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Studies on Phase Distribution in (O′ + β′)-Sialon Composites

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Abstract

By pressureless sintering powder mixtures of silicon nitride, silica and alumina, using Y_2O_3 as a densifying additive, O′-sialon (O′) formation begins at about 1400°C and increases with increasing temperature up to 1600°C β-Sialon (β′) formation then increases rapidly at the expense of unreacted α-Si_3N_4 and O′ The ratio of O′/β′ at higher temperatures (above 1700°C) depends on the aluminium concentration The more alumina which is present in the starting materials, the less O′ remains in (O′ + β′)-ceramics

The stability of O′ in composite (O′ + β′)-sialon has been studied, and the results show that the reduction of O′ at temperatures above 1700°C may be attributed to the formation of a liquid phase which dissolves O′ and produces β′ while cooling down The stability of synthesized Si_2N_2O with and without Al_2O_3 has also been determined and the results indicate that Si_2N_2O and O′ decompose significantly into Si_3N_4 and β′ respectively only at temperatures above 1800°C

Pulvermischungen von Siliziumnitrid, Silika und Aluminiumoxid mit Y_2O_3 als Sinterhilfsmittel wurden drucklos gesintert Dabei wird ab c *1400°C O′-Sialon gebildet Ab dieser Temperatur steigt die β-Sialonbildung schnell auf Kosten von noch nicht abreagiertem α-Si_3N_4 und O′ an Das Verhaltnis O′/β′ bei Temperaturen oberhalb 1700°C hangt von der Al_2O_3-Konzentration ab Je mehr Al_2O_3 im Ausgangspulver vorhanden ist, desto weniger O′ verbleibt in (O′ + β′)-Keramiken*

Die Stabilitat von O′ in O′ + β′-Sialon-Komposites wurde untersucht und die Ergebnisse zeigen, daß die Reduktion von O′ bei Temperaturen oberhalb 1700°C auf die Bildung einer Flussigphase zuruckzufuhren ist, die O′ lost und beim abkuhlen β′ bildet Die Stabilitat von syntetisiertem Si_2N_4O mit und ohne Al_2O_3 wurde ebenfalls bestimmt und die Ergebnisse zeigen, daß Si_2N_2O und O′ sich nur oberhalb von 1800°C deutlich in Si_3N_4 und β′ zersetzen

Lors du frittage naturel à l'aide d'Y_2O_3 de mélanges de poudres de nitrure de silicium, de silice et d'alumine, la formation du sialon O′ commence vers 1400°C et se poursuit lors du chauffage jusqu'à 1600°C Dès lors, il se forme rapidement du sialon β′ à partir du Si_3N_4 α en excès et de la phase O′ Le taux O′/β′ à haute température (supérieure à 1700°C) dépend de la concentration en aluminium plus il y a d'aluminium présent au départ et moins il reste de phase O′ dans les céramiques (O′ + β′) La stabilité du O′ dans le sialon composite (O′ + β′) a été étudiée, et les résultats montrent que la réduction de O′ à des températures supérieurs à 1700°C peut être attribuée à la formation d'une phase liquide qui dissout le O′ et produit le β′ au refroidissement La stabilité du Si_2N_2O synthétisé avec et sans Al_2O_3 a également été déterminée et les résultats montrent que la décomposition de Si_2N_2O et O′ respectivement en Si_3N_4 et β′ ne devient significative qu'à des températures supérieures à 1800°C

1 Introduction

O′-Sialon (O′) ceramics are known to possess good oxidation resistance[1,2] and β′-sialon (β′) ceramics with excellent mechanical properties are currently manufactured for a range of engineering applications The incorporation of β′-sialon into O′-sialon offers the possibility of improving the mechanical properties, since many of the properties of a composite material are additive. Previous phase relationships[3] in the Y–Si–Al–O–N system show that O′, β′ and $Y_2Si_2O_7$ form a compatibility region

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However, previous work by Sun *et al*[4] indicates that both yttrium aluminium garnet (YAG) and $Y_2Si_2O_7$ can be crystallized out as intergranular phases in $(O' + \beta')$-sialon composites. Recent work on phase relationships of $(O' + \beta')$-sialon in the Y–Si–Al–O–N system[5] revised the previous work[3] and indicates that three compatibility tetrahedra are involved in the O'–β' region and the sub-solidus phase relationships depend on temperature. At 1550°C the phase relationships are as follows

$$Si_3N_4 + Si_2N_2O + O'(Si_{2-x}Al_xN_{2-x}O_{1+x},\ x = 0{\cdot}3) + H$$
$$Si_3N_4 + O'(x = 0{\cdot}3) + H + YAG$$
$$Si_3N_4 + \beta'(Si_{6-z}Al_zO_zN_{8-z},\ z = 0{\cdot}8) + O'\ (x = 0{\cdot}3) + YAG$$

On firing at higher temperatures (above 1700°C), the H-phase completely dissolves and the phase relationships after devitrification at 1200–1300°C are changed with $Y_2Si_2O_7$(Y 2S) appearing instead of H, as shown in Fig 1. For the fabrication of dense nitride ceramics, sintering temperatures are usually around 1700–1800°C. Therefore, in an $(O' + \beta')$- composite sialon with Y_2O_3 as additive, there is a choice between $Y_2Si_2O_7$ and YAG or a combination of both as the grain-boundary phases.

Two-phase materials also provide the advantage that if, during fabrication, the two phases form at different rates or at different temperatures, it is possible to tailor the microstructure to full advantage. Previous work by Sun *et al*[4] shows that, by pressureless sintering powder mixtures of Si_3N_4, SiO_2 and Al_2O_3 using Y_2O_3 as a densifying additive, O' formation starts at about 1400°C and increases with increasing temperature up to about 1600°C, β' formation then increases rapidly at the expense of unreacted α-Si_3N_4 and some O'-sialon. Further work by Sun *et al* both at Newcastle and at Shanghai indicates that the ratio of O'/β' at temperatures above 1700°C depends on the aluminium concentration. If the starting materials contain more alumina, more O' is consumed and the phase distribution which is in equilibrium at sub-solidus temperatures cannot be reached.

The present paper attempts to study the reaction sequence, phase distribution and densification in different compatibility phase regions and then to explore the cause for the decrease of O' in $(O' + \beta')$-ceramics at higher temperatures. To explore the possibility of fabricating $(O' + \beta')$-composite sialons with YAG as the only grain-boundary phase is also the aim of the present paper.

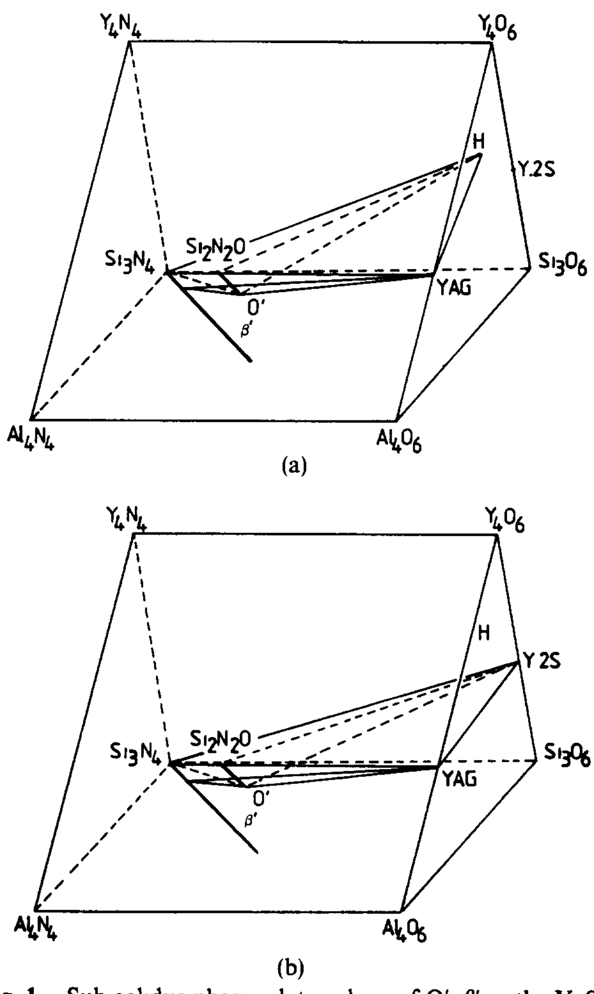

Fig. 1. Sub-solidus phase relationships of O'–β' in the Y–Si–Al–O–N system (a) below 1550°C and (b) at devitrifying temperature. H, $Y_{10}(SiO_4)_6N_2$, Y 2S, $Y_2Si_2O_7$, YAG, $3Y_2O_3 \cdot 5Al_2O_3$

2 Experimental

Crushed quartz crystal, alumina and yttria, all of 99·9% purity, were ball-milled using alumina media with silicon nitride (Starck LC for the Y-series samples, and laboratory-made powder containing 1·4% O for the G-series samples) in isopropyl alcohol for 25 h. Powder mixes were dried and uniaxially pressed in a steel die, then cold isostatically pressed at 200 MPa and, after embedding in Si_3N_4 SiO_2 powder to suppress volatilization of silicon monoxide and nitrogen, fired in a nitrogen atmosphere. Weight losses of the fired samples were all less than 1%. Silicon oxynitride prepared in the Shanghai Institute of Ceramics, containing 16·4% oxygen, was used for the determination of the stability of Si_2N_2O and O'.

Matrix compositions with O' $\beta' = 1{\cdot}1$ within the two-phase region of the Si–Al–O–N system, as shown in Fig. 2, plus extra 15 wt% $Y_2Si_2O_7$ or 15 wt% YAG, respectively, making a total of nine

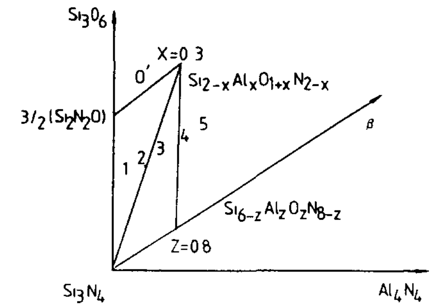

Fig 2 The O'–β' region of the Si–Al–O–N system showing the tie line joining Si_3N_4–O'($x = 0\ 3$) and the compositions explored

compositions distributed in different compatibility tetrahedra, as listed in Table 1, were explored Y-series experiments were carried out at Newcastle and G-series samples were prepared and experimented upon at Shanghai

Phase identification and quantitative analysis of phase compositions were made by X-ray diffraction

3 Results and Discussion

3.1 Reaction sequence

Reaction sequences for compositions within different phase regions, as shown in Table 1, were determined by quantitative measurement of phase compositions after sintering different specimens for 0 5–1 h (1 h for composition G-4) at 100°C intervals in the range 1300 or 1400 to 1800°C Intermediate heat-treatments at 1600°C for 0 5 h were used for the determination of compositions Y-5 and G-4 at above 1600°C Compositions within the $Si_3N_4 + Si_2N_2O + O'(x = 0\ 3) + Y_2Si_2O_7$ (phase region 1)

Table 1. Sample composition and phase region located

Sample	*Matrix composition*[a]	*Extra additive (wt %)*		*Phase region located*[b]
		$Y_2Si_2O_7$	*YAG*	
Y-1	1	15		1
Y-2	2	15		1
Y-3	3	15		2
Y-4	4	15		2
Y-5	5	15		3
G-1	1		15	2
G-2	2		15	2
G-3	3		15	3
G-4	4		15	4

[a] See Fig 1

[b] 1 $Si_3N_4 + Si_2N_2O + O'(x = 0\ 3) + Y_2Si_2O_7$

2 $Si_3N_4 + O'(x = 0\ 3) + Y_2Si_2O_7 + YAG$

3 $Si_3N_4 + O'(x = 0\ 3) + \beta'(z = 0\ 8) + YAG$

4 $O'(x + 0\ 3) + \beta'(z = 0\ 8) + X + YAG$

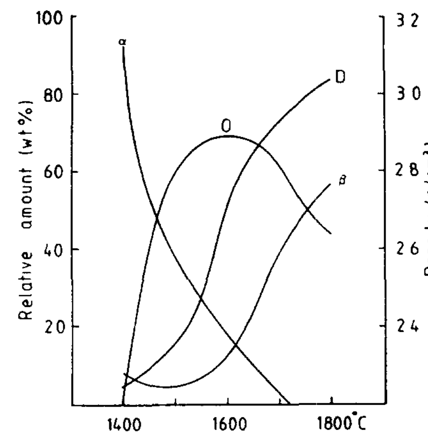

Fig. 3 Reaction sequence and densification for composition Y-3 after Ref 4 α, α-Si_3N_4, D, density

and the $Si_3N_4 + O'(x = 0\ 3) + Y_2Si_2O_7 + YAG$ (phase region 2) tetrahedra have a similar reaction sequence Composition Y-3 is typical, as shown in Fig 3 O' formation starts at about 1400°C and increases with increasing temperature up to about 1600°C β' formation then increases rapidly at the expense of unreacted α-Si_3N_4 and some O' to achieve the final equilibrium phase distribution Compositions within the $Si_3N_4 + O'(x = 0\ 3) + \beta'(z = 0\ 8) + YAG$ tetrahedron (phase region 3) have different behaviour at high temperatures As shown in Fig 4, most of the O' is exhausted at 1800°C and the expected 50 50 ratio of O' to β' cannot be obtained If the compositions are shifted further to the alumina-side, the extreme of having no O' appearing in the whole temperature range would occur, as shown in Fig 5 According to the chemical composition of G-4, which is just outside phase region 3 and goes into the $O'(x = 0\ 3) + \beta'(z = 0\ 8) + X + YAG$ tetrahedron (phase region 4), O' should still exist as a main phase From the tendency of the density curve, it is clear that in this region the liquid

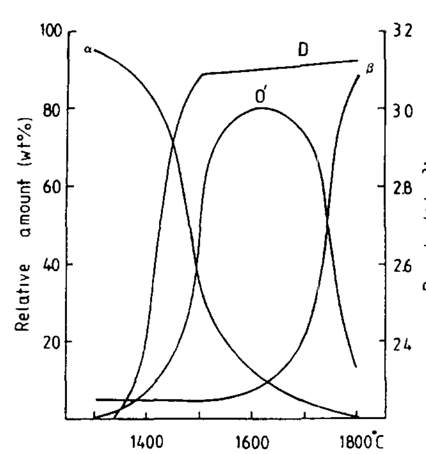

Fig. 4. Reaction sequence and densification for composition Y-5 α, α-Si_3N_4, D, density

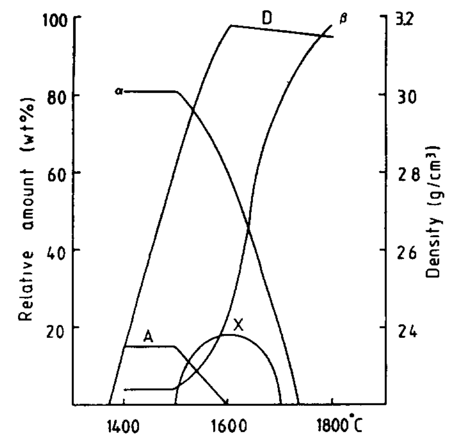

Fig. 5. Reaction sequence and densification for composition G-4 α, α-Si_3N_4, D, density, X, X-phase, A, Al_2O_3

phase forms at much lower temperatures, which promotes rapid densification below 1600°C and prevents the formation of O′ which is usually produced in large quantities at temperatures of 1500–1600°C

3.2 Densification and phase distribution

Densities and phase distributions of the compositions explored after firing at 1600°C for 0 5 h and 1700°C for 1 h are listed in Table 2 Some of the compositions were hot-pressed (at 1700–1750°C) and the densities which are assumed to be close to fully dense materials are also listed in Table 2 for comparison In the present work, intermediate heat-treatments at about 1600°C for 0 5 h were used to minimize bloating at higher firing temperatures. For all compositions within phase regions 3 and 4, bloating occurs above 1600–1700°C and becomes more severe at higher temperatures As can be seen from Figs 4 and 5, compositions in these regions densify rapidly at temperatures below 1600°C, which implies excessive liquid formation at lower temperatures. Bloating may be caused by the generation of a vapour mix of SiO plus N_2 from the liquid phases formed that become less stable at higher temperatures Matrix compositions 1 and 2 with either $Y_2Si_2O_7$ or YAG as sintering additives cannot be fired to full density Obviously, densities increase with increasing aluminium concentration in the matrix compositions The maximum density of the alumina-rich composition G-4 occurs at 1600°C and bloating at higher temperatures cannot be completely suppressed by using intermediate heat-treatments at 1500–1600°C, thus resulting in slightly decreasing densities at temperatures above 1600°C

Table 2. Density and phase composition under firing conditions of 1600°C for 0 5 h and 1700°C for 1 h

Sample	*Density* (*g/cm³*)	*Phase composition*[b]
Y-1	2 72	β′(s), O′(s)
Y-2	2 90	β′(s), O′(s)
Y-3	2 98 (3 09)[a]	β′(s), O′(s)
Y-4	3 09	β′(s), O′(m)
Y-5	3 11	β′(s), O′(m)
G-1	2 63 (3 16)	O′(s), β′(m)
G-2	2 72 (3 16)	β′(s), O′(m)
G-3	3 14	β′(s), O′(w)
G-4	3 14	β′(s)

[a] Obtained from hot-pressed samples
[b] s, Strong, m, medium, w, weak (from X-ray diffraction)

Phase distributions close to the equilibrium ratio for compositions within phase regions 1 and 2 can be achieved in the temperature range 1700–1750°C, but cannot be reached easily for compositions within phase region 3 As shown in Table 2, the more alumina existing in the starting materials, the less O′ remains in the fired compositions. Therefore, for the fabrication of dense (O′ + β′)-sialon with an equilibrium phase distribution, it is important to optimize the alumina content in the starting materials. Too high an alumina content would reduce O′-sialon content in the fired products and too low an alumina content brings difficulty in densification. It appears that compositions in phase region 2 (Si_3N_4 + O′ ($x = 0$ 3) + $Y_2Si_2O_7$ + YAG) are favorable to fabricate (O′ + β′)-sialon composites with high density and phase distributions not far away from equilibrium

3.3 Decomposition of Si_2N_2O and O′-sialon

The stability of Si_2N_2O and Si_2N_2O plus 10 wt% Al_2O_3 were determined by measurement of weight loss after firing different specimens in N_2 atmospheres, with and without a powder bed of Si_3N_4 SiO_2, for 1 h at 100°C intervals in the range 1500–1800°C The results (Fig 6) indicate that decomposition of both Si_2N_2O and O′ in a powder bed

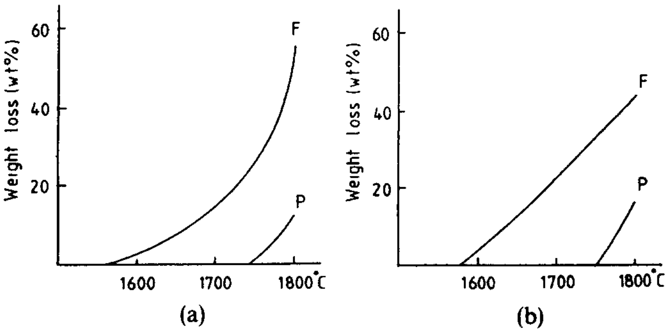

Fig. 6. Weight loss of (a) Si_2N_2O and (b) O′ F, Fired without packing, P, fired by embedding in Si_3N_4 SiO_2

starts at 1750°C and becomes severe at 1800°C However, both Si_2N_2O and O' fired without packing decompose severely at 1700°C and result in Si_3N_4 (mainly α-form with less β-form), and β' with a trace of α-Si_3N_4, respectively Gaseous phase compositions were not identified However, N_2 and SiO are presumed to be predominant [1]

Therefore, during the fabrication of (O' + β')-ceramics at 1700°C, the decrease in O' content in the alumina-rich compositions cannot be attributed to decomposition, since the pellets were embedded in a powder bed with very little or no weight loss

3.4 Dissolution of O'-sialon

Work at Shanghai on the Si_2N_2O–Al_2O_3–Y_2O_3 system[6] shows a liquid phase region on the O'–YAG join (Fig 7) The eutectic composition is Y_2O_3 $2Al_2O_3$ $2Si_2N_2O$ with $T_{eu} \sim 1450$°C Work at Newcastle on the β'–YAG plane[7] also indicates a large liquid region through the line joining Si_3N_4–YAG at 1700°C (Fig 8), which after devitrification at 1350°C, produces β' and YAG If devitrification takes place at 1050°C, β' and B-phase (Y_2SiAlO_5N) are produced The liquid regions indicated by both investigations are, in fact, different intersections with very similar compositions of the same liquid-forming region, which is just located in the composition region explored The formation of this liquid may facilitate the dissolution of the preformed O' while crystallizing out β', in addition to those formed at firing temperatures during cooling down The more liquid which forms during firing, the less O' would survive in the (O' + β')-sialon composite This is consistent with the observation that Al_2O_3-rich compositions have higher densities

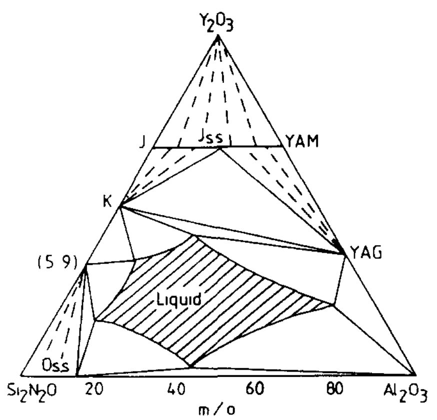

Fig. 7 Isothermal section at 1550°C in the Si_2N_2O–Al_2O_3–Y_2O_3 system (T_{eu} = 1450°C) After Ref 6 J = $2Y_2O_3$ Si_2N_2O, J_{ss} = solid solution between J and YAM, YAM = $2Y_2O_3$ Al_2O_3, O_{ss} = O'-sialon, K = Y_2O_3 Si_2N_2O, YAG = $3Y_2O_3$ $5Al_2O_3$

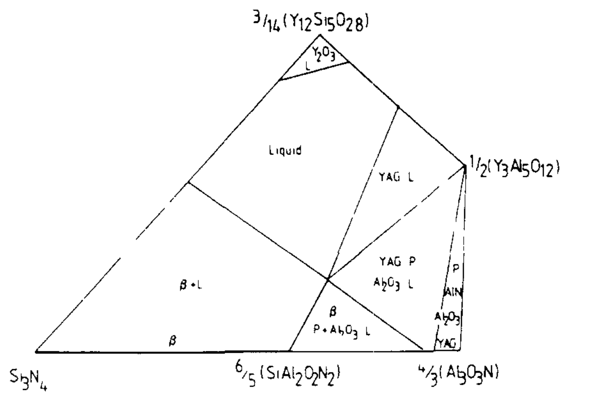

Fig. 8 Phase relationships in the β'–YAG plane at 1700°C After Ref 7 L = Liquid, P = AlN polytype

and lower O'-sialon contents Therefore, to fabricate (O' + β')-sialon composites with YAG as the only intergranular phase could not be realized Although the sub-solidus phase relationships indicate that this is possible, in fact this is not the case in practice, since firing temperature is usually above the liquidus temperature and heat treatment at sub-solidus temperatures cannot restore the corresponding equilibrium phases

4 Conclusion

O'-Sialon in alumina-rich (O' + β')-compositions is unstable at high temperatures due to the formation of a Y-sialon liquid phase which dissolves the preformed O' and gives β' during cooling down For the fabrication of dense (O' + β')-sialon composite ceramics with a phase distribution close to equilibrium, alumina content should be carefully controlled It is rather difficult to fabricate (O' + β')-composites with YAG as the only grain-boundary phase, although the sub-solidus phase relationships indicate the possibility

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