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Decomposition of some Si-Al-O-N powders during plasma spheroidization

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An attempt to prepare Si–Al–O–N glasses with compositions lying along the mullite–Si_3N_4 junction, by subjecting powders to rapid melting in a nitrogen plasma followed by quenching ($\simeq 10^6$ C sec^{-1}), resulted in their decomposition. Powders (− 53, + 37 μm) containing SiO_2/Si_3N_4 in the ratio 3/1 tended to decompose to give spheroidized γ-Al_2O_3/δ-Al_2O_3 particles, SiO and N_2. For $SiO_2/Si_3N_4 > 3$ the particles consisted of γ-Al_2O_3 stabilized by the presence of SiO_2 in solution, whereas if $SiO_2/Si_3N_4 < 3$, the particles consisted predominantly of the Al_2O_3–AlN spinel. Larger particle size powders (− 75, + 53 μm) did not decompose to the same extent and there was evidence that a nitrogen-containing glass was formed with a devitrification temperature of $\simeq$ 1100° C compared with $\simeq$ 1000° C for Al_2O_3–SiO_2 glasses.

1. Introduction

Alumina–silica glasses may be prepared with Al_2O_3 contents up to $\simeq 85$ mol% by splat quenching or by rapidly cooling a stream of molten droplets produced by flame or plasma spraying [1–3]. A mixture of glass and γ-Al_2O_3 may be prepared by rapid quenching of liquids containing 80 to 95 mol% Al_2O_3 [1]. The extent of glass formation depends upon the cooling rate and particle size; in the case of mullite composition powders spheroidized by combustion flame spraying into water, a completely glass product is produced of particle sizes less than $\simeq 20$ μm and this rapidly crystallizes to mullite on reheating to 1000° C [3]. It has been suggested that replacement of some of the oxygen in silicate glasses by nitrogen could result in a significant increase in the devitrification temperature [4] leading to useful high temperature materials. The possibility of preparing mullite glasses containing substituted nitrogen has therefore been investigated using powders spheroidized by means of a nitrogen plasma torch.

The Si–Al–O–N system contains a compound, generally referred to as phase *X*, which was originally termed a nitrogen mullite with the composition $3Al_2O_3 \cdot 2Si_3N_4$ [5]. Later work showed that this was not correct and that phase *X* contained much less nitrogen [6]. The exact composition however remains uncertain although the most recent work suggests $Si_{12}Al_{18}O_{39}N_8$ (or $3Al_2O_3 \cdot 2SiO_2 \cdot 2/3Si_3N_4$) lying on the mullite–$Si_3N_4$ join [7, 8]. The melting point of phase *X* is also uncertain but is probably about 1750° C [7]. The most likely section of the Si–Al–O–N system, based on the latter composition for *X*, is shown in Fig. 1 using the reciprocal salt method of representation. Estimated liquidus data are also shown [9] together with the various proposed compositions of phase *X* [5–11]; more recent work suggests that the liquidus region is larger and extends further towards the N-rich region of the diagram [7]. The present investigation concentrated on compositions in the vicinity of the mullite–Si_3N_4 join.

2. Experimental procedure

Starting materials for the spheroidization experiments were prepared by firing mixtures of Si_3N_4 (< 53 μm, Goodfellow Metals), reagent grade calcined alumina (< 37 μm, Unilab), and precipitated amorphous SiO_2 (Ajax Chemicals) powders. The powders were mixed by tumbling as a slurry with alcohol, dried and pressed into

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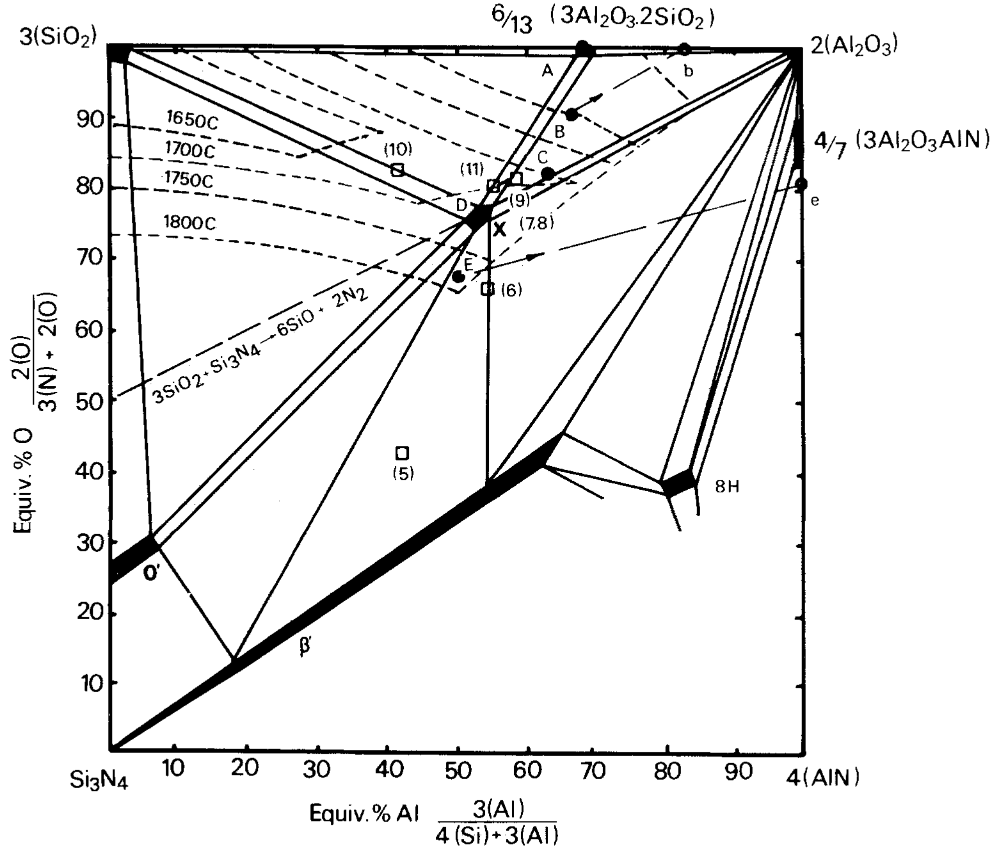

Figure 1 Si–Al–O–N phase diagram using the reciprocal salt representation based on a composition for phase *X* of $3Al_2O_3 \cdot 2SiO_2 \cdot 2/3Si_3N_4$. Numbers in parentheses are references to various reported compositions of *X*. The letters A to E refer to initial powder compositions used in the present study. The points b and e correspond to compositions of B and E after complete decomposition. Liquidus data from [9].

compacts at a pressure of ≃ 350 MPa. The compacts were packed in Si_3N_4 powder in Al_2O_3 crucibles and fired in a nitrogen atmosphere at temperatures in the range 1500 to 1800° C using either a Mo wound furnace or induction heated graphite susceptor. The fired compacts were ground using a high speed laboratory mill with WC blades and separated into various size fractions by screening. Phase constitution was determined by X-ray diffraction using CuKα radiation in a Philips diffractometer. The initial compositions of the powders are given in Table I and also represented in the phase diagram of Fig. 1. Samples of spheroidized pure Al_2O_3 (− 53 μm, + 37 μm) and a sample of γ-Al_2O_3 prepared by plasma spraying 20 μm α-Al_2O_3 powder onto a cold substrate were also examined.

Powders were spheroidized using the apparatus illustrated in Fig. 2 which consisted of a d.c. plasma torch (A) and water cooled reaction chamber (B) sealed from the atmosphere to prevent oxidation of the powder which was injected radially into the torch anode through the inlet (C) in a stream of Ar. Additional gas (He) could be injected radially into the reaction chamber by means of the quench ring (D). The gas–particle stream was then directed through a water-cooled conical section (E) into a water-cooled cyclone (F) which allowed collection of the spheroidized powder. The plasma torch was operated on nitrogen at ≃ 16 kW electrical input.

Typical conditions were:

Voltage	110
Current	150 amp
Nitrogen flow rate	30 l min^{-1}
Quenching gas (He) flow rate	60 l min^{-1}

Initial experiments showed that the particle size of the powder influenced its structure after spheroidization and all subsequent work made use of two feed powder size fractions: − 75 + 53 μm and − 53 + 37 μm. The spheroidized

TABLE I Initial powder compositions and phases present after firing and spheroidization

Powder	Initial composition	Al_2O_3 (wt%)	SiO_2	Si_3N_4	Phases after firing (minor phases in brackets)	Phase present after spheroidization	
						$-53, +37\,\mu m$	$-75, +53\,\mu m$
A	$3Al_2O_3 \cdot 2SiO_2$	73	27	0	mullite (α-Al_2O_3)	mullite, glass	mullite, glass
B	$13.3Al_2O_3 \cdot 6.9SiO_2 \cdot Si_3N_4$	72.5	20.7	6.8	X, mullite, α-Al_2O_3	δ-Al_2O_3/γ-Al_2O_3 (α-Al_2O_3, mullite)	α-Al_2O_3, mullite (δ-Al_2O_3)
C	$6.8Al_2O_3 \cdot 3SiO_2 \cdot Si_3N_4$	67.4	18.5	14.1	X, α-Al_2O_3 (β'-SiAlON)	γ-Al_2O_3 (α-Al_2O_3)	γ-Al_2O_3 (α-Al_2O_3)
D	$4.5Al_2O_3 \cdot 3SiO_2 \cdot Si_3N_4$	60.8	22.3	16.9	X, (β'-SiAlON)	γ-Al_2O_3, δ-Al_2O_3	γ-Al_2O_3, X-SiAlON (mullite, α-Al_2O_3)
E	$3.3Al_2O_3 \cdot SiO_2 \cdot Si_3N_4$	64.9	10.7	24.4	X, β'-SiAlON (α-Al_2O_3)	γ-Al_2O_3, X-Al_2O_3/AlN (β'-SiAlON, α-Al_2O_3)	γ-Al_2O_3, α-Al_2O_3 (β'-SiAlON, X-Al_2O_3/AlN)

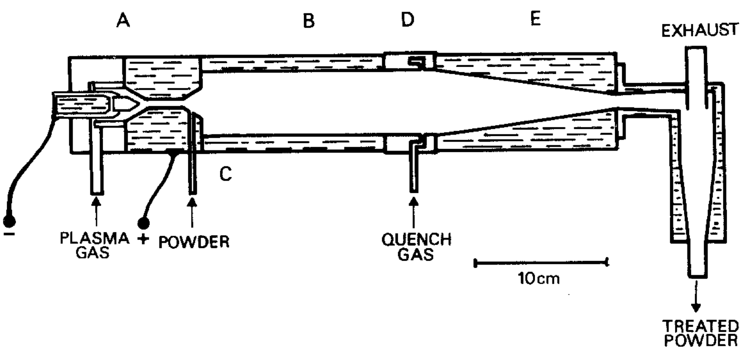

Figure 2 Plasma spheroidization apparatus: A plasma torch; B reaction chamber; C powder injection inlet; D gas quenching ring; E conical section and F cyclone.

powders were examined by X-ray diffraction, differential thermal analysis (DTA) and transmission optical microscopy. The DTA experiments were performed using a "Rigaku" micro-DTA apparatus at a heating rate of 20° C min^{-1} under a nitrogen atmosphere. Powders were dispersed in a liquid of comparable refractive index (bromoform) between a microscope slide and cover slip for optical microscopy using a Zeiss Ultraphot microscope.

It was found that the equilibrium phases expected from the phase diagrams shown in Fig. 1 could be prepared by heating the compacts for 1 to 2h at $\simeq 1600°$ C; the phases present in the as-fired compacts and after spheroidization are shown in Table I.

The spheroidized Al_2O_3 powder consisted of a mixture of δ-Al_2O_3 and α-Al_2O_3 with no detectable γ-Al_2O_3. DTA gave a rather broad exotherm with a peak at 1250° C and X-ray diffraction of a sample heated to just above the peak showed that it consisted of α-Al_2O_3 and a trace of θ-Al_2O_3. The sample prepared by plasma spraying α-Al_2O_3 powder onto a cold substrate consisted predominantly of γ-Al_2O_3 with some α-Al_2O_3 but no detectable δ-Al_2O_3 and DTA gave a large exotherm at 1150° C corresponding to transformation to α-Al_2O_3. The mullite composition powder gave a mixture of mullite and glass after spheroidization, as expected from previous studies [3]. Many of the particles were dumbell-shaped and consisted of small crystals of mullite in a glass matrix (Fig. 3). A large, sharp exotherm was observed at 1000° C in DTA experiments which X-ray diffraction showed corresponded to crystallization of the glass to mullite.

The spheroidization products of the nitrogen containing powders were brown in colour and the reaction chamber and cyclone walls were also covered with a fine brown powder. Optical microscopy showed that the products consisted of transparent spherical particles, with some of the fine brown powder on the surface; only a small proportion of the powders were unmelted. X-ray diffraction revealed that samples of the powder collected from the reaction chamber walls were amorphous and heating to $\simeq 1500°$ C resulted in the appearance of cristobalite suggesting that it was the condensation product of SiO vapour, which does not exist as a crystalline phase but forms a brown amorphous powder on cooling [12].

Significant differences in the structure of the two size fractions of the nitrogen-containing powders were observed after spheroidization. X-ray diffraction showed that the -53, $+37\,\mu$m fraction of powder D, initially predominantly phase X, consisted of γ-Al_2O_3 plus a trace of δ-Al_2O_3 after spheroidization. DTA experiments gave a broad exotherm between 910 and 1020° C (peak $\simeq 980°$ C) but X-ray diffraction after heating to 1100° C showed no apparent structural change. No other DTA peaks were observed although the powder consisted of a mixture of mullite and α-Al_2O_3 after heating to 1400° C. Optical microscopy showed that the powder consisted of spherical, optically isotropic particles with evidence of surface and internal patterns consistent with them being crystalline rather than amorphous. The -75, $+53\,\mu$m fraction of powder D again consisted predominantly of γ-Al_2O_3 but also contained some α-Al_2O_3 and phase X together with traces of δ-Al_2O_3 and mullite. DTA revealed an exotherm with a peak at 1120° C but X-ray diffraction of a sample heated to 1200° C showed that the main change was an increase in the proportion of phase X. After heating to 1500° C alumina was present predominantly as α-Al_2O_3 with some δ-Al_2O_3 and a trace of γ-Al_2O_3 with no other apparent structural change. It was difficult to detect the

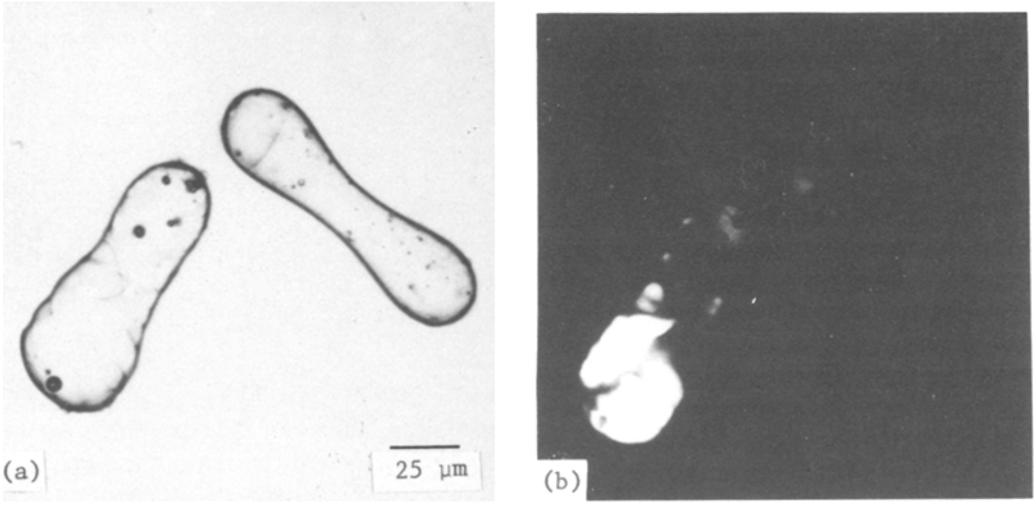

Figure 3 Optical micrograph, spheroidized powder A (mullite) (a) normal illumination and (b) crossed Polaroids.

presence of an amorphous phase with certainty by X-ray diffraction, however, there was evidence of a broad hump between 20 and 30°, 2θ in the pattern from spheroidized powder which was absent after heating to 1500° C.

Other nitrogen-containing compositions gave generally similar results, namely the appearance of γ-Al_2O_3/δ-Al_2O_3 as the major phase after spheroidization of the smaller size fraction with complete disappearance of phase X, a small DTA peak between 920 and 1000° C, and gradual transformation of γ/δ-Al_2O_3 to α-Al_2O_3 on heating over the range 1200 to 1500° C. The only significant differences observed between the various compositions were the formation of γ-Al_2O_3 in powder E (initially $X + \beta'$) together with additional lines which were found to correspond to the "X" metastable Al_2O_3–AlN phase reported by Lejus [13]. No DTA exotherms were observed for this powder after spheroidization and the γ-Al_2O_3 phase persisted on heating to 1500° C at 20° C min^{-1} in DTA experiments. Heating at 1500° C for 90 min in N_2 resulted in the formation of a mixture of α-Al_2O_3 and AlN with some residual γ-Al_2O_3. The larger particle size powders all showed the presence of residual phases in addition to γ/δ-Al_2O_3 after spheroidization and DTA gave only one exotherm with a peak temperature of $\simeq$ 1100° C.

3. Discussion

The results obtained for the spheroidized mullite composition material are very similar to previous work using flame spheroidization [1, 3]. The major difference is the presence of dumbell-shaped particles showing that break-up of the liquid droplets occurs, probably because of the turbulent conditions produced by gas quenching. Glass was also observed in larger particles in the present study and, although mullite has nucleated in many of the dumbell-shaped particles, the cooling rate has been sufficiently rapid to prevent significant crystal growth. The cooling rate is therefore probably greater than that achieved by flame spraying into water. The observation of δ-Al_2O_3 in spheroidized alumina is also consistent with previous studies, its formation rather than γ-Al_2O_3 being explained by transformation during cooling [14] whereas γ-Al_2O_3 is observed in plasma sprayed coatings because of the higher cooling rate resulting from the small thickness of the lamellae formed on impact and the high heat transfer coefficient between the flattened particle and substrate [15]. The fact that the -53, $+37\,\mu$m fraction of spheroidized Al_2O_3 consisted predominantly of δ-Al_2O_3 also suggests that the cooling rate achieved with He quenching is greater than that obtained by other techniques which tend to result in the formation of δ-Al_2O_3 only in particles of size less than $\simeq 20\,\mu$m diameter [14]; the cooling rate in the present study is therefore probably of the order of 10^{6} °C sec^{-1}.

The formation of γ-Al_2O_3 and SiO as the major products of spheroidization of the smaller size fraction phase X powder indicates that decomposition occurs on melting, even within the very short time interval available between reaching the melting point and quenching ($\simeq 0.1$ sec). The most likely decomposition reaction is

$$3Al_2O_3 \cdot 2SiO_2 \cdot 2/3Si_3N_4 \rightarrow 3Al_2O_3 + 4SiO + 4/3N_2, \qquad (1)$$

resulting in the formation of liquid Al_2O_3 droplets and the gases SiO and N_2. The SiO would condense to the fine amorphous brown powder observed and the liquid Al_2O_3 would freeze as γ-Al_2O_3 or δ-Al_2O_3 because of the more favourable nucleation kinetics of the metastable phases under these conditions [14]. Calculation of the free energy change for the reaction,

$$Si_3N_4 + 3SiO_2 \rightarrow 6SiO + 2N_2, \qquad (2)$$

using available thermodynamic data [16], confirms that the reaction will proceed to the right at temperatures greater than $\simeq 1800°$ C, that is close to the melting point of phase X. The line corresponding to the ratio $SiO_2 : Si_3N_4 = 3$ is shown on the phase diagram (Fig. 1). Along this line complete decomposition would result in pure Al_2O_3 as the solid product. Powders C and D both lie on the line and give γ-Al_2O_3/δ-Al_2O_3 as the major crystalline phase however no exotherm was observed corresponding to the transformation to α-Al_2O_3, which occurs at $\simeq 1150°$ C for γ-Al_2O_3 and $\simeq 1250°$ C for δ-Al_2O_3 although complete transformation had taken place between 1100 and 1400° C. This is similar to the behaviour of γ-Al_2O_3 containing small quantities of SiO_2 which transforms slowly to α-Al_2O_3 between 1200 and 1400° C [2], suggesting that spheroidized powders C and D contain some residual SiO_2 in solution.

Above the 3:1 line complete decomposition would result in the formation of liquid Al_2O_3 containing SiO_2 in solution giving a γ-Al_2O_3/SiO_2 solid solution after solidification. Powder B falls in this region and complete decomposition would give γ-Al_2O_3–15 wt% SiO_2 (b in Fig. 1). Previous studies [2] have shown that at this composition, γ-Al_2O_3 is stabilized to high temperatures and transforms to α-Al_2O_3 only after heating for some time at 1400° C which is consistent with the present observation that only partial transformation occurred after heating to 1500° C at 20° C min^{-1}.

Complete decomposition of compositions below the 3:1 line would result in elimination of Si and the formation of an Al_2O_3–AlN liquid (the reaction: $Al_2O_3 + Si_3N_4 \rightarrow 3SiO + 2AlN + N_2$ is also thermodynamically favourable at temperatures greater than $\simeq 1900°$ C). Thus powder E would decompose to give the composition $2Al_2O_3 \cdot AlN$ (e in Fig. 1), which falls within the region of high temperature stability of the γ-Al_2O_3/AlN (spinel) phase, plus the "X"-Al_2O_3/AlN phase of the Al_2O_3-AlN system [13]. Again this is consistent with the present results which show the presence of γ-Al_2O_3, plus "X"-Al_2O_3/AlN after spheroidization with no structural change on heating to 1500° C but partial transformation to α-Al_2O_3 + AlN on heating at 1500° C for 90 min.

The evidence therefore suggests that the − 53, + 37 μm fractions of nitrogen-containing powders almost completely decompose during plasma spheroidization to give γ-Al_2O_3/δ-Al_2O_3 containing residual SiO_2 and/or N depending upon the initial composition. The larger size fraction (− 73, + 53 μm) nitrogen-containing powders however do not completely decompose during spheroidization. The appearance of a large exotherm at $\simeq 1100°$ C in all of these powders is significant: X-ray diffraction showed that it could not be associated with transformation of γ-Al_2O_3 and the absence of any other structural change suggests that it corresponds to the crystallization of an amorphous phase. Since the crystallization of SiO_2–Al_2O_3 glasses occurs at temperatures in the range 920 to 1020° C [1, 2] the exotherm at 1100° C cannot be from glasses in this composition range and the conclusion must therefore be reached that the larger size fraction powders contain some Si–Al–O–N glass which crystallizes at $\simeq 1100°$ C, probably to phase X. The composition of the glass is unknown because of partial decomposition during melting, however, the result is consistent with the suggestion that nitrogen tends to increase the devitrification temperature [4].

4. Conclusions

Although glasses can be formed by plasma spheroidization and quenching of mullite an attempt to extend this method to nitrogen-containing compositions results in decomposition to γ-Al_2O_3, containing SiO_2 and/or N. There is some evidence that nitrogen-containing glasses can be formed under conditions which minimize decomposition and these crystallize at $\simeq 1100°$ C.

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