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Phase Relationships Involving Mixed O'–β' Sialons in the Y–Si–Al–O–N System

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SUMMARY

As a preliminary to investigating O'–β' *phase relationships in the Y–Si–Al–O–N system, sub-solidus phase relationships in the* Si_2N_2O–AlN–Y_2O_3 *system have been studied. The results show that two AlN-containing triangles and eight tetrahedra, of which seven contain YAG, occur in this system, namely:* Y_2O_3–J–AlN; J–K–AlN; H–Si_3N_4–O'_{ss}–Si_2N_2O; K–Si_3N_4–H–YAG; K–Si_3N_4–AlN–YAG; H–Si_3N_4–O'_{ss}–YAG; Si_3N_4–O'_{ss}–$\beta'(z=0{\cdot}8)$–YAG; O'_{ss}–β' $(z=0{\cdot}8)$–X–YAG; X–β' $(z=0{\cdot}8)$–β' $(z=4)$–YAG; Si_3N_4–β' $(z=4)$–AlN–YAG.

Phase relationships involving O'–β' *sialon in the Y–Si–Al–O–N system have been revised. In the Si–Al–O–N system, the* O'–β' *two-phase region consists of two compatibility triangles:* Si_3N_4–Si_2N_2O–$O'_{ss}(x=0{\cdot}3)$ *and* Si_3N_4–$\beta'(z=0{\cdot}8)$–$O'_{ss}(x=0{\cdot}3)$. *In the Y–Si–Al–O–N system, there are three compatibility tetrahedra involved in the* O'–β' *region, and the sub-solidus phase relationships depend on temperature. At 1550°C, these three compatibility tetrahedra are* Si_3N_4–Si_2N_2O–$O'_{ss}(x=0{\cdot}3)$–H, Si_3N_4–$O'_{ss}(x=0{\cdot}3)$–H–YAG *and* Si_3N_4–$\beta'(z=0{\cdot}8)$–$O'_{ss}(x=0{\cdot}3)$–YAG. *At devitrification temperatures (1200–1300°C), they are:* Si_3N_4–Si_2N_2O–$O'_{ss}(x=0{\cdot}3)$–$Y_2Si_2O_7$, Si_3N_4–$O'_{ss}(x=0{\cdot}3)$–$Y_2Si_2O_7$–YAG *and* Si_3N_4–$\beta'(z=0{\cdot}8)$–$O'_{ss}(x=0{\cdot}3)$–YAG.

1 INTRODUCTION

In recent years two-phase ceramics have received more and more attention, since they offer the advantage over single phase materials that their

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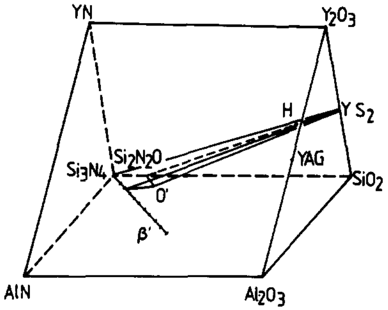


Fig. 1. The compatibility pyramid Si_3N_4–Si_2N_2O–β′(z = 0·8)–O'_{ss}–$Y_2Si_2O_7$ from Naik *et al.*[4] YAG = $3Y_2O_3.5Al_2O_3$, $YS_2 = Y_2Si_2O_7$, $H = Y_{10}(SiO_4)_6N_2$.

properties can be tailored extensively. β′-Sialon has already been established as a good high-temperature engineering ceramic with excellent mechanical properties. O′-Sialon $(Si_2N_2O)_{ss}$ ceramics either hot-pressed[1] or pressureless sintered[2] possess good oxidation resistance up to 1350–1400°C. O′–β′ composite sialons offer good prospects for development as ceramic materials, combining the mechanical properties of β′ with the good oxidation resistance of O′. Dense O′–β′ sialons[3] have been fabricated by pressureless sintering using Y_2O_3 as an additive. Most of the intergranular glassy phase can be devitrified to produce $Y_2Si_2O_7$ and YAG by sequential

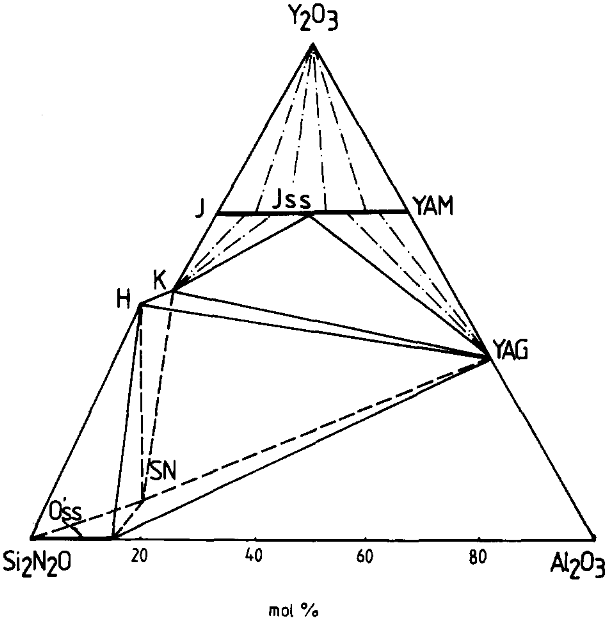


Fig. 2. Sub-solidus diagram of the Si_2N_2O–Al_2O_3–Y_2O_3 system from Cao *et al.*[5] J = $2Y_2O_3.Si_2N_2O$; K = $Y_2O_3.Si_2N_2O$; SN = Si_3N_4; YAM = $2Y_2O_3.Al_2O_3$.

heat treatments and the oxidation resistance of the devitrified specimens is good up to at least 1300°C.

The crystalline products from the intergranular glass are determined by phase relationships. Previous phase relationships[4] show that O′–β′ and $Y_2Si_2O_7$ form a compatibility region, as shown in Fig. 1. However, Cao's work[5] on phase relations in the Si_2N_2O–Al_2O_3–Y_2O_3 system indicates that O′-sialon should be in equilibrium with YAG and also with Si_3N_4 and H-phase, as shown in Fig. 2. The present paper attempts to clear up this confusion.

The Si_2N_2O–AlN–Y_2O_3 plane is considered to be mainly concerned with phase relationships involving O′–β′ sialons. Like β′-sialon which can be synthesized from AlN and SiO_2[6], O′–β′ composite sialons can also be produced by reacting AlN and Si_2N_2O. For these reasons phase relationships in the Si_2N_2O–AlN–Y_2O_3 system were studied, and also taken as a continuation of our previous work on phase equilibrium studies in the Si_2N_2O-containing system.[5]

2 EXPERIMENTAL

Aluminium nitride, as one of the starting materials, was prepared in our laboratory, and contained 1·4% oxygen. The details of other starting powders used and preparation of specimens are the same as described in our previous paper.[5] The hot-pressing temperature used was 1700–1750°C for the compositions on the line joining Si_2N_2O and AlN, and 1600°C for ternary Y_2O_3-containing compositions. The phase compositions of the specimens after hot-pressing were determined by X-ray diffraction analysis.

3 RESULTS AND DISCUSSION

3.1 Phase relationships in the Si_2N_2O–AlN system

As shown in the Si–Al–O–N phase diagram of Fig. 3, Si_2N_2O, O'_{ss}, Si_3N_4 and β'_{ss} form a compatibility region. The solubility limit of Al_2O_3 in Si_2N_2O was determined to be 15 mol/% (i.e. $x = 0{\cdot}3$ in the formula $Si_{2-x}Al_xN_{2-x}O_{1+x}$).[5] The upper limit of β′-sialon coexisting with O'_{ss} was detected to be $z = 0{\cdot}8$ in the formula $Si_{6-z}Al_zO_zN_{8-z}$.[3] Our previous work[5] shows there should be a tie line joining $O'_{ss}(x = 0{\cdot}3)$ to Si_3N_4. Therefore the Si_2N_2O–AlN join would cut across four tie lines: Si_3N_4–O'_{ss}, $\beta'(z = 0{\cdot}8)$–O'_{ss}, $\beta'(z = 0{\cdot}8)$–x and Si_3N_4–$\beta'(z = 4)$ at Si_2N_2O:AlN mol ratios of 4·3:1, 3:1, 1·6:1 and 1:1 respectively, forming five different phase regions: Si_2N_2O–O'_{ss}–Si_3N_4, Si_3N_4–O'_{ss}–$\beta'(z = 0{\cdot}8)$, O'_{ss}–$\beta'(z = 0{\cdot}8)$–x, x–$\beta'(z = 0{\cdot}8)$–$\beta'(z = 2)$ and $\beta'(z = 2)$–AlN (and

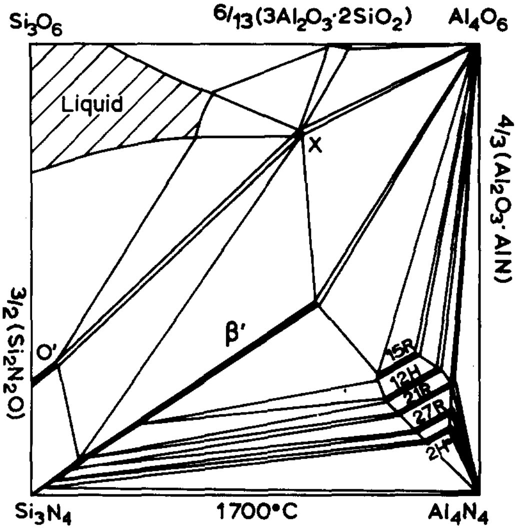


Fig. 3. Phase relationships in the Si_3N_4–SiO_2–Al_2O_3–AlN system at 1700°C after Thompson *et al.*[8]

polytypes). The present work using Si_2N_2O and AlN as starting materials has confirmed the existence of these phase regions. The temperature used was 1700–1750°C, since above 1750°C the decomposition of Si_2N_2O occurs according to the reaction:

$$4Si_2N_2O(S) \rightarrow \beta'\text{-}Si_3N_4(S) + Si(L) + 4SiO(G) + 2N_2(G)$$

Compositions between Si_2N_2O and 4·3 Si_2N_2O:AlN contain Si_2N_2O (and/or O'_{ss}) and β'–Si_3N_4 (with small amounts of α-Si_3N_4). Pure $\beta'(z = 2)$ can be obtained at the Si_2N_2O:AlN composition at 1750°C but below this temperature the reaction is not complete. The compositions between Si_2N_2O:AlN and AlN give $\beta'(z = 2)$ and AlN with a little 15R. The appearance of AlN instead of polytypes is expected, since the temperature used was not high enough to produce polytypes which are generally formed at above 1800°C if no or only a little liquid phase is present. The above results indicate that O'–β' sialon and $\beta'(z = 2)$ can be synthesized from Si_2N_2O and AlN mixtures.

3.2 Phase relationships in two Y_2O_3-containing binary systems

The two systems Y_2O_3–Si_2N_2O and Y_2O_3–AlN have been studied in our previous work[5,7] and it is unnecessary to repeat them. In the Y_2O_3–Si_2N_2O system, there are two compounds $2Y_2O_3 . Si_2N_2O$(J) and $Y_2O_3 . Si_2N_2O$(K), as shown in Fig. 2. At the Si_2N_2O-rich corner, Si_2N_2O reacts at 1550°C with

Y_2O_3 to form $Y_{10}(SiO_4)_6N_2$(H) and Si_3N_4 (mainly α-form, with a little β) by the following reactions:

$$10Si_2N_2O + 6Y_2O_3 \rightarrow Y_{10}(SiO_4)_6N_2 + 4Si_3N_4 + Y_2O_3 . Si_2N_2O$$
$$9Si_2N_2O + 5Y_2O_3 \rightarrow Y_{10}(SiO_4)_6N_2 + 4Si_3N_4$$

The existence of the compatibility region Si_2N_2O–O'_{ss}–Si_3N_4–h is contrary to other authors' results. The contradiction is caused mainly by the different experimental conditions used. Our previous work shows that H-phase completely disappears above 1700°C to form the glassy phase which can be devitrified to give $Y_2Si_2O_7$. The fact that different products are obtained by different experimental conditions emphasizes the point that sub-solidus phase relationships are not temperature invariant.

The system Y_2O_3–AlN does not produce any quaternary compounds.

3.3 Sub-solidus phase relationships in the Si_2N_2O–AlN–Y_2O_3 system

The temperature used inside the triangle was 1600°C which did not give any liquid in the compositions explored. The results obtained were used to construct the phase diagrams shown in Figs 4–6. Within this system, there exists two AlN-containing compatibility triangles J–Y_2O_3–AlN and K–J–AlN. In the Si_2N_2O-rich area, the phase relationships are rather complicated; K, H, Si_3N_4, O'_{ss} ($x = 0{\cdot}3$), β'_{ss} and AlN are all compatible with YAG, thus forming seven YAG-containing compatibility tetrahedra. Altogether there exist eight tetrahedra involved in this system:

H–Si_3N_4–O'_{ss}–Si_2N_2O
K–Si_3N_4–AlN–YAG
K–Si_3N_4–H–YAG
H–Si_3N_4–O'_{ss}–YAG
Si_3N_4–O'_{ss}–$\beta'(z = 0{\cdot}8)$–YAG
O'_{ss}–$\beta'(z = 0{\cdot}8)$–X–YAG
X–$\beta'(z = 0{\cdot}8)$–$\beta'(z = 4)$–YAG
Si_3N_4–$\beta'(z = 4)$–AlN–YAG

The results obtained are in good agreement with our previous work,[5] but contrary to the phase relationships obtained by Naik *et al.*[4] who reported the whole Si_3N_4–Si_2N_2O–O'_{ss}–$\beta'(z = 0{\cdot}8)$ region to be coexisting with $Y_2Si_2O_7$, as shown in Fig. 1. The determination of phase relationships of this ternary system is beneficial for the fabrication of O′–β′ composite ceramics from Si_2N_2O and AlN using Y_2O_3 as an additive.

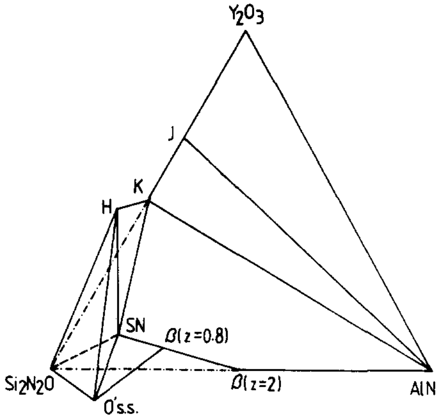


Fig. 4. Sub-solidus diagram of the Si_2N_2O–AlN–Y_2O_3 system.

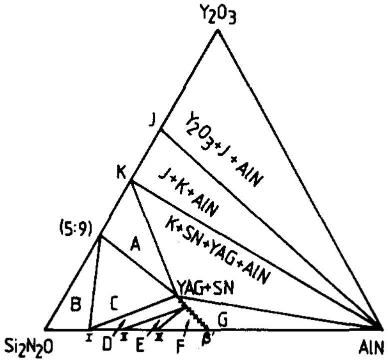
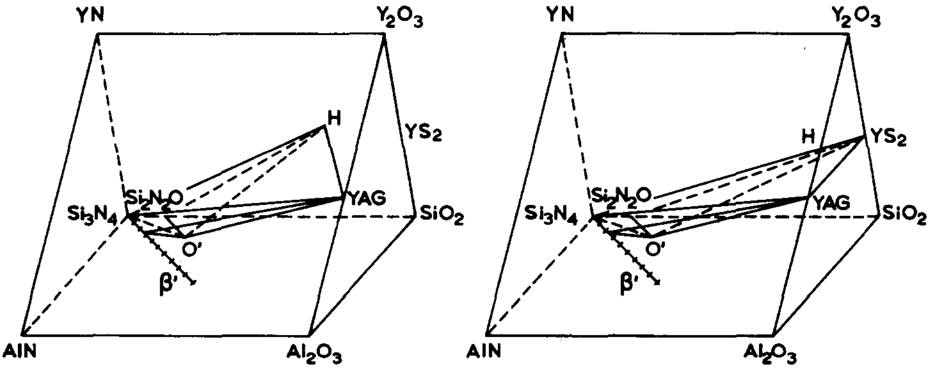


Fig. 5. Sub-solidus diagram of the Si_2N_2O–AlN–Y_2O_3 system. I = $O'_{ss} + Si_3N_4$; II = $O'_{ss} + \beta'(z = 0{\cdot}8)$; III = $\beta'(z = 0{\cdot}8) + x$; (5:9) = H + Si_3N_4; A = K + H + Si_3N_4 + YAG; B = H + $Si_3N_4 + Si_2N_2O + O'_{ss}$; C = H + $Si_3N_4 + O'_{ss}$ + YAG; D = $Si_3N_4 + O'_{ss} + \beta'(z = 0{\cdot}8)$ + YAG; E = $O'_{ss} + \beta'(z = 0{\cdot}8)$ + X + YAG; F = X + $\beta'(z = 0{\cdot}8) + \beta'(z = 4)$ + YAG; G = $Si_3N_4 + \beta'(z = 4)$ + AlN + YAG.



(a) (b)

Fig. 6. Phase relationships of O′–β′-sialon in Y–Si–Al–O–N system (a) at 1550°C, (b) at devitrifying temperatures 1200–1300°C.

3.4 Phase relationships involving O′–β′ sialon in the Y–Si–Al–O–N system

O′–β′ Phase relationships can be summarized as follows:

$$Si_3N_4\text{–}\beta'(z = 0{\cdot}8)\text{–}O'_{ss}(x = 0{\cdot}3)\text{–}YAG$$

$$Si_3N_4\text{–}O'_{ss}(x = 0{\cdot}3)\text{–}YAG\text{–}Y_2Si_2O_7(\text{or H})$$

$$Si_3N_4\text{–}Si_2N_2O\text{–}O'_{ss}(x = 0{\cdot}3)\text{–}Y_2Si_2O_7(\text{or H})$$

The two triangles Si_3N_4–Si_2N_2O–$O'_{ss}(x = 0{\cdot}3)$ and Si_3N_4–$O'_{ss}(x = 0{\cdot}3)$–YAG at lower temperatures (about 1550°C) join to H-phase. At higher temperatures (about 1700°C) H-phase dissolves into liquid phase and $Y_2Si_2O_7$ can then be crystallized from the liquid if sequential heat treatment is used. So the phase relationships of O′–β′ sialon are temperature dependent. For the fabrication of dense O′–β′ sialon ceramics, the temperature used for sintering is usually above 1700°C and $Y_2Si_2O_7$ is expected to be the intergranular crystalline phase instead of H-phase. The revised phase relationships can satisfactorily explain the appearance of YAG in O′–β′ sialon ceramics[3] and indicated that there is a choice of either $Y_2Si_2O_7$, YAG or both of these as grain-boundary phases for O′–β′ sialons.

4 CONCLUSIONS

(1) The sub-solidus phase diagram of the Si_2N_2O–AlN–Y_2O_3 is presented. Within this system no new compound has been found but two ternary phase regions and eight quaternary tetrahedra are identified.

(2) Phase relationships involving O′–β′ sialons in the Y–Si–Al–O–N system have been revised. The phase relationships are temperature dependent. Three compatibility tetrahedra, Si_3N_4–Si_2N_2O–O'_{ss}–$Y_2Si_2O_7$ (or H), Si_3N_4–O'_{ss}–$\beta'(z = 0{\cdot}8)$–YAG and O'_{ss}–Si_3N_4–YAG–$Y_2Si_2O_7$(or H) have been found.

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