Letters

Composition and stability of Y–Si–Al–O–N solid solutions based on α-Si_3N_4 structure

The existence of a whole range of joint solid solubilities of oxygen and aluminium, magnesium, yttrium (for example) in the β-Si_3N_4 lattice has been the matter of several structural and chemical studies [1–4]. A thermochemical computation [5] clearly suggested that the atmosphere (in which volatile silicon monoxide SiO appeared to be the major species beside nitrogen) played a dominant role in the formation and the stability of those so-called "β′-sialon" solutions and that no satisfactory understanding of the corresponding mechanisms could be expected unless vapour transfers were assumed.

It has also been suggested that new classes of materials might similarly be based on other structures built up of SiN_4 tetrahedra, such as the α-Si_3N_4 structure. In fact, α-Si_3N_4 expanded structures have been observed in the Li–Si–Al–O–N and Mg–Si–Al–O–N systems [1]. More recently there have been indications of the possible existence and composition of such "α′-sialon" solutions in the Y–Si–Al–O–N system [6]. These results have now seemingly been confirmed and it has been determined from crystallographic considerations that α′-sialon should be a 3M:4X structure with a general unit cell composition close to:

$$M_x\,(\mathrm{Si,\,Al})_{12}\,(\mathrm{O,\,N})_{16}$$

and additional metallic element M incorporated into large holes [7]. However, direct experimental evidence for this theory is to our knowledge still limited.

The available information about the stability of yttrium α′-sialon suggests that alumina reacts with α′ to give β′ and that conversely aluminium nitride reacts with β′ to give α′ [7]. So far the α′ ↔ β′ transformation has been thus more or less explicitly assumed to result from reactions between the condensed phases only, i.e. with no participation of the atmosphere in the reaction mechanisms. In the present paper, further expermental data about the composition and stability of α′-sialon will be brought and it will be shown that gas–solid interactions must *a priori* be taken into account in discussions about the phase stability in the Y–Si–Al–O–N system as well as in the Si–Al–O–N system.

The samples used in this study were obtained from compacted 90% α-Si_3N_4*, 99% AlN*, 99% Y_2O_3† blends. The initial compositions to be considered here consisted of 75 wt% Si_3N_4 and 25% Y_2O_3 $(AlN)_x$ with $x = 3,6$ or 9. The compacts were heated in the alumina core of a graphite resistor furnace. Two alternative temperature programmes were used: 3 h at 1680° C followed by one hour at 1720° C or 4 h at 1720° C. The atmosphere of the furnace was static nitrogen (total pressure: 1 atm.) which was in some cases SiO enriched in the presence of a $Si_3N_4 + Al_2O_3$ mixture at the vicinity of the samples within the furnace.

At the end of the heat treatments parts of the samples were ground for X-ray diffraction recordings. Special attention was devoted to quantitative electron microprobe analyses. Those were made on polished sections using a CAMEBAX MBX-2SI operating at 10 kV with a beam current of $(50.0 \pm 0.1) \times 10^{-9}$ A. Such conditions were found necessary for obtaining meaningful data on the lighter elements. Single crystal alumina and hot-pressed silicon nitride were used as standards. Surfaces of standards and samples had been made conducting by graphite plating. Si and Al were detected with a TAP crystal whereas for N and O, a lead stearate multilayer analyser was used. Weight contents of these elements in the samples were estimated following a ZAF procedure which had been specially developed for very light elements [8] and was recently modified to be applicable to any species [9]. The yttrium content in the samples was finally calculated as the difference between the sum of the contents of Si, Al, O and N and unity.

Results are given in Table I as functions of the composition of the starting mixture, of the tem-

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TABLE I Results

Starting mixture: 75 wt % Si_3N_4	Temperature programme	Atmosphere composition	β'/α	α' unit cell dimensions (Å)*	α' unit cell composition
$x = 3$	3 h at 1680° C + 1 h at 1720° C		1.8	$a = 7.794 \pm 0.003$ $c = 5.677 \pm 0.015$	$Y_{0.27 \pm 0.02}Si_{10 \pm 0.14}Al_{1.60 \pm 0.03}O_{1.88 \pm 0.03}N_{14.12 \pm 0.20}$ or $Y_{0.27 \pm 0.02}(Si, Al)_{11.6 \pm 0.17}(O, N)_{16 \pm 0.23}$
$x = 6$	As above	N_2 + SiO	1.3	$a = 7.794 \pm 0.004$ $c = 5.678 \pm 0.006$	$Y_{0.33 \pm 0.02}Si_{10.02 \pm 0.14}Al_{1.90 \pm 0.03}O_{1.6 \pm 0.02}N_{14.4 \pm 0.22}$ or $Y_{0.33 \pm 0.02}(Si, Al)_{11.9 \pm 0.17}(O, N)_{16 \pm 0.24}$
$x = 9$	As above	N_2 + SiO	1.2	$a = 7.796 \pm 0.002$ $c = 5.679 \pm 0.042$	$Y_{0.10 \pm 0.02}Si_{9.53 \pm 0.14}Al_{2.04 \pm 0.03}O_{1.4 \pm 0.02}N_{14.4 \pm 0.22}$ or $Y_{0.10 \pm 0.02}(si, Al)_{11.57 \pm 0.17}(O, N)_{16 \pm 0.24}$
	4 h at 1720° C	N_2 + SiO	0.3	$a = 7.801 \pm 0.002$ $c = 5.689 \pm 0.013$	$Y_{0.15 \pm 0.02}Si_{9.67 \pm 0.14}Al_{1.97 \pm 0.03}O_{1.33 \pm 0.02}N_{14.67 \pm 0.22}$ or $Y_{0.15 \pm 0.02}(Si, Al)_{11.67 \pm 0.17}(O, N)_{16 \pm 0.24}$
	4 h at 1720° C	N_2	0 (pure α')	$a = 7.803 \pm 0.006$ $c = 5.695 \pm 0.013$	$Y_{0.24 \pm 0.02}Si_{9.46 \pm 0.14}Al_{2 \pm 0.03}O_{1.44 \pm 0.02}N_{14.56 \pm 0.22}$ or $Y_{0.24 \pm 0.02}(Si, Al)_{11.46 \pm 0.17}(O, N)_{16 \pm 0.24}$

*To be compared with "pure" α-Si_3N_4 cell dimensions determined in the same conditions: $a = 7.746 \pm 0.003$ Å; $c = 5.646 \pm 0.005$ Å.

perature programme and of the composition of the gas-phase. α'-sialon could be detected in all the samples with no significant difference between the electron-probe analyses. Those are in agreement with the theoretical unit cell composition mentioned above. β'-sialon appeared to be also present in most cases and the β'/α' ratio was estimated using the intensities of the 1 0 1 and 2 1 0 (in fact combined 2 1 0 and 1 2 0) diffraction peaks for β' and those of the 1 0 2 and 2 1 0 peaks for α' and assuming that the relation:

$$\beta/\alpha = \frac{I_{101}(\beta) + I_{210}(\beta)}{I_{102}(\alpha) + I_{210}(\alpha)}$$

which is applicable to the case of pure β- and α-Si_3N_4 [10] is still valid. This ratio was found to decrease as the AlN content of the starting mixture was increased, everything else being the same, which is in agreement with previous results [7]. A major decrease was however observed as the firing temperature was increased for given atmosphere and starting mixture compositions. This was drastically amplified as the SiO content of the atmosphere was simultaneously decreased.

It is thus clear that the stability of α'-sialon is closely dependent on the silicon monoxide partial pressure: decreasing this pressure favours the $\beta' \rightarrow \alpha'$ transformation. A similar effect is obtained when the AlN content of the starting mixture is increased. These results can be compared to the computed stability conditions of β' in the Si–Al–O–N system [11]: it had been shown that decreasing P_{SiO} (which appeared to be equivalent to increasing P_{N_2} for a given total pressure) resulted in moving from β' stability field to those of phases observed in the AlN rich corner of the pseudo-quaternary Si_3N_4–SiO_2–Al_2O_3–Aln. The present results also suggest that the extent of the α' stability field in the Y–SI–Al–O–N system increases at the expense of β' when the temperature is increased.

In summarizing, the present work is believed to confirm the recent theory concerning the composition of yttrium α'-sialon and to show the importance of atmosphere compositions in setting the existence and stability conditions of this phase. It follows that gas transfers within the compacts or exchanges with the environment are more than likely to take place during the practical reaction and sintering treatments involving compounds of the Y–Si–Al–O–N system.

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