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A synthesis of mono-crystalline silicon nitride filaments

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A catalytic process for synthesis of pure, mono-crystalline α-Si_3N_4 filaments, with iron particles of some micrometres in diameter as catalyst, was investigated. Silicon subhydrides, produced *in situ* by reaction of silicon powder with hydrogen at 1300 °C, were used as the silicon source. Experiments with molecular nitrogen as the nitrogen source failed, but the use of ammonia was successful. At 1300 °C mono-crystalline α-Si_3N_4 filaments up to some micrometres in diameter and some centimetres in length were successfully produced. These filaments exhibit tensile strength values between 30 and 50 GPa, and Young's modulus values between 550 and 750 GPa.

1. Introduction

Monolithic ceramics developed during the last decade exhibit excellent mechanical properties. For applications at very high temperatures, creep still represents a problem. A more general disadvantage of monolithic ceramics, however, results from their limited damage tolerance. Both problems can only be overcome by the use of fibre-reinforced materials, so-called ceramic matrix composites. Reinforcement fibres available for the production of such materials are of limited usefulness. Carbon fibres are mechanically stable up to at least 2000 °C, but suffer severe oxidation above 500 °C. Therefore the problem is shifted to complex oxidation protection systems. The silicon carbide-based fibres, which are produced in an analogous way to the carbon fibre via the polymer route, are non-stoichiometric, amorphous or polycrystalline. Alumina- and mullite-based fibres, produced by various routes, are subject to similar problems. As a consequence, the high temperature properties are poor, mainly because of recrystallization and reactions between the components of the fibre material. Whiskers (which are monocrystalline) and platelets are of limited usefulness for other reasons, such as low volume fraction, orientation problems and cancerous properties [1–3].

The problem may be solved with monocrystalline filaments, which can easily be produced via the vapour-liquid-solid (VLS) process [4–6]. They are monocrystalline like whiskers, but exhibit a length-to-diameter ratio which is orders of magnitudes higher, i.e. they exhibit a length of some centimetres and a diameter of some micrometres.

For all these reasons, we investigated the possibility of producing silicon nitride filaments [7]. The idea was to use iron particles as catalyst and, for environmental reasons, silicon hydrides instead of silicon chlorides as the silicon source. Molecular nitrogen and ammonia were studied as the nitrogen source.

2. Experimental procedure

2.1. Reactor

The experimental reactor is shown in Fig. 1. The silicon hydrides are produced by reacting silicon powder with hydrogen at 1200 °C. At a hydrogen pressure of 0.1 MPa, formation of monosilane should be favoured for thermodynamic reasons, but silicon subhydrides, SiH_x, are formed exclusively. The iron particles of some micrometres in diameter are placed on an alumina ceramic substrate. The reaction temperature was 1300 °C in all cases. In the absence of nitrogen and especially ammonia, crystalline silicon filaments are obtained. This result emphasizes that the ratio between SiH_x and NH_3 in the gas phase is decisive for the formation of stoichiometric silicon nitride.

2.2. Analytical methods

Scanning electron microscopy (SEM) was used for analysing the morphologies and growth features of the catalyst particles and the filaments. Electron probe microanalysis (EPMA) was employed for analysing the silicon content of the catalyst particles at the top of the filaments, and the filaments themselves. The crystalline perfection of the filaments was studied by X-ray diffraction (XRD) using CuK_α radiation. In order to analyse the silicon nitrogen bonds in the filaments, infrared studies were performed using the KBr technique. Finally, the strength of the filaments was measured using an Instron machine. The filaments investigated had a diameter of $\sim 3\ \mu m$ and a gauge length between 6 and 10 mm.

3. Thermodynamics

The overall reactions of Si_3N_4 formation from silicon subhydrides, SiH_x, and N_2 or NH_3, respectively, are as follows:

$$3SiH_x + 2N_2 \rightarrow Si_3N_4 + 3x/2H_2 \quad (1)$$

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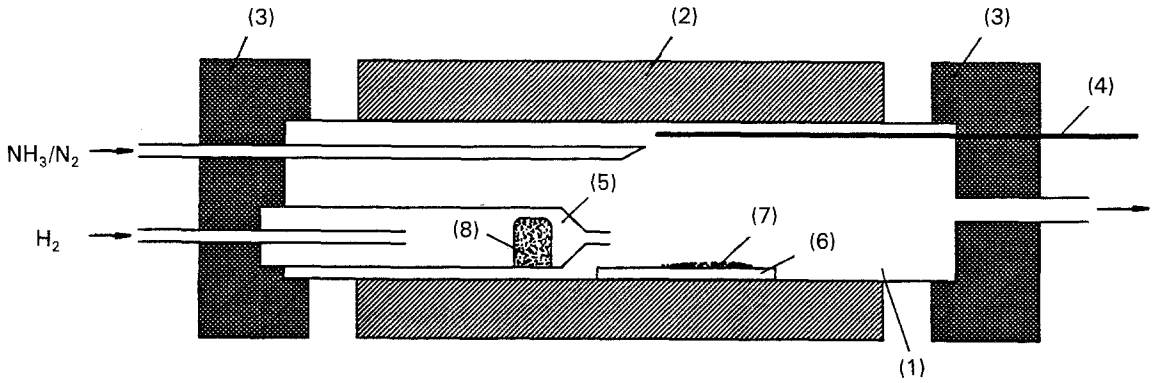

Figure 1 Diagram of the experimental reactor. (1) Reactor tube, (2) furnace, (3) water-cooled flanges, (4) thermocouple, (5) internal reactor tube for SiH_x production, (6) substrate (alumina), (7) catalyst particle, (8) silicon powder.

$$3SiH_x + 4NH_3 \rightarrow Si_3N_4 + (6 + 3x/2)H_2 \quad (2)$$

Both reactions are strongly exergonic up to very high temperatures. In the presence of a catalyst such as iron the single steps of the catalysed reaction are as follows.

1. Dissociative adsorption of SiH_x at the catalyst surface and formation of an iron–silicon alloy, Fe_ySi_z.
2. Dissociative adsorption of N_2 or NH_3, respectively, at the catalyst surface and diffusion of nitrogen atoms through the catalyst particle.
3. Precipitation of Si_3N_4 from the catalyst particle.

For discussion of step 1, the iron–silicon phase diagram is presented in Fig. 2. At the reaction temperature of 1300 °C, dissolution of silicon in iron yields a solid alloy up to 22 at %. With still higher silicon contents, up to about 37 at %, a melt is formed. Further silicon dissolution by dissociation of SiH_x is only possible by simultaneous precipitation of free silicon. The driving force of silicon precipitation is given by the reactions 3 to 5:

$$Fe_ySi_z + SiH_x \rightarrow Fe_ySi_{z+1} + x/2H_2 \quad (3)$$

$$Fe_zSi_{y+1} \rightarrow Fe_ySi_z + Si \quad (4)$$

$$SiH_x \rightarrow Si + x/2H_2 \quad (5)$$

Reaction 5 is strongly exergonic. The Gibbs free enthalpy at 1300 °C amounts to $-230\,kJ\,mol^{-1}$.

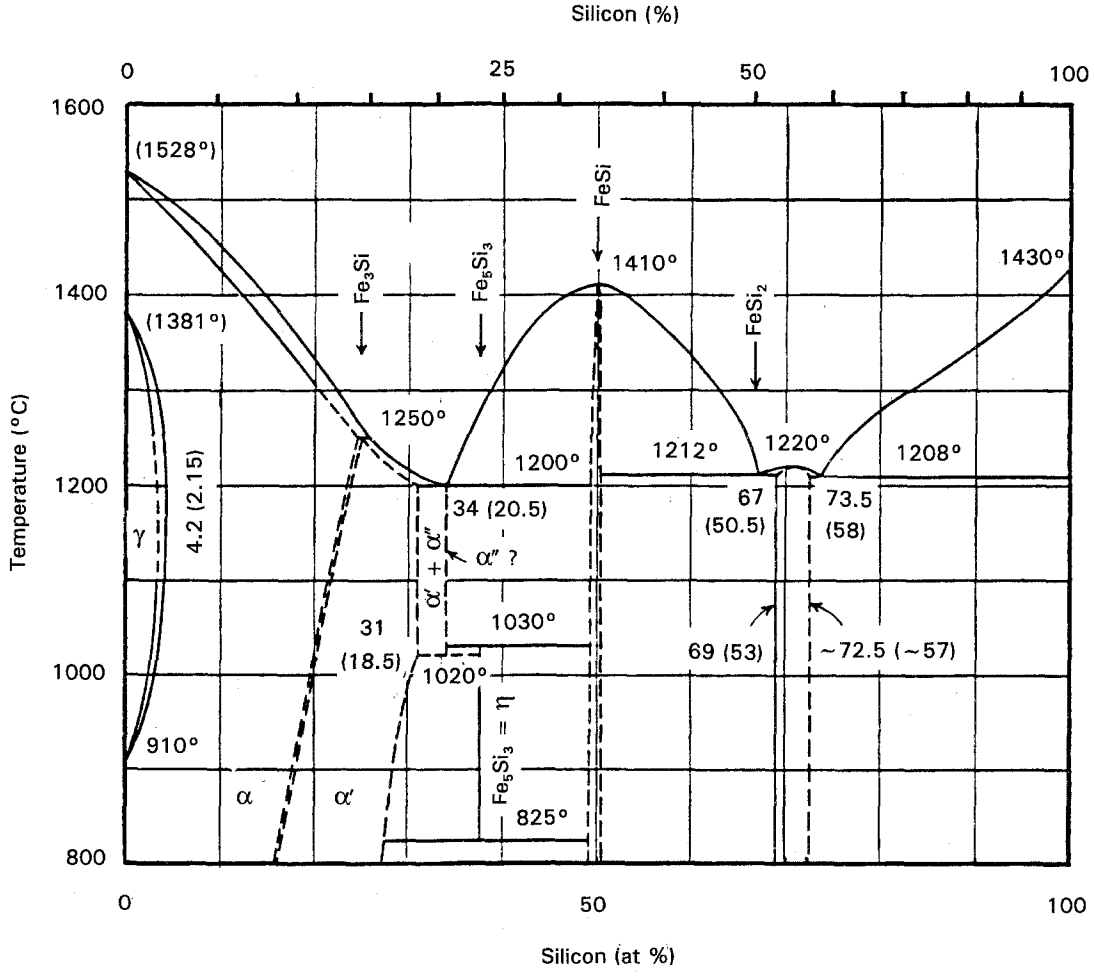

Figure 2 The iron-silicon phase diagram [8].

Consideration of the dissociation of N_2 or NH_3, respectively, shows significant differences. The Gibbs free enthalpies of dissociation at 1300 °C are as follows: N_2, + 373 kJ mol^{-1}; NH_3, − 132 kJ mol^{-1}. Experimental results on filament formation showed that the filaments are not hollow, but massive. For this reason, volume diffusion of nitrogen atoms has to be assumed. Solubility data of nitrogen in pure iron are shown in Fig. 3. At 1300 ° C the solubility of nitrogen in γ-iron is very low. In the presence of silicon the nitrogen solubility is further decreased. From these thermodynamic considerations it may be concluded that the growth rate of Si_3N_4 filaments is kinetically controlled by the low nitrogen solubility in the possible ferrosilicon alloys.

4. Results and discussion

4.1. Influence of the substrate

For the vapour-liquid-solid process it is essential that the catalyst particle is located at the tip of the growing filament. This can only occur if the substrate material is not wetted by the catalyst material. Experiments in flowing hydrogen atmosphere with Al_2O_3, TiN, glassy carbon and graphite showed wetting of TiN and complete wetting of the graphite (including partial gasification). A non-wetting situation was found with Al_2O_3 and glassy carbon. These results were expected, because wetting requires strong selective interactions which, in the case of iron, can only result from electron/electron interactions. The work of adhesion W_{SL} is given by [10]:

$$W_{SL} = W_{SL}^{LW} + W_{SL}^{E} \quad (6)$$

W_{SL}^{LW} = Lifshitz-van der Waals interactions; W_{SL}^{E} = electron/electron interactions. Glassy carbon, which represents a semi-conductor only, and Al_2O_3, which represents an insulator, are thus not wetted. For all further experiments an alumina ceramic was used as the substrate material.

4.2. Formation of filaments

Experiments on filament growth were performed at normal pressure, 1300 °C, various flow rates and partial pressures of SiH_x and N_2 or NH_3, respectively. Deposition of pure silicon was studied with hydrogen volume flows of 5 and 8.7 l h^{-1} (ntp). According to the preceding *in situ* formation of SiH_x the concentrations of SiH_x in hydrogen were 0.068 and 0.04%. With 5 l h^{-1} hydrogen flow, the conversion of the SiH_x on

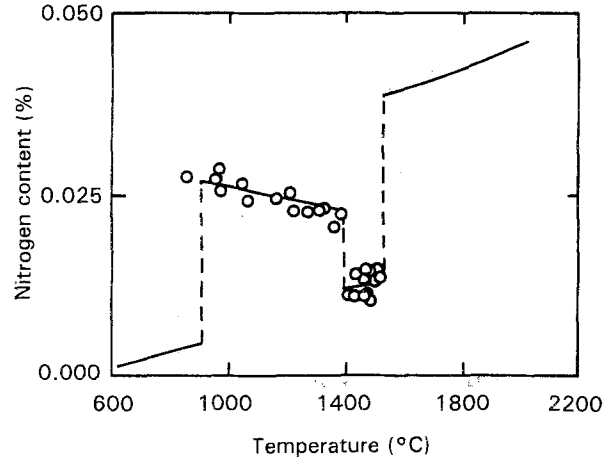

Figure 3 Solubility of nitrogen in pure iron [9].

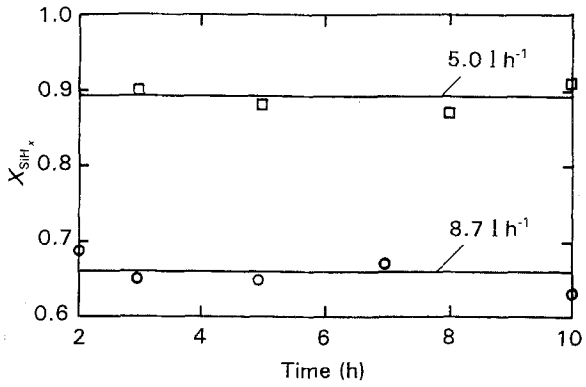

Figure 4 Degree of SiH_x conversion at the iron catalyst particles as function of the reaction time; hydrogen flow rates of 5.0 and 8.7 l h^{-1} (ntp); 1300 °C reaction temperature.

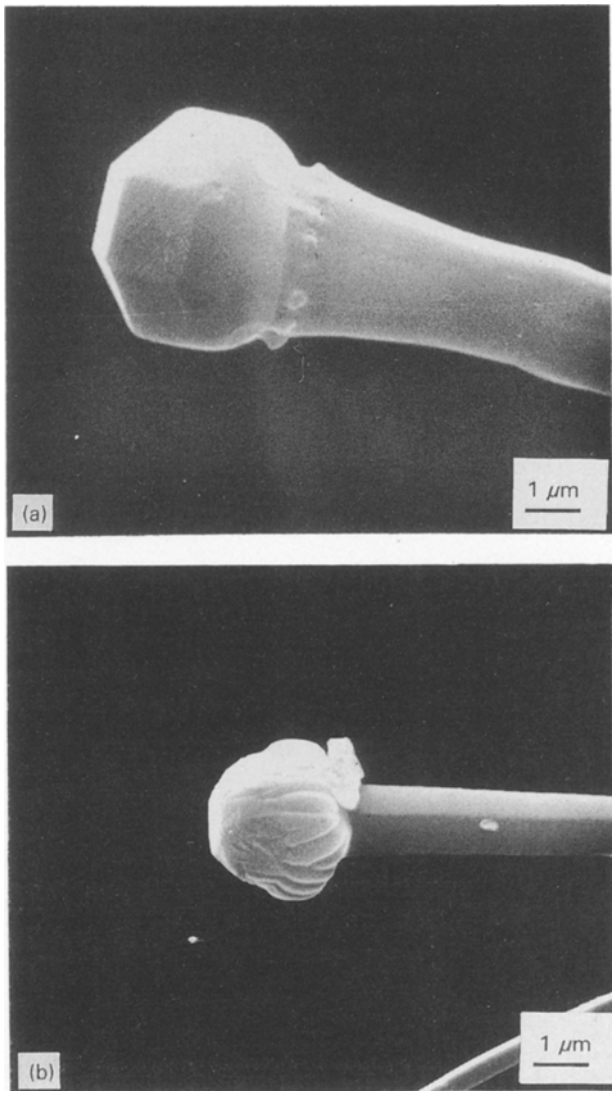

Figure 5 Scanning electron micrographs of filaments obtained at hydrogen flow rates of (a) 5 and (b) 8.7 l h^{-1}; 1300 °C reaction temperature.

the catalyst was ~ 0.9, with $8.7\,l\,h^{-1} \sim 0.65$ (Fig. 4). This result reveals that the silicon deposition is mainly controlled by the residence time. X-ray examinations of the filaments grown were not performed, but it can be assumed that they are crystalline.

With the addition of nitrogen only, the growth rate of Si_3N_4 filaments was extremely low. For this reason the filaments could not be characterized by X-ray, but only with i.r. The i.r. analysis showed the presence of α-Si_3N_4. Further studies were focused on ammonia, where nitrogen was used as diluent or carrier gas (volume ratio 1:1). Typical deposits using hydrogen flows of 5 and $8.7\,l\,h^{-1}$ and $1.7\,l\,h^{-1}$ of the N_2/NH_3 mixture are shown in Fig. 5. After 5 h of deposition, the length of the filaments was 15 mm (H_2 flow $8.7\,l\,h^{-1}$) and 10 mm (H_2 flow $5\,l\,h^{-1}$). The catalyst particles (filament heads) and the filament shafts were analysed by EPMA. Representative results found for the filament heads are shown in Fig. 6a and b. A quantitative analysis yielded 18–24% Si for the low hydrogen flow of $5\,l\,h^{-1}$ and 5–8% Si for $8.7\,l\,h^{-1}$. This result explains the different morphologies of the catalyst particles as shown in Fig. 5a and b. With the lower silicon content the catalyst particles are operating in the solid state, but with the higher silicon content in the liquid state (see Fig. 2).

The emission spectrum of the filament shafts in Fig. 6c only shows the silicon peak; nitrogen could not be analysed by EPMA. In order to determine the phase content of the filament shafts, X-ray studies were performed. The results with filaments produced at hydrogen flows of 5, 6 and $8.7\,l\,h^{-1}$ are presented in Fig. 7a–c. At all hydrogen flows, α-Si_3N_4 is formed, but at the two low hydrogen flows free silicon is precipitated in addition. In this case the filaments exhibit a circular cross-section, whereas a hexagonal cross-section is typical for filaments of pure, monocrystalline α-Si_3N_4. This result illustrates that an excess of ammonia favours the formation of the desired

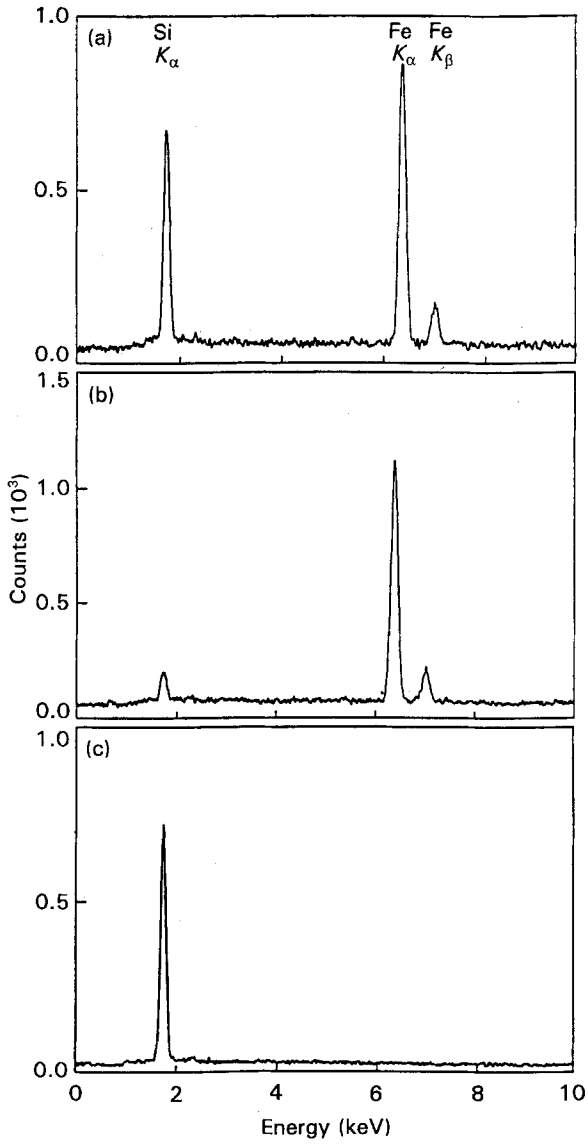

Figure 6 X-ray emission spectra of filament heads obtained with (a) 5 and (b) $8.7\,l\,h^{-1}$ hydrogen flow, and (c) a filament shaft; 1300 °C reaction temperature.

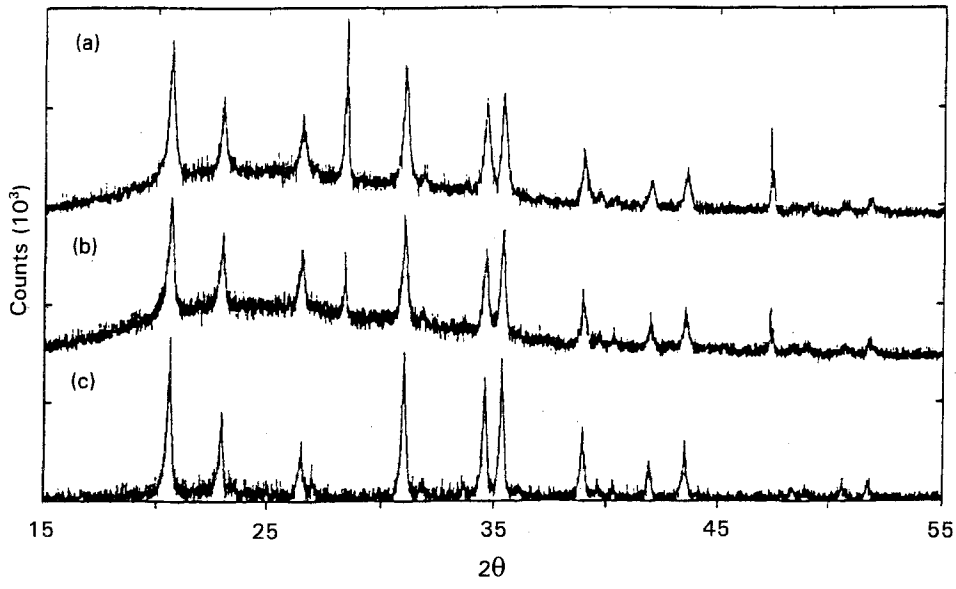

Figure 7 X-ray diffraction patterns of filament shafts obtained with (a) 5, (b) 6 and (c) $8.7\,l\,h^{-1}$ hydrogen flow.

monocrystalline α-Si_3N_4 filaments. However, with SiH_x/NH_3 ratios lower than 0.006, non-catalysed reactions resulting in the formation of Si_3N_4 powder are possible.

The negative results with nitrogen and the positive results with ammonia can clearly be attributed to the strongly different adsorption probabilities of the two gases at an iron or ferrosilicon surface, which differ from each other by approximately several orders of magnitude [11].

4.3. Strength of the filaments

Mechanical properties of filaments with various diameters are shown in Table I. The maximum values found for Si_3N_4 whiskers in the literature are presented for comparison. According to our knowledge, the monocrystalline Si_3N_4 filaments exhibit the highest strength values ever reported. The strain-to-failure values of these filaments are higher than 0.05. The theoretical value according to the Griffith theory is only twice as high. This result additionally underlines the crystalline perfection of the filaments synthesized.

TABLE I Results of tensile strength investigation of the filaments; values of whiskers according to the literature are presented for comparison

Filament diameter (μm)	Type	Young's modulus (GPa)	Tensile strength (GPa)
4–5	"amorphous"	200–300	5–9
1–3	crystalline	550–750	30–50
0.5–2	whisker	380	14

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