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DEVELOPMENT OF STRUCTURAL CERAMIC MATERIALS SILICON NITRIDE AND SIALON

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Abstract: The activity on the development of the structural ceramic materials silicon nitride and sialons is highlighted. Special emphasis has been given to explore new methods and to develop low cost processes for the synthesis of these materials. An analysis of the oxygen content in various samples of α-silicon nitride has been made to show how the bulk oxygen content can vary depending on the method of preparation.

Key words : silicon nitride, sialon, structural ceramics

1. INTRODUCTION

Silicon nitride and sialons are modern man made ceramic materials although they are made up of some of the most abundant elements on the earth silicon, nitrogen, aluminium and oxygen. These materials have an interesting combination of properties making them suitable for high temperature structural applications. They have very high strength at high temperatures, low density, high corrosion and wear resistance, low thermal expansion coefficient and high hardness. These materials find applications in high temperature ball and roller bearings, rocket nozzles, combustion and wear parts in engines such as pistons, cylinders, valves and turbochargers[1]. They are also widely used in cutting tools, molten metal handling, welding nozzles, pump seals etc[2]. Currently there is also a great interest in the development of these materials in the form of whiskers and fibres for use in ceramic matrix and metal matrix composites as reinforcements[3-5].

Ceramic products using these materials are generally made by sintering of shaped green compacts of fine powder. The properties of the sintered product depend on its microstructure. In order to achieve the required microstructure, the starting powder should meet certain criteria such as high purity, high specific surface area, equiaxed particle morphology and low oxygen content[6]. Though these powders are commercially available, use of these materials has been limited to only high technology areas because of their high cost. The main objectives of taking up this project have been (1) to develop low cost processes for the synthesis of these powders, (2) to explore various chemical reactions that could lead to new methods of synthesis and (3) to prepare these materials in the form of whiskers and fibres.

For the synthesis of these materials, the strategy has been to use silica, silicon tetrachloride or kaolinite as a source of silicon and to use ammonia for nitridation. Unlike using nitrogen gas for nitridation, the use of ammonia has been shown to be more efficient because of the liberation of nascent nitrogen at the reaction temperature. There are several critical parameters for successfully carrying out these reactions like purity and particle size of the starting material, temperature and duration of the reaction, the ambient atmosphere, the rate of flow of the reacting gases and the substrate material. Some of the interesting results of our work are discussed below.

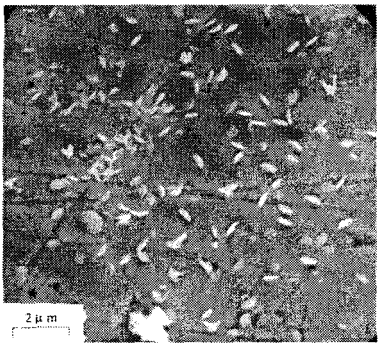

Fig. 1. Electron micrograph of the powder of α-silicon nitride

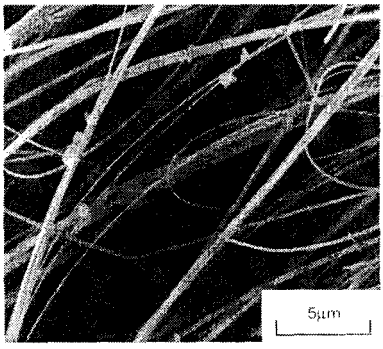

Fig. 2 . Electron micrograph of α-silicon nitride fibres

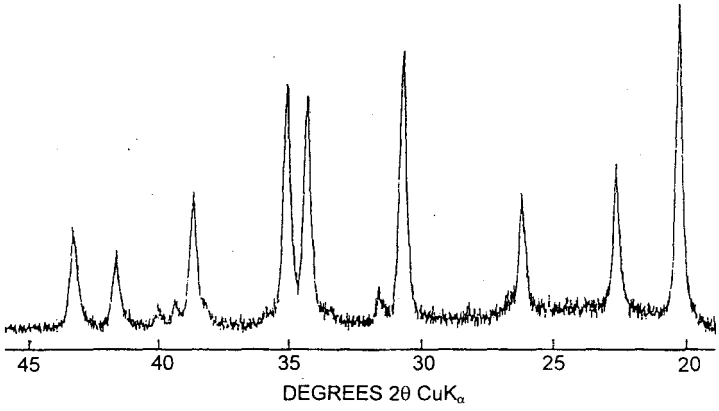

Fig. 3 X-ray diffraction pattern of powder of α-silicon nitride

2. SYNTHESIS OF SILICON NITRIDE BY THE REACTION BETWEEN SILICON TETRACHLORIDE AND AMMONIA

This is a reaction which has attracted the attention of a number of laboratories all over the world. In Japan, detailed studies on this reaction have led to the development of a liquid phase process (Ube process). This is basically a reaction between liquid ammonia and liquid silicon tetrachloride at temperatures of less than 25^0C. The products of this reaction are silicon diimide and ammonium chloride. The silicon diimide is first converted to amorphous silicon nitride and then crystallised to α-silicon nitride by heating at temperatures between 1300-1500^0C. The reactions involved are given below :

$$SiCl_4 + 6NH_3 \xrightarrow{<25^\circ C} Si(NH)_2 + 4NH_4Cl$$

$$6Si(NH)_2 \xrightarrow{900-1200^\circ C} 2Si_3N_4(amorphous) + 4NH_3$$

$$Si_3N_4(amorphous) \xrightarrow{1300-1500^\circ C} \alpha - Si_3N_4$$

The problems associated with this process are (1) the removal of the large excess of ammonium chloride and (2) the extreme sensitivity of the diimide to moisture which leads

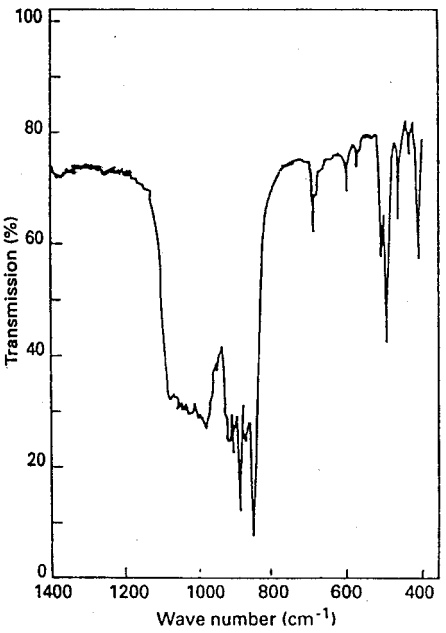

Fig.4 IR absorption spectrum of α-silicon nitride

to the formation of silica. We have studied the reaction between the vapour of silicon tetrachloride and gaseous ammonia in the temperature range of 1200-1400°C and observed that the formation of ammonium chloride can be avoided by diluting the reactants with hydrogen. The reaction taking place under these conditions can be written as

$$4NH_3 + 3SiCl_4 \xrightarrow{H_2,1200-1400^\circ C} Si_3N_4 + 12HCl$$

This reaction has been used to prepare either powder or fibres of α-silicon nitride by controlling the reaction temperature and the dwell time of the gases in the hot zone. Lower temperature and short dwell time lead to the formation of powder whereas fibres are formed with higher temperatures and larger dwell time. Both powder and fibres are white in appearance. The dimensions of the powder particles are less than a micrometer and the diameter of the fibres is less than a micrometer and the length is more than 2 mm. These materials have been characterised for the composition by wet chemical methods. The nitrogen content ranges between 36.5 and 39.2 wt % suggesting the presence of small amounts of oxygen. Phase purity of this materials has been determined by both X-ray diffraction and infrared absorption. The α-phase content in these materials is up to 98 %, the remaining being β-phase. Figures 1 to 4 show the typical micrographs, XRD pattern and IR absorption spectrum.

3. SYNTHESIS OF SILICON NITRIDE BY THE REDUCTION AND NITRIDATION OF SILICA USING AMMONIA

Starting from silica, silicon nitride is manufactured by carbothermal reduction and nitridation process wherein silica is mixed with large excess of carbon and heated in nitrogen atmosphere at temperatures of 1400-1500°C. However, in this process small amounts of silicon carbide also form especially when the reaction temperature exceeds 1450°C. Moreover, the excess carbon has to be removed which is often not complete. Presence of traces of free carbon affects the sinterability of the powder. By using ammonia for reduction and nitridation, these problems can be eliminated. Also, the inherent advantages of solid-gas reaction can be made use of. Therefore, we have studied the reaction between silica and ammonia under different conditions. The effect of various experimental parameters such as the time and temperature of the reaction, particle size of the starting silica, flow rate of ammonia, container material etc. have been studied in detail. These studies have shown that (1) the hydrogen produced by the decomposition of ammonia can effectively reduce silica. At high temperatures (about 1400°C) this leads to the formation of long fibres of α-silicon nitride. At lower temperatures (about 1300°C) the formation of silicon monoxide vapour is negligible and under these conditions α-silicon nitride powder is formed. (2) The reaction temperature

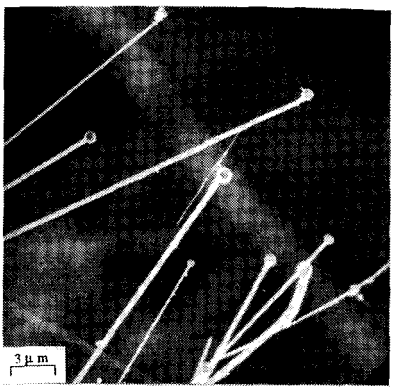

Fig. 5. Drop-like structures at the tips of the fibres

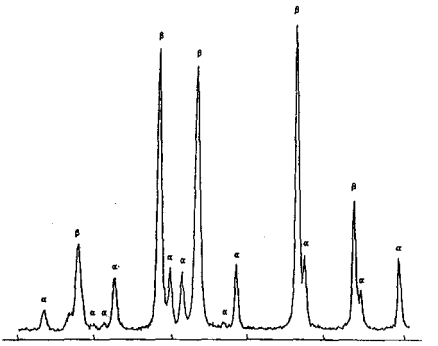

Fig. 6. X-ray diffraction pattern of α -silicon nitride powder

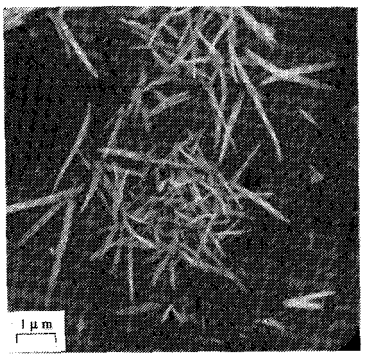

Fig. 7. Electron micrograph of α-silicon nitride powder

can be brought down to 1200°C by adding small quantities of iron to the starting silica. However, only fibres are formed under these conditions. Electron microscopic examination of these fibres has clearly shown that they have drop-like structure at the tips. EDX analysis of these droplets has shown that they have large concentrations of iron. This suggests that these fibres grow by vapour-liquid-solid mechanism. Figure 5 shows the electron micrograph of the drop-like structure at the fibre tips. (3) The partial pressure of oxygen plays a crucial role in this reaction. This necessitates the use of very dry ammonia and non-oxide container for silica. (4) Certain alkaline earth oxides when added to the starting silica enhance the formation of β-silicon nitride and under optimum conditions the β-phase can be as high as 85 %. The product is always a free flowing powder with needle shaped particles. The length of the particles varies from 0.5 to 2.5 μm and the thickness varies from 0.1 to 0.2 μm. Figure 6 shows the XRD pattern of this material and Figure 7 shows the morphology of the particles.

4. SYNTHESIS OF β–SIALON FROM KAOLINITE

β-sialons are obtained from β-silicon nitride by the partial replacement of silicon and nitrogen by aluminium and oxygen. These are represented by the formula $Si_{6-z}Al_zO_zN_{8-z}$. These materials have properties very similar to that of silicon nitride. The sialon with a composition in which z= 3 has the best properties for high temperature structural applications. Sialons are commercially prepared by reacting together silicon nitride, silica, alumina and aluminium nitride. However, this process is expensive. There have been attempts to use cheaper materials such as naturally occurring clay minerals for the synthesis of sialons. We have done a detailed study on the reduction and nitridation with ammonia of kaolinite which has the formula $Al_2O_3.2SiO_2.2H_2O$ in the temperature range of 1300-1400°C. These studies gave the following results. (1) When the reaction is done at 1400°C for a short period, the product is a mixture of mullite, β-sialon and X-phase with β-sialon as minor phase. (2) When the reaction is done for long periods, more β-sialon forms. (3) After an optimum duration of the reaction, the product is only β-sialon . (4) Prolonged reactions give a mixture of β-sialon, aluminium nitride and α-silicon nitride. This clearly shows that pure β-sialon can be obtained by the reaction between kaolinite

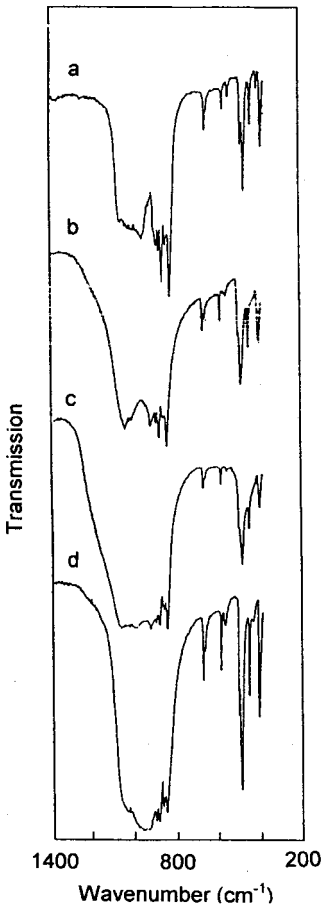

Fig. 8. IR absorption spectra of four different samples of α-silicon nitride

and ammonia. These results have led us to standardise the process for preparing pure β-sialon from kaolinite in a reproducible manner. Here also, either powder or fibres can be prepared by adjusting the experimental parameters.

5. STUDIES ON THE OXYGEN CONTENT IN DIFFERENT SAMPLES OF α-SILICON NITRIDE

α-silicon nitride prepared by different processes has always a certain amount of oxygen in it. This is considered very useful for better sintering because the oxide reacts with the sintering additives to form liquid phase in which α-silicon nitride dissolves and reprecipitates as β-silicon nitride. We have prepared α-silicon nitride by different methods (1) ammonolysis of silicon powder[7], (2) nitridation of equimolar mixture of silicon and silica, (3) carbothermal reduction and nitridation of silica and (4) nitridation of silicon whsikers[8]. Though these samples have identical XRD patterns, there are conspicuous differences in their infrared absorption spectra. This has prompted us to analyse the data in more detail. The IR absorption spectra of the 4 samples are shown in Figure 8. It can be seen that the spectra of the samples prepared by methods 1 and 2 surprisingly do not have the characteristic absorption band at 950 cm^{-1} which corresponds to Si-N-Si antisymmetric stretching mode. Sample 4 has the highest absorption at this wave number. The nitrogen content of these samples has been analysed by wet chemical method and the following values are obtained: (1) 36.3 %, (2) 37.2 %, (3) 38.7 % and (4) 39.2 %. Thus samples 1 and 2 which show low IR absorption at 950 cm^{-1} have considerably lower nitrogen content. Since all the samples have been prepared from pure starting materials, it can be surmised that these samples may contain correspondingly more oxygen. If this oxygen is due to the presence of silica, the IR absorption spectra should have shown either the lines of crystalline silica or the diffuse halos of amorphous silica. Moreover, the IR absorption spectrum of a mixture of silicon nitride and silica cannot account for a lower absorption especially at 950 cm^{-1}. Therefore, the oxygen present must be in the bulk. To confirm this a few grams of sample 1 has been mixed with excess of carbon and heated at 1450°C, for 5 hours while passing ammonia. The excess carbon has been removed later by heating in air at 800°C. The IR absorption spectrum of this material has shown the characteristic absorption at 950 cm^{-1} similar to that of sample 4. This clearly shows that oxygen is present in the silicon nitride samples 1 and 2 and it is indeed in the bulk. These studies clearly show that although it is not necessary that α-silicon nitride should have bulk oxygen to stabilise its structure, it can accommodate a considerable amount of oxygen without becoming oxynitride structurally[9].

Silicon carbide is another important high temperature structural ceramic material. Presently, studies on the synthesis of fibrous silicon carbide and submicron size silicon carbide powder are being done in this laboratory.

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