detectable trace of $MgCl_2 \cdot 2H_2O$, while $MgCl_2 \cdot 2H_2O$ was very pronounced in the powder obtained at 950° C. Temperature was not seen to affect the size of silicon. However, the desired Si_3N_4 was not detected in any of the tests.

The powders prepared at 1050 °C were selected for further purification studies. Two purification methods, vacuum distillation and acid leaching, were tested. Both techniques show that the purified powders contained a primary phase of silicon and minor phases of $TiSi_2$, TiN and FeSi, while $MgCl_2$ and magnesium were not detected. It is believed that the $TiSi_2$, TiN and FeSi contaminations were caused by the bottom part of a reactor baffle made of titanium and by the stainless steel reactor. During silicon formation, some of the silicon reacted with titanium and iron and some of the titanium was nitrided. This contamination could be prevented by using a suitable material such as Si_3N_4 or SiC to line the reactor and to construct the baffle.

The vacuum-distilled powder was nitrided at 1150 °C for 15 min using a mixture of 50 vol% NH_3 and 50 vol % N_2. X-ray diffraction data show that the powders contain a primary phase of α-Si_3N_4, minor

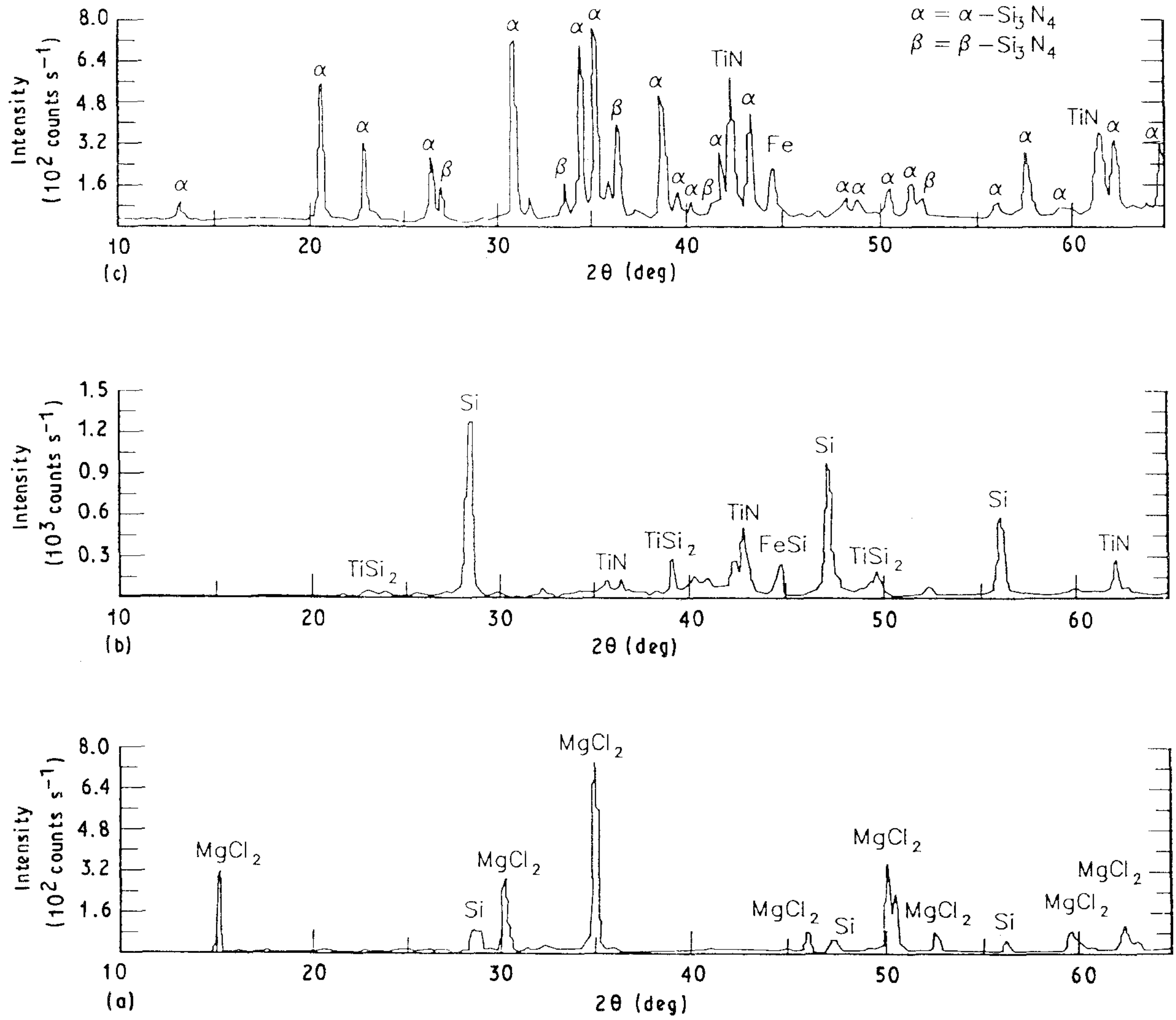

Figure 4 X-ray diffraction patterns of (a) powder obtained from reaction of $SiCl_4$ and magnesium at 1050 °C, (b) vacuum-distilled powder at 880 °C, and (c) nitrided silicon powder at 1150 °C.

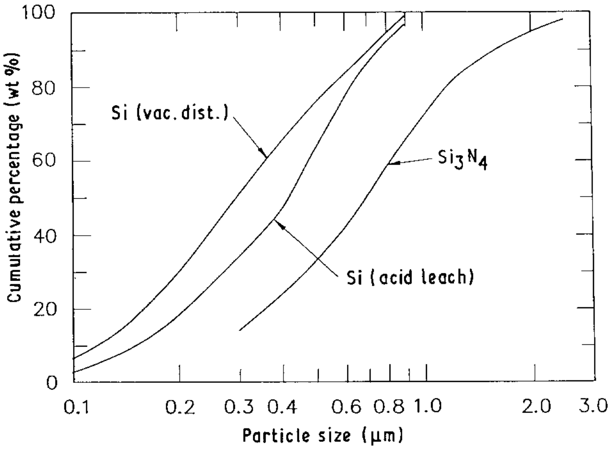

Figure 5 Particle-size distributions of vacuum-distilled and acid-leached silicon powders and Si_3N_4 powder.

phases of β-Si_3N_4 and TiN and a trace of iron. Thus, the silicon was easily nitrided to produce the desired phase of α-Si_3N_4 at 1150 °C, a much lower temperature than used for nitriding commercial silicon. Commercial silicon is nitrided at a temperature ranging from 1200–1500 °C for a longer duration [6, 8]. The phases developed during the reaction of $SiCl_4$ and magnesium at 1050 °C, vacuum distillation, and nitridation steps described above, are shown in Fig. 4.

Median particle sizes of the vacuum-distilled silicon, acid-leached silicon and Si_3N_4 powders were found to be, respectively, 0.29 ± .32 μm, 0.42 ± .26 μm and 0.65 ± .57 μm. The size of acid-leached silicon was larger than the size of vacuum-distilled silicon, which may be due to agglomeration. The size of Si_3N_4 powder was twice as large as the original size of silicon used for nitridation. Typical particle-size distributions of the powders are shown in Fig. 5. The size of the Si_3N_4 ranges from 0.1–3 μm, while the size of commercial Si_3N_4 ranges from 0.1–8 μm for an identical median particle of Si_3N_4. However, the Si_3N_4 was not ground, while commercial Si_3N_4 is often obtained by grinding coarse Si_3N_4.

4. Conclusion

These studies show that submicrometre-sized silicon can be produced by vapour-phase reaction of $SiCl_4$ and magnesium in the presence of NH_3 at a temperature ranging from 950–1050 °C. Silicon powder and by-product $MgCl_2$ can be separated by vacuum distillation or acid leaching. The silicon powder can be nitrided to form submicrometre sized Si_3N_4 at 1150 °C which is relatively lower than the temperature used by industries for nitriding the commercial silicon.

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