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Formation of β'-sialon in the $Al–SiO_2–N_2$ system

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Abstract

Reaction processes which form β'-sialon by reaction between SiO_2 and Al in an N_2 atmosphere up to 1440°C were studied by means of DTA and X-ray diffraction techniques. Stoichiometric mixtures of Al and SiO_2 powders, for the oxidation–reduction reaction $4Al + 3SiO_2 \rightarrow 3Si + 2Al_2O_3$, and mixtures containing 50% Al in excess were used. With the stoichiometric mixture, as well as β'-sialon, the X sialon phase and mullite were formed as minor constituents. In contrast, the mixture containing Al in excess produced as secondary phase a 15R sialon phase or "Y" phase. The addition of Al in excess made it possible to obtain a product enriched in β'-sialon.

INTRODUCTION

The sialons are phases of the Si–Al–O–N system. Some of them, such as the β'-sialons, are being explored for their excellent thermal, mechanical, chemical and electrical properties.

The β'-sialons have a structure derived from β-Si_3N_4, corresponding to the composition $Si_{6-z}Al_zO_zN_{8-z}$ with $0 < z \leqslant 4.2$; z denotes the number of atoms of Si and N replaced by Al and O respectively in the initial Si_3N_4 structure.

In general, the sialons are obtained by carbothermal reduction of natural aluminosilicates. The reaction between SiO_2 and Al in an N_2 atmosphere is an alternative route. This reaction has been studied partially in respect of the final composition of the product [1–3], but the mechanism by which the $Al–SiO_2–N_2$ reaction system proceeds has not been the subject of attention.

In this work, the reaction processes which lead to the formation of β'-sialon by reaction between fumed silica and Al in an N_2 atmosphere, according to the oxidation–reduction reaction $4Al + 3SiO_2 \rightarrow 3Si +$

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$2Al_2O_3$, were studied by means of differential thermal analysis (DTA) and X-ray diffraction (XRD).

The addition of 50% Al in excess of the stoichiometric ratio was also investigated.

EXPERIMENTAL

Fumed silica of submicrometre particle size, provided by Elkem S.A. (Brazil), was used. It has the following characteristics: humidity, 1%; organic matter, 1%; Fe oxides, traces (20 ppm).

The Al powder (retained fraction on 325 ASTM sieve (44 μm) = 8%) was 99.9% pure.

Nitrogen of high purity (99.998%) was used, containing < 5 ppm of O_2, < 5ppm of H_2O, and < 10 ppm of Ar.

Two types of sample were prepared: (a) stoichiometric mixtures of Al and SiO_2 powders for the oxidation–reduction reaction

$$4Al + 3SiO_2 \rightarrow 3Si + 2Al_2O_3$$

and (b) mixtures containing 50% Al in excess over the amount in the first set.

The synthesis of β'-sialon was carried out in a Netzsch thermal analysis apparatus under an N_2 atmosphere. The enthalpy changes of the process were simultaneously recorded. Sample holders made from Al_2O_3 and Pt–Pt/Rh 10% thermocouple wires were used. The heating rate was 10°C min^{-1} and the sensitivity was 0.2 mV. The N_2 pressure used was 0.20 kg cm^{-2} above the atmospheric pressure and the N_2 flow rate was 600 cm^3 min^{-1}. In all the tests 320 mg of mixture was weighed and α-Al_2O_3 was used as reference material.

The thermograms were recorded up to 1440°C, samples being maintained for 4 h at this temperature in order to obtain the maximum conversion to β'-sialon. The DTA curves of the stoichiometric mixture (curve a) and that with 50% excess Al (curve b) are shown in Fig. 1.

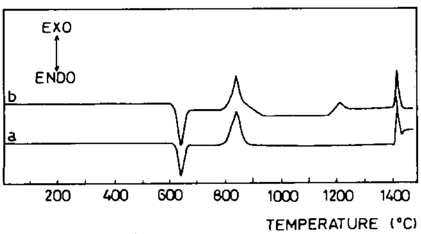

Fig. 1. DTA curves of the different mixtures of Al and SiO_2 powders: curve a, stoichiometric mixture; curve b, mixture with 50% Al in excess.

In the thermogram corresponding to the stoichiometric mixture (Fig. 1, curve a) three peaks were observed at the following temperatures: 640°C (endo), 840°C (exo) and 1420°C (exo). The DTA curve of the mixture with Al excess (Fig. 1, curve b) shows, besides the mentioned peaks, a small exothermic band with its maximum a 1210°C.

In order to investigate the sequence of reactions indicated by DTA, the mixtures were heated in an N_2 atmosphere at lower and higher temperatures than those corresponding to the maximum of each peak, and in each case the XRD spectra were recorded.

The diffraction measurements were made in a Philips PW 1140/00 apparatus with Cu Kα radiation and an Ni filter. The 2θ scanning rate was $2° \ min^{-1}$.

RESULTS AND DISCUSSION

Figure 2 shows the diffractograms of the stoichiometric mixture thermally treated at 800, 950, 1250, 1340, 1370, 1400 and 1440°C, and after the corresponding treatment at 1440°C for 4 h.

The endothermic peak at 640°C (Fig. 1, curve a) corresponds to the melting of Al (melting point 660°C).

The diffractograms obtained at 800 and 950°C (Fig. 2) indicate that the exothermic peak at 840°C (Fig. 1, curve a) is produced by two simultaneous reactions:

(a) the oxidation–reduction reaction between Al and SiO_2

$$4Al + 3SiO_2 \rightarrow 3Si + 2Al_2O_{3T} \quad (1)$$

(b) the formation of AlN

$$Al + 0.5N_2 \rightarrow AlN \quad (2)$$

The transitional aluminas of low crystallinity are named in a generic manner with the subscript T. The η and δ forms were observed in this work.

The DTA curve of an Al–α-Al_2O_3 mixture which has the same Al mass as that of the stoichiometric mixture (Al–SiO_2) is shown in Fig. 3. There is an exothermic effect at 820°C corresponding to the conversion of Al to AlN, which confirms the formation of AlN at such a temperature. The DTA peaks generated by reactions (1) and (2) cannot be resolved at the sensitivity used, as they are both exothermic and easily masked.

By X-ray diffraction the percentages of Si and AlN present at 950°C were determined using standards of such compounds. The values obtained were 10% Si and 16% AlN.

The oxidation–reduction reaction is more exothermic than that of AlN formation, so the main caloric contribution at 840°C corresponds to the production of Si.

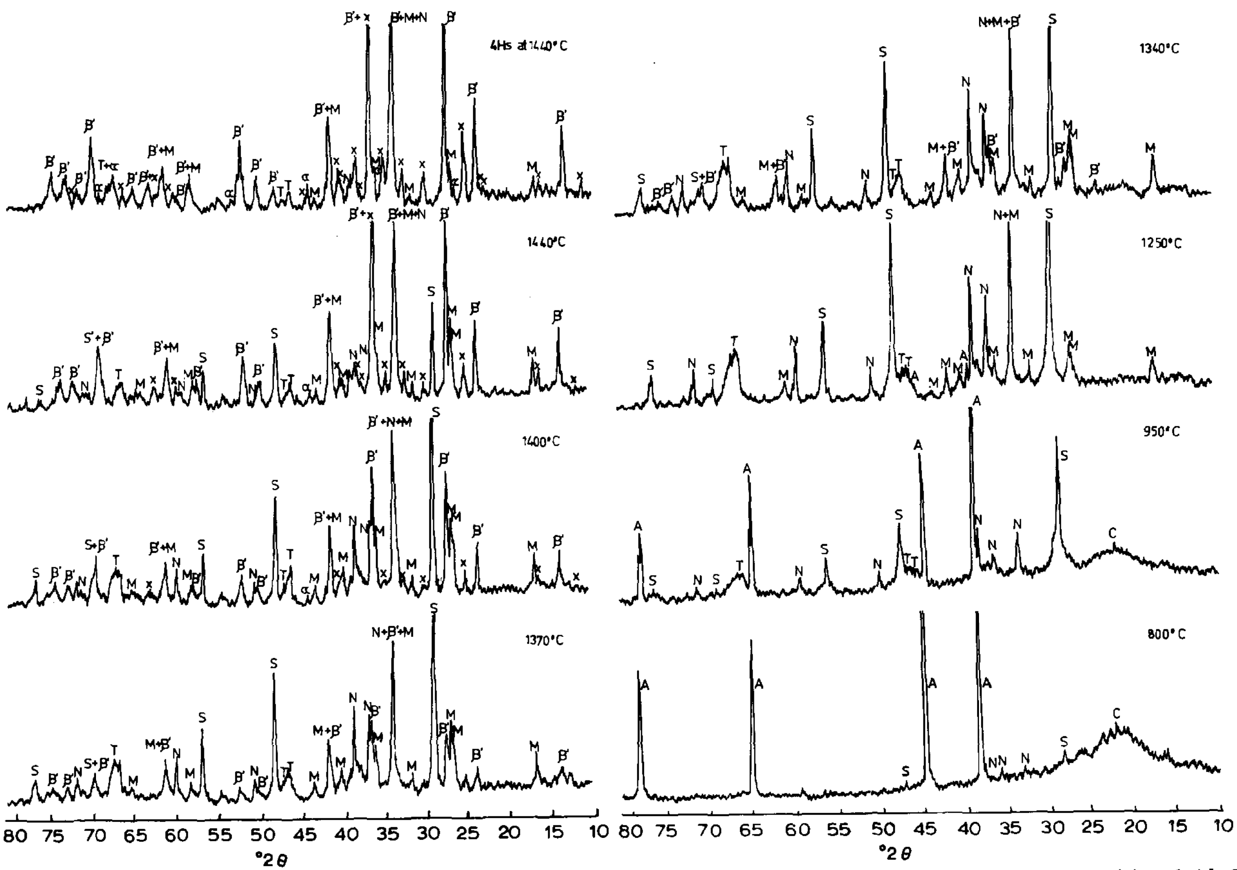

Fig. 2. X-ray diffractograms of the stoichiometric mixture Al–SiO_2: A, Al; C, fumed silica; N, AlN; T, transitional Al_2O_3; S, Si; M, $3Al_2O_3 \cdot 2SiO_2$; β', $Si_3Al_3O_3N_5$ (β'-sialon); X, $Si_{12}Al_{18}O_{39}N_8$ (X sialon phase); α, α-Al_2O_3.

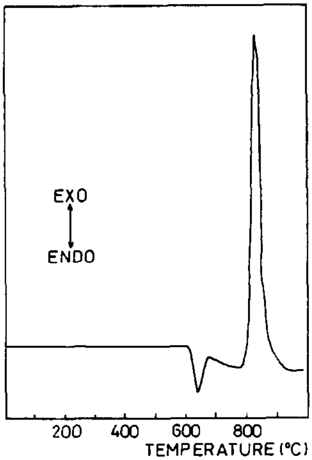

Fig. 3. DTA curve of the mixture of Al and α-Al_2O_3.

The reactions (1) and (2) progress up to 1250°C (Fig. 2). At this temperature practically all the Al has reacted. The SiO_2 which remains is converted into mullite at such a temperature (Fig. 2) according to the reaction

$$2SiO_2 + 3Al_2O_{3T} \rightarrow 3Al_2O_3 \cdot 2SiO_2 \qquad \text{(mullite)} \qquad (3)$$

As this reaction is controlled by diffusion, there is no appreciable thermal effect associated with it, as shown in Fig. 1, curve a.

At 1340°C (Fig. 2) the β'-sialon phase begins to appear. Its formation corresponds to the exothermic peak with its maximum at 1420°C (Fig. 1, curve a). The stability region of β'-sialon is shown in Fig. 4; here the Si–Al–O–N system is represented according to ref. 4. The reflections

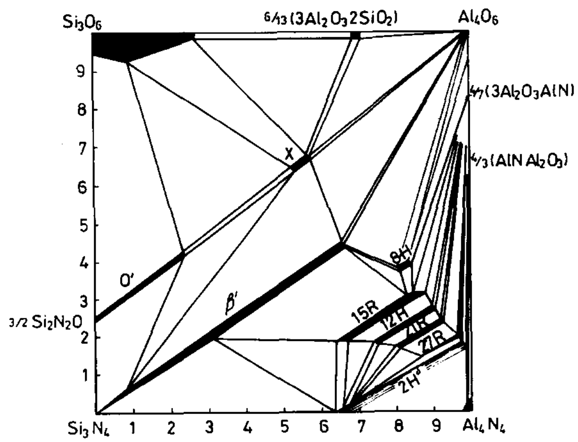

Fig. 4. The Si_3N_4–AlN–Al_2O_3–SiO_2 system according to ref. 4.

observed by XRD correspond to β'-sialon with $z = 3$ (formula $Si_3Al_3O_3N_5$ [5]).

Between 1340 and 1400°C the XRD spectra (Fig. 2) indicate that the appearance of the β'-sialon phase is accompanied by an increase in the formation of $3Al_2O_3 \cdot 2SiO_2$ and a progressive decrease in the Si, Al_2O_{3T} and AlN reflections. According to these results, the following reaction scheme is suggested:

$$3Si + 2N_2 + Al_2O_{3T} + AlN \rightarrow Si_3Al_3O_3N_5 \quad (4)$$

$$30Si + 20N_2 + 12Al_2O_{3T} \rightarrow 8Si_3Al_3O_3N_5 + 6SiO_2 \quad (5)$$

$$6SiO_2 + 9Al_2O_{3T} \rightarrow 3[3Al_2O_3 \cdot 2SiO_2] \quad (6)$$

The reactions (4) and (5) for the formation of β'-sialon were observed by Jack [6].

The combination of reactions (4), (5) and (6) yields the following global reaction for the temperature interval 1340–1400°C:

$$33Si + 22N_2 + 22Al_2O_{3T} + AlN \rightarrow 9Si_3Al_3O_3N_5 + 3[3Al_2O_3 \cdot 2SiO_2] \quad (7)$$

The global reaction (7) and other global reactions which will be postulated indicate the observed tendency, but none of them progresses to complete conversion.

The large quantity of β'-sialon produced at 1420°C is evident from XRD at 1440°C (Fig. 2). Nevertheless, at this temperature the reflections of $3Al_2O_3 \cdot 2SiO_2$ are not increased and β'-sialon formation is accompanied by the generation of a SiO_2-rich "X" sialon phase (Fig. 4) as a minor constituent. The reflections of this X phase correspond to a triclinic structure of composition $Si_{12}Al_{18}O_{39}N_8$ [7].

The X phase may be formed in this system starting from $3Al_2O_3 \cdot 2SiO_2$ according to the reaction

$$3[3Al_2O_3 \cdot 2SiO_2] + 6Si + 4N_2 \rightarrow Si_{12}Al_{18}O_{39}N_8 \quad (8)$$

The changes occurring between 1400 and 1440°C may be interpreted by means of a combination of the reactions (7) and (8), leading to the overall reaction

$$39Si + 26N_2 + 22Al_2O_{3T} + AlN \rightarrow 9Si_3Al_3O_3N_5 + Si_{12}Al_{18}O_{39}N_8 \quad (9)$$

The treatment at 1440°C for 4 h (Fig. 2) leads to the disappearance of Si and a decrease of Al_2O_{3T}, AlN and $3Al_2O_3 \cdot 2SiO_2$, with production of β'-sialon and the X phase.

It is considered that the overall reaction (9) takes place, and that part of the mullite existing in the system is converted into X phase.

The transformation of the existing $3Al_2O_3 \cdot 2SiO_2$ according to eqn. (8), together with reaction (9), gives the global reaction (10):

$$45Si + 30N_2 + 22Al_2O_{3T} + AlN + 3[3Al_2O_3 \cdot 2SiO_2](\text{existing}) \rightarrow 9Si_3Al_3O_3N_5 + 2Si_{12}Al_{18}O_{39}N_8 \quad (10)$$

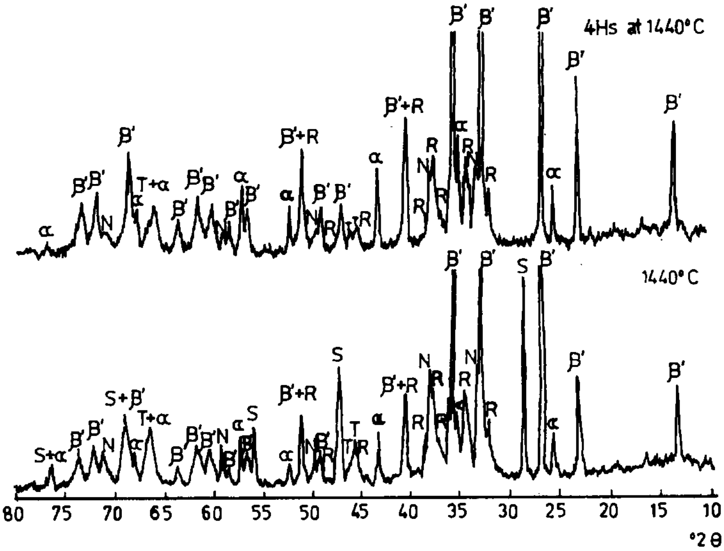

Fig. 5. X-ray diffractograms of the mixture Al–SiO_2 with 50% Al in excess (R, 15R sialon phase; the other symbols have the same meaning as in Fig. 2).

With respect to the mixture with 50% Al in excess, its thermogram (Fig. 1, curve b) shows a small exothermic peak at 1210°C. The other peaks are interpreted in the same way as the ones shown in Fig. 1, curve a.

Figure 5 shows the diffractograms of the mixture with excess Al treated up to 1440°C and for 4 h at 1440°C. At 1440°C greater production of Si, Al_2O_{3T}, α-Al_2O_3 and AlN is detected by XRD with respect to the stoichiometric mixture at the same temperature (Fig. 2) but without formation of $3Al_2O_3 \cdot 2SiO_2$.

The presence of α-Al_2O_3 permits the peak at 1210°C to be associated with the phase transformation

$$Al_2O_{3T} \rightarrow \alpha\text{-}Al_2O_3 \qquad (11)$$

This change usually occurs at temperatures of at least 1200°C [8].

The SiO_2-rich X sialon phase is not observed together with the β'-sialon phase at 1440°C (Fig. 5). According to this it is estimated that the only way to form β'-sialon at 1420°C is the one suggested in reaction (4).

Because of the high AlN concentration present in the system, together with β'-sialon, an AlN-rich sialon phase appears. It was identified as a 15R polytype of AlN, or "Y" phase [6].

Gauckler et al. [9], prepared six sialon phases nearer to the AlN corner of the Si_3N_4–AlN–Al_2O_3–SiO_2 system (Fig. 4) with ranges of homogeneity extending along lines of constant M/X ratio (M = metal, X = non-metal). These phases have now been identified as polytypes of AlN [6]. The 15R

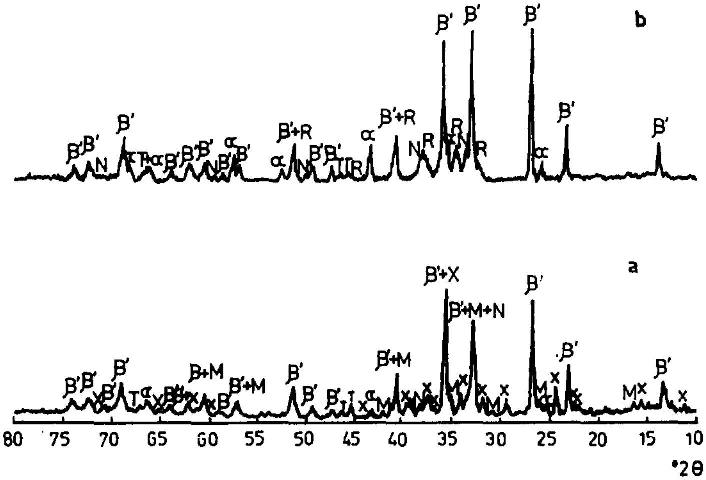

Fig. 6. X-ray diffractograms of the different Al–SiO_2 mixtures treated for 4 h at 1440°C: (a) stoichiometric mixture; (b) mixture with 50% Al in excess (the symbols have the same meaning as in Figs. 2 and 5).

polytype or "Y" phase has an M/X ratio of 5/6 and is frequently found as a minor phase in the hot-pressing of AlN-rich β'-sialon compositions [6].

Umebayashi and Kobayashi [1] reported the formation of β'-sialon and an unknown phase as products of the reaction between volcanic ash and Al powder in N_2 at 1400°C. The unknown phase had d values corresponding to the strongest X-ray reflections of the 15R phase, and its intensity was increased with increasing Al content.

In the XRD spectrum of the sample with Al excess treated at 1440°C during 4 h (Fig. 5), a maximum conversion to β'-sialon is observed without any increase in the 15R phase.

This phase is not generated owing to the low concentration of AlN remaining at this temperature. The decrease of Al_2O_{3T} and AlN and the disappearance of Si support the reaction (4) as the way of β'-sialon formation. Also, part of the transitional Al_2O_3 which remained is converted into α-Al_2O_3 according to eqn. (11). Combining reactions (4) and (11), the following global reactions is obtained:

$$3Si + 2N_2 + 2Al_2O_{3T} + AlN \rightarrow Si_3Al_3O_3N_5 + \alpha\text{-}Al_2O_3 \qquad (12)$$

Figure 6 shows, for comparison, the diffractograms of the reaction products of the stoichiometric mixture and the one with 50% Al excess after 4 h at 1440°. It is evident that the addition of 50% Al in excess over the stoichiometry of eqn. (1) has two effects (Fig. 6): (a) it produces a product richer in β'-sialon; (b) it produces an AlN-rich secondary sialon phase. In contrast, the stoichiometric mixture leads to a SiO_2-rich sialon phase and mullite as minor constituents.

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