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The Influence of Different Oxides on the Formation of Si_2N_2O from SiO_2 and Si_3N_4

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Abstract

Si_2N_2O powder has been produced by reacting SiO_2 and Si_3N_4 in the presence of a liquid phase obtained by the addition of Al_2O_3, Y_2O_3, and MgO. The phase changes occurring during the reaction have been quantified by X-ray diffraction. The reaction has been studied at different temperatures and periods of time. The grain size of the starting materials has a large influence on the conversion to Si_2N_2O, and, by using a fine-grained SiO_2, a substantial conversion to Si_2N_2O was obtained within 1 h at 1500°C for the Y_2O_3-containing material.

Si_2N_2O-Pulver wurde durch die Reaktion von SiO_2 und Si_3N_4 in Gegenwart einer Flüssigphase hergestellt, die Zusätze von Al_2O_3, Y_2O_3 bzw. MgO enthielt. Die während der Reaktion auftretenden Änderungen der Phasenzusammensetzung wurden mit der Röntgenbeugungsmethode quantitativ bestimmt. Die Reaktion wurde bei verschiedenen Temperaturen und Zeiten untersucht. Die Korngröße des Ausgangsmaterials hat einen großen Einfluß auf die Umwandlung in Si_2N_2O und mit einem feinkörnigen SiO_2 konnte eine weitgehende Umwandlung in Si_2N_2O innerhalb 1 h bei 1500°C für das Y_2O_3-haltige Material erreicht werden.

On a préparé de la poudre de Si_2N_2O par réaction entre SiO_2 et Si_3N_4 en présence d'une phase liquide obtenue par l'addition de Al_2O_3, de Y_2O_3 ou de MgO. Les changements de phase se produisant pendant la réaction ont été mesurés par diffraction X. On a étudié la réaction en faisant varier les paramètres temps et température. La granulométrie des réactifs exerce une influence notable sur la conversion en Si_2N_2O. L'utilisation d'une poudre fine de SiO_2 et le dopage par Y_2O_3 conduisent à un taux de conversion élevé après un traitement d'1 h à 1500°C.

1 Introduction

Silicon oxynitride ceramics should be regarded as promising high-temperature materials because of their good oxidation and thermal-shock resistance.[1–4]

Si_2N_2O ceramics may in principle be prepared in two different ways. One method is to sinter SiO_2, Si_3N_4, and the appropriate sintering aid and have Si_2N_2O formed during the sintering. Another method is to sinter presynthesized Si_2N_2O together with a sintering aid. This second technique seems to be more advantageous because it permits more suitable processing.

According to the literature, the following routes have been used to prepare Si_2N_2O powders:

$$3Si + SiO_2 + 2N_2 \rightarrow 2Si_2N_2O \quad (1)$$

$$2SiO_2 + 3C + N_2 \rightarrow Si_2N_2O + 3CO \quad (2)$$

$$2SiO_2 + 2NH_3 \rightarrow Si_2N_2O + 3H_2O \quad (3)$$

$$Si_3N_4 + SiO_2 \rightarrow 2Si_2N_2O \quad (4)$$

In 1971 Billy *et al.*[5] prepared 95% pure Si_2N_2O (containing 5% β-Si_3N_4) according to the reaction of eqn (1). The mean particle size was 3 μm and the size was always below 20 μm.

The carbothermal reaction in eqn (2) has been applied to produce low-cost Si_2N_2O powders by using an impure SiO_2:C source, 'black ash', which is the product of combustion of rice husks in an oxygen-deficient atmosphere.[6] Besides the impurities present in the 'black ash', CaO was added to enhance the Si_2N_2O formation. However, the presence of CaO will, of course, limit the use of these

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powders to lower temperatures. Bolech *et al.*,[7] using purer starting materials, studied the influence of different oxide additives on the carbothermal reaction. By adding 1–3% of CaO, SrO or BaO, Si_2N_2O powders were prepared at 1400–1450°C. However, Si_2N_2O ceramics made of these powders will have an inferior high-temperature strength.

As long ago as 1967, Marchand and Lang[8] tried to synthesize Si_2N_2O by nitridation of amorphous SiO_2 with NH_3. However, when they tried to crystallize the product, Si_2N_2O appeared in small amounts contaminated with Si_3N_4. Recently, Sjöberg *et al.*[9] nitrided a spray-dried commercial pure silica sol by using NH_3. The resulting powders were amorphous. However, by sintering the amorphous powder with large amounts of sintering aids, Y_2O_3 and Al_2O_3, a 90% dense Si_2N_2O material was formed.

The fourth preparation route, eqn (4), involves a direct reaction between SiO_2 and Si_3N_4. However, even if thermodynamics predict[10] the reaction to start at about 1140°C, the reaction is extremely sluggish. Si_2N_2O powders have therefore been prepared by adding Al_2O_3[1] or MgO[11] in order to enhance the reaction rate by forming a liquid phase. Barta *et al.*[11] used MgO because they were mainly concerned with the dielectric properties of Si_2N_2O and a final application at temperatures below 800°C. By using equimolar amounts of SiO_2 and Si_3N_4 and with the addition of 3 wt% MgO, a nearly full conversion was obtained at 1650°C. In the work by Huang *et al.*[1] an equimolar mix of SiO_2 and Si_3N_4 and 3 mol% of Al_2O_3 were used, resulting in a 75% conversion to Si_2N_2O at 1700°C.

From the discussion above, it is evident that an oxide additive that forms a liquid phase with the SiO_2 and Si_3N_4 should enhance the formation rate of Si_2N_2O. Presumably, the liquid enhances the dissolution of Si_3N_4 and in that way promotes the formation of Si_2N_2O.[1,12]

The intention of this paper is primarily to compare the influence of different oxide additives on the formation of Si_2N_2O powders. The oxide additives studied are Al_2O_3, MgO, and Y_2O_3. The yttrium oxide was included because it produces a more refractory glass phase than the other compounds. The influence of different starting materials has also to some extent been studied. For example, the influence of the coarseness of the SiO_2 powder was studied for one composition. Results obtained by using β-Si_3N_4 instead of α-Si_3N_4 are also presented.

Table 1. Chemical composition (mol%) of the mixtures studied

Specimen	Si_3N_4	SiO_2	Al_2O_3	Y_2O_3	*MgO*
O	50	50	—	—	—
A	48·5	48·5	3	—	—
Y	48·5	48·5	—	3	—
M	48·5	48·5	—	—	3

2 Experimental

The raw materials used are α-Si_3N_4 (BET surface area = $20\,m^2/g$ and $\alpha/\beta = 95/5$; Kema Nord Industrikemi, Ljungaverk, Sweden), SiO_2 (Quartz, Pro analysi, M 7536; BET surface area = $0{\cdot}03\,m^2/g$; E. Merck, Darmstadt, FRG), Al_2O_3 (Pro analysi, Fi A-591; Fisher Scientific Co., Fair Lawn, NJ, USA), Y_2O_3 (99·98% Y_2O_3; H. C. Starck, FRG) and MgO (Pro analysi, M 5865; E. Merck, Darmstadt, FRG). Equimolar amounts of Si_3N_4 and crushed SiO_2 were dry-mixed together with the appropriate sintering aid in a mixer mill (sample mixer mill, M 280; Glen Creston, Stanmore, Middx, UK). The compositions of the mixtures used are listed in Table 1.

The mixed powders were uniaxially pressed into cylindrical pellets. The pellets were embedded in BN powder in BN-lined graphite crucibles. The heat treatment was done in a graphite resistance furnace in static nitrogen, generally for 1 h at 1500–1800°C.

The reaction products were identified by X-ray diffraction. A qualitative estimate of the relative amounts of the different phases was obtained by using

$$i\% = \frac{I_i}{\sum I_i} \qquad (5)$$

where I_i is the peak height of phase i. The criteria for choosing a specific peak were based on good resolution, sufficient intensity, and freedom from peak overlap. The following peaks were used: (020) for Si_2N_2O, (201) for α-Si_3N_4, (101) for β-Si_3N_4, and (101) for cristobalite.

The sintered pellets were crushed and ground by hand for 20 min by using an agate mortar and pestle. The morphology of the powder obtained was characterized by SEM (JSM-840; Jeol, Tokyo, Japan).

3 Results and Discussion

From the thermodynamic information given by Hendry,[10] Si_2N_2O should form at 1140°C. However, the X-ray results for specimen O indicates that no

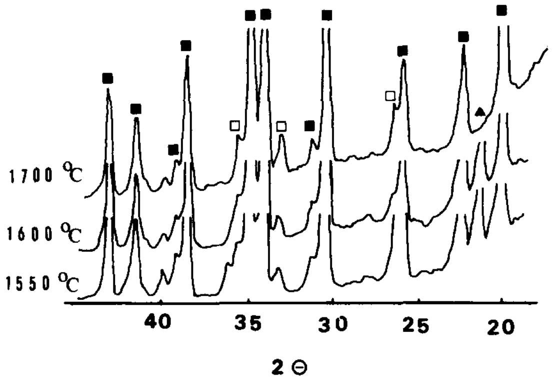

Fig. 1. X-ray diffractograms for composition O, heat treated for 1 h. ■, α-Si_3N_4; □, β-Si_3N_4; △, cristobalite.

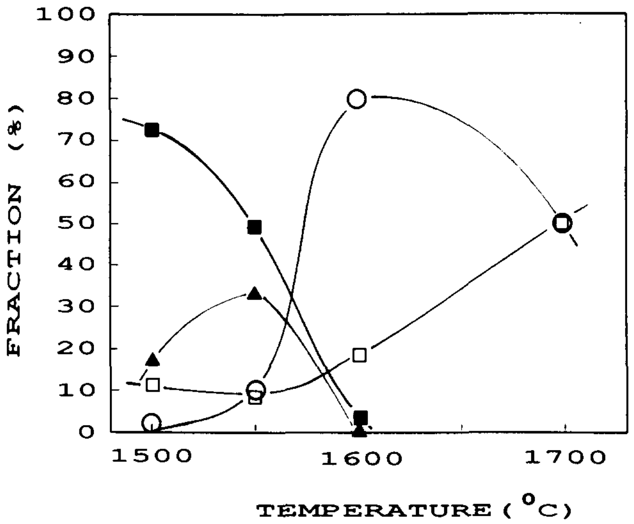

Fig. 3. Fraction of phases obtained in composition Y (3 mol% Y_2O_3) after heat treatment for 1 h as a function of temperature. ○, Si_2N_2O; ■, α-Si_3N_4; □, β-Si_3N_4; ▲, cristobalite.

Si_2N_2O is formed between 1550 and 1700°C (see Fig. 1). Furthermore, Fig. 1 shows that some transformation of α- to β-Si_3N_4 has occurred at 1700°C but not at 1600°C. Besides this, no cristobalite peak can be seen at 1700°C. With increasing temperature, a reaction will occur between SiO_2 and Si_3N_4, resulting in the volatile formation of SiO and N_2,[13] which presumably accounts for the major part of the weight losses shown below in Fig. 5. The reaction may explain why the α-Si_3N_4 and cristobalite contents decrease with increasing temperature, especially if we consider that α-Si_3N_4 is less stable than β-Si_3N_4[10] and therefore will be more prone to take part in the volatilization reaction. However, besides the apparent increase in the amount of β-Si_3N_4 owing to the evaporation, a certain amount must have been formed, as seen in the X-ray diffractogram. Presumably, some SiO_2 is present as an amorphous phase, which at temperature provided the liquid phase necessary for the α-to-β transformation.

The effect of small additions (2 mol%) of Al_2O_3, Y_2O_3, and MgO was also studied. By using eqn (5), the relative amount of the phases was estimated from the X-ray diffraction data. The results shown in Figs 2–4 were obtained after a heat treatment time of 1 h. The oxide additions show a large influence on the formation of Si_2N_2O. From the X-ray diffraction data, traces of Si_2N_2O were found at 1500°C for the Y_2O_3 and MgO additions, while Si_2N_2O started to form at about 1550°C for the Al_2O_3 addition.

The amount of Si_2N_2O increases with increasing temperature to reach a value of about 55% at 1700°C for the Al_2O_3 addition (see Fig. 2). In

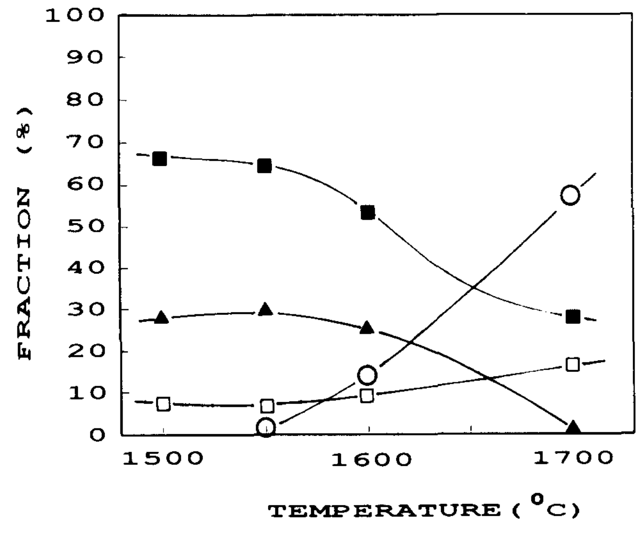

Fig. 2. Fraction of phases obtained in composition A (3 mol% Al_2O_3) after heat treatment for 1 h as a function of temperature. ○, Si_2N_2O; ■, α-Si_3N_4; □, β-Si_3N_4; ▲, cristobalite.

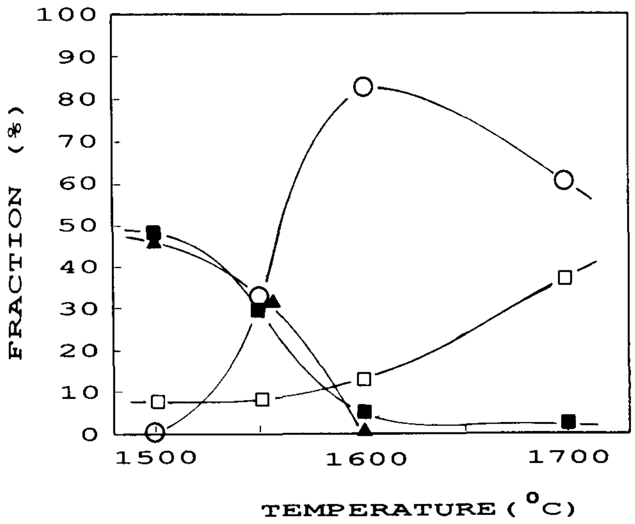

Fig. 4. Fraction of phases obtained in composition M (3 mol% MgO) after heat treatment for 1 h as a function of temperature. ○, Si_2N_2O; ■, α-Si_3N_4; □, β-Si_3N_4; ▲, cristobalite.

contrast, the Y_2O_3 and MgO additions give a maximum amount of about 80% at a temperature of about 1600°C (see Figs 3 and 4). The decrease in the amount of Si_2N_2O corresponds well with the increase in β-Si_3N_4. At the higher temperatures, Si_2N_2O presumably has decomposed to SiO, N_2, and Si_3N_4. This type of decomposition has previously been observed by others, e.g. Lortholary and Billy.[14]

Furthermore, the transformation of α- to β-Si_3N_4 also coincides with the formation of Si_2N_2O. We therefore believe that a liquid phase is necessary for the reaction between SiO_2 and Si_3N_4 to occur. Further support for this hypothesis is obtained from work by Hampshire and Jack.[15] In their paper, the liquid formation temperature for a Si_3N_4 with 4 wt% surface silica was found to be 1470, 1440 and 1390°C, respectively, for a 5 wt% addition of Al_2O_3, Y_2O_3 and MgO. A liquid phase is thus believed to form at a higher temperature for the Al_2O_3 case (Fig. 2), and Si_2N_2O therefore starts to form at a higher temperature than for the Y_2O_3 and MgO cases. Tsai and Raj[16] have suggested a model for the dissolution of Si_3N_4 and the resulting growth of Si_2N_2O in a Mg–Si–O–N glass, which, slightly modified, should be applicable in the present case. The growth of Si_2N_2O is a process suggested to consist of the following three steps. First, Si_3N_4 and SiO_2 are dissolved into the melt as silicon, nitrogen and oxygen, which, secondly, then diffuse through the melt towards the growing Si_2N_2O and finally attach to these growing crystals. Because the Al_2O_3-containing liquid is believed to have the highest viscosity, the growth of Si_2N_2O and the α to β transformation should be more difficult than in Y_2O_3- and MgO-containing liquids.

It is also of interest to look at the weight losses observed for the compositions studied. In Fig. 5 is shown the weight loss as a function of temperature for a heat treatment time of 1 h. The weight loss increases strongly with increasing temperature. Because of the large weight loss, it should thus be of no interest to form Si_2N_2O at temperatures above 1600°C. It is interesting to note that the Al_2O_3-containing material has the lowest weight loss, which we interpret as if the liquid of this material has the highest viscosity.

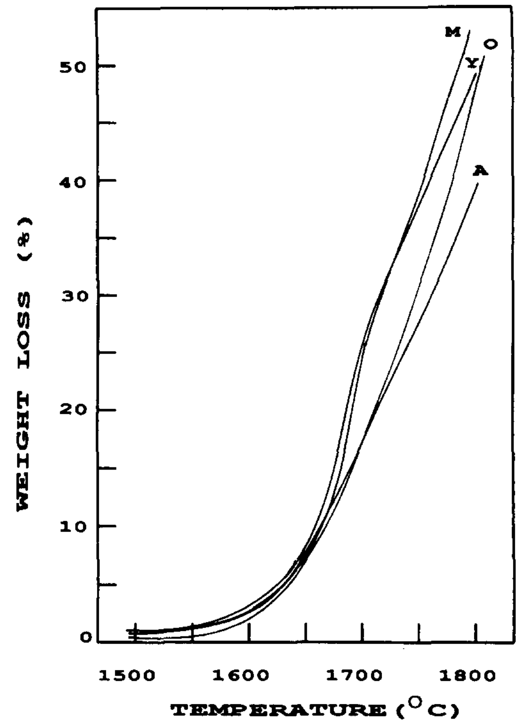

Fig. 5. Weight losses after heat treatment for 1 h as a function of temperature. O, Specimen O; A, specimen A; Y, specimen Y; M, specimen M.

Besides temperature, heat treatment time has a large influence on the Si_2N_2O formation. By using a time of 8 h, significant amounts of Si_2N_2O were obtained at 1430°C for the Y_2O_3 and MgO additions (see Table 2). After 8 h at 1500°C the Al_2O_3 added material also showed a significant transformation (see Table 3).

In Figs 2–4 it was seen that the α- to β-Si_3N_4 transformation occurs during the Si_2N_2O formation, and, in order to see if this transformation might influence the Si_2N_2O formation, a β-Si_3N_4 (Denka SN-BS, lot no. 1002; BET surface area 4·5 m^2/g and >90% β-Si_3N_4; Denka, Tokyo, Japan) was used instead of α-Si_3N_4. It was found that the X-ray diffraction patterns obtained by using α- and β-Si_3N_4 in the Y_2O_3 composition were roughly the same at 1600°C. It therefore seems reasonable to assume that there is no significant effect of using β-Si_3N_4 instead of α-Si_3N_4, which seems natural in view of the small difference in Gibbs energy between the two Si_3N_4 modifications.[10]

Table 2. Relative amounts (%) of phases after 8 h at 1430°C

Composition	*Si_2N_2O*	*α-Si_3N_4*	*β-Si_3N_4*	*Cristobalite*	*$Y_2Si_2O_7$*
Y	37	26	7	22	8[a]
M	48	21	11	20	—

[a] The amount of $Y_2Si_2O_7$ was evaluated by using the (021) peak.

Table 3. Relative amounts (%) of phases after 8 h at 1500°C

Composition	*Si_2N_2O*	*α-Si_3N_4*	*β-Si_3N_4*	*Cristobalite*	*$Y_2Si_2O_7$*
A	46	31	7	16	—
Y	78	2	12	—	8[a]
M	51	27	7	15	—

[a] The amount of $Y_2Si_2O_7$ was evaluated by using the (021) peak.

As discussed previously, the oxide additive will initially form an oxynitride liquid by a reaction with SiO_2 and Si_3N_4. When the liquid becomes supersaturated with respect to Si_2N_2O, this phase will precipitate. Its further growth will be described by the modified model discussed earlier. The rate controlling step may thus be dissolution of either SiO_2 or Si_3N_4, transport of ions through the liquid to the growing Si_2N_2O crystals, or the attachment of ions to these crystals. The SiO_2 powder used was extremely coarse-grained, and its dissolution may therefore have been rate controlling. In order to test this hypothesis, a fine-grained SiO_2 was used in a few experiments.

The mixing conditions were as follows: Si_3N_4 α-Si_3N_4, grade LC10; BET surface area 11·8 m^2/g; H. C. Starck, FRG), quartz (Quartz no. 4651, >99·35% SiO_2; BET surface 1·1 m^2/g; Carl Roth KG Chemische Fabrik, Karlsruhe, FRG) and Y_2O_3 were wet milled in propanol for 30 min. After evaporating the liquid, cylindrical pellets were pressed as discussed earlier. The formation of Si_2N_2O was significantly enhanced by using more fine-grained quartz and a more appropriate mixing technique. For a sintering temperature of 1500°C and a time of 1 h, about 85% Si_2N_2O, 5% β-Si_3N_4 and 10% β-$Y_2Si_2O_7$ were formed. (These fractions were not significantly changed by increasing the sintering time to 3 h.) As was seen in Fig. 3, only traces of Si_2N_2O were formed when using coarse-grained SiO_2. Thus improved processing and a finer-grained SiO_2 had a most impressive effect on the formation of Si_2N_2O. We believe that an appropriate liquid phase was formed much more easily in the present case, and thus the growth of Si_2N_2O was drastically enhanced.

The X-ray results clearly demonstrate that Si_2N_2O can be formed at rather low temperatures provided that suitable raw materials and an appropriate processing technique are used. The Si_2N_2O powder was found to be submicron even after formation at 1600°C for the Y_2O_3-containing material. By reacting at lower temperatures, very fine-grained Si_2N_2O powder should thus be obtained.

4 Conclusions

(1) Si_2N_2O powder can be produced by reacting SiO_2 and Si_3N_4 in the presence of a liquid phase formed by the addition of Al_2O_3, Y_2O_3 and MgO.
(2) About 80% conversion to Si_2N_2O was obtained at 1500°C for a time of 8 h when Y_2O_3 additions were used.
(3) The particle size of the raw material has a large influence on the formation of Si_2N_2O.
(4) By improved processing and the use of a fine-grained SiO_2, a substantial conversion to Si_2N_2O was obtained at 1500°C after only 1 h by using Y_2O_3 additions.
(5) Submicron Si_2N_2O particles have been obtained after reaction at 1600°C for the Y_2O_3-containing material.
(6) The conversion rate to Si_2N_2O is directly related to the liquid formation temperature. The degree of conversion for a given time and temperature increases with decreasing liquid formation temperature.
(7) The conversion rate to Si_2N_2O is much higher for Y_2O_3 and MgO additions than for Al_2O_3 additions.

Acknowledgement

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