MICROSTRUCTURAL CONTROL AND OXIDATION BEHAVIOUR OF Gd-SiAlON CERAMICS

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ABSTRACT

The purpose of the present work are to investigate the possibility of controlling the microstructure of Gd α/β-SiAlON composite materials by controlling the starting composition and to study the oxidation behaviour of these ceramics. A series of Gd α/β-SiAlON composites were prepared by pressureless sintering at 1750 ^{o}C for 4 h. Additions of SiO_2 were made to a selected composition to explore the potential mechanisms for controlling the microstructural development. Investigation on oxidation resistance of selected materials was carried out isothermally at 1350 ^{o}C in air. It was found that materials in the as-sintered state comprised a high proportion of equiaxed α' phase and a small amount of β' and AlN polytypoid. The additions of up to 5 wt% of SiO_2 was found to be effective in promoting the development of β-SiAlON. The oxidation studies show that Gd α-SiAlON based materials exhibit greater oxidation resistance at 1350 ^{o}C compared to β+YAG material. The oxidation process of Gd α/β-SiAlONs was found to follow a parabolic relationship with respect to time. The parabolic rate constant for these materials is dependent on the microstructure of the ceramics.

INTRODUCTION

Silicon nitride has great potential for high temperature applications due to excellent high temperature properties such as high decomposition temperature, high strength, good chemical properties and high oxidation resistance. One of the problems associated with silicon nitride is densification. Sintering agent such as MgO [1] and Y_2O_3 [2] have been used to facilitate densification via liquid phase sintering, which always results in the formation of undesired residual glass in the microstructure.

The discovery of silicon nitride's solid solution, SiAlONs, opened the new hope of producing glass `free' ceramics by pressureless sintering. Unlike silicon nitride, the SiAlON ceramics have the ability to consume most of the elements contained in the residual glass, although, in reality there is always small amount of residual glass left in the microstructure. SiAlON exists in two major phases: α-SiAlON (α') and β- SiAlON (β'). α' is formulated as $Me_xSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$ where m(Si-N) are replace by m(Al-N) and n(Si-N) by n(Al-O). The charge discrepancy introduced by these substitutions is compensated by the metal ion, Me^{p+}, with m = px. Among the Me elements which have been reported to stabilise α' are Ca [3], Li [4], Y [5] and a selected lanthanide metals such as Sm, Nd, Dy and Yb [6-10]. The other structure in the SiAlON system is β-SiAlON (β') phase which is formed by substitution of the Al-O bond for the Si-N bond. β' has an overall composition of $Si_{6-z}Al_zO_zN_{8-z}$ with z varies from 0 to 4.2 [11]

Although pressureless sintered β' ceramics have been widely investigated and used commercially, the prospect of α'/β' composites is brighter. The main advantage of an α'/β' material is that its microstructure can be controlled, either by compositional change or by heat treatment, thus allowing the tailoring of mechanical properties to the desired

values. Moreover, the presence of α' in the microstructures provide greater control over residual phase crystallisation.

In the Lanthanide series, most of the reported rare earth α-SiAlON stabilising cations have concentrated on Nd, Sm, Dy and Yb. Rare-earth elements located in the middle of the series, such as Er and Gd received less attention. The objective of the present work was to demonstrate the ability to synthesis and control the microstructure of Gd doped α/β - SiAlON composites via altering initial composition selection. In addition, the effect of residual glass on the oxidation resistance of Gd-SiAlON ceramics was also investigated.

EXPERIMENTAL PROCEDURES

The raw materials used in making the investigated ceramic systems are α-Si_3N_4 (UBE-SNE10), AlN (Starck C), Al_2O_3 (Alcoa, purity 99.8%), SiO_2 (BDH-Merck, purity 99.8%) and Gd_2O_3 (BDH, purity 99.8%) which were added as a presynthesised glass (of composition Gd_2O_3. Al_2O_3. $2SiO_2$)

The starting α' and β' composition were calculated using a computer programme, with the assumption that all the Gd^{3+} will be incorporated in the α' structure. The computer programme selects the cation level to form a desired α' content in the final ceramic with predicted Al-N and Al-O bond substitution level. Corrections were made for the small amount of oxygen present in Si_3N_4 and AlN powders. After subtracting the total Si, Al, O, N and Gd required to form α', the remaining elements are assumed to form β' and the necessary equivalance of O and Al adjusted in the initial mixture via alteration of the AlN content. The range of overall compositions for Gd α/β-SiAlONs are shown in Figure 1, projected on to the base of Janecke prism, and are listed in Table 1. Compositions were designed to produce three SiAlON materials with varying α'/β' ratios. In each case, the values of m and n were 1.50 and 0.75 respectively.

Addition of 2wt% or 5wt% of silica were made directly to the starting compositions of sample Gd3 in an attempt to investigate the effect of increasing liquid content in the system on the β-SiAlON formation. The introduction of silica actually shifts the overall compositions, as shown in Figure 1, off the α' formation plane, towards the β' formation line and thus provides stronger compositional basis for β' evolution.

An appropriate amount of the required powders for 50 g batch SiAlON materials were milled in Si_3N_4 media for 72 hours, using isopropyl alcohol (IPA) and sieved through the 38μ mesh. The dried powders were isostatically pressed at 150 MPa for 10 seconds and pressureless sintered in nitrogen atmosphere for 4 hours at 1750°C.
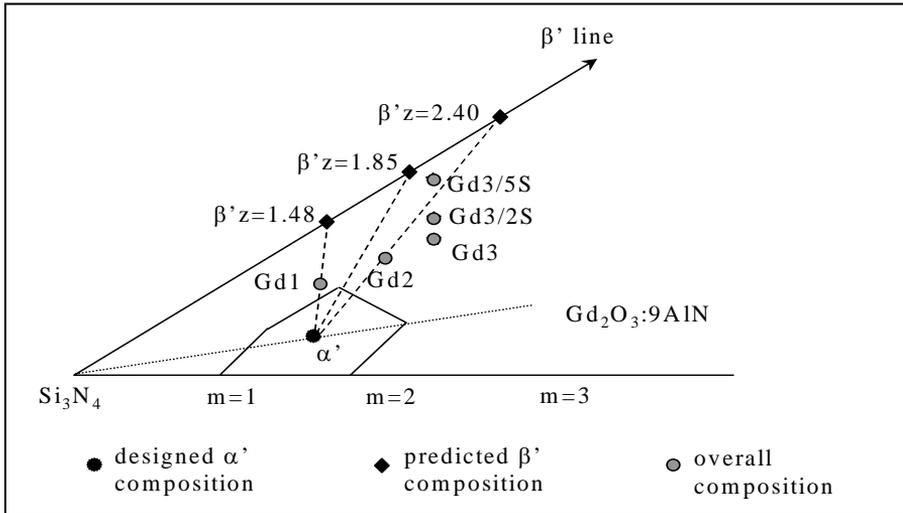
Figure 1.   The projection of composition prepared for Gd-SiAlONs.

The oxidation resistance test of Gd-SiAlON ceramics was carried out for a period up to 50 hours at 1350^oC on Gd3 with added SiO_2 series materials only. The test bars were placed on iridium sheet inside an air oven and removed at various time intervals. The weight gained at each interval was recorded before replacing the specimen in the oven. Materials were sliced and characterised by XRD (Philips PW 1700) and SEM (JEOL 6100).

Table 1. The composition (in wt%) prepared for Gd-SiAlON ceramics.

Sample	Predicted $\alpha':\beta'$	α-Si_3N_4	AlN	Gd-glass	SiO_2
Gd1	50:50	71.89	16.35	12.43	-
Gd2	65:35	63.88	19.82	16.30	-
Gd3	75:25	59.41	21.94	18.65	-
Gd3/2S	-	59.41	21.94	18.65	2.00
Gd3/5S	-	59.41	21.94	18.65	5.00

RESULTS AND DISCUSSION

1. As-Sintered Materials

The XRD phase analysis on the as-sintered material revealed that the only crystalline phases detected were α' and β' plus a small fraction of AlN polytypoid, namely 12H. The increment in Gd level in the starting charge has resulted in the increment of α':β' phase ratio, from around 78:22 in sample Gd1, to nearly 100% in sample Gd3 (Table 2).

Table 2. The density and phase of Gd-SiAlONs after pressureless sintering.

Sample	Density (g/cm^3)	Observed α':β'
Gd1	3.11	78:22
Gd2	3.33	90:10
Gd3	3.34	95:5
Gd3/2S	3.36	85:15
Gd3/5S	3.35	50:50

The α':β' ratios obtained in the Gd α/β-SiAlON materials were always higher compared to the predicted ratios. The higher α' content observed indicates that Gd is a good α' former, which can be attributed to the smaller ionic radii of the Gd^{3+} cation (~0.9 nm) [6]. This also indicates that the Gd stabilised α' has better stability than Nd or Sm α' with virtually no α'→β' transformation during furnace cooling.

Microstructure of as-sintered materials Gd1 and Gd3 are presented in Figure 2a and 2b. These materials consist of small, elongated dark grey β' crystals (~2μm long) thinly distributed in a light grey equiaxed α' matrix. The α' phase has the grain size ranging from ~0.5 to 1.5 μm and is surrounded by a layer of white glassy phase. The low density of material Gd1 is manifested by the existence of ~ 5% porosity in the size ~5 μm in diameter. A small amount of 12H AlN polytypoid was also observed, displaying its typical rectangular black grains with a grain size of approximately 3μm.

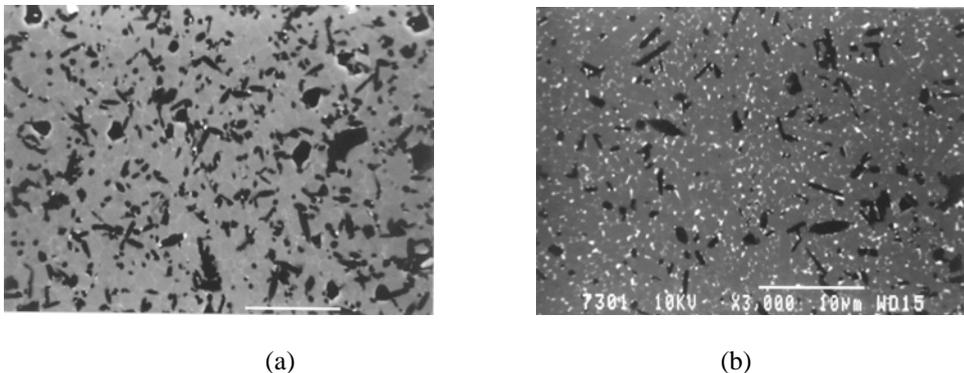(a)   (b)

Figure 2.   The SEM micrographs of as-sintered (a) Gd1 and (b) Gd3. The scale bar is equivalent to 10μm.

The series with increasing added SiO_2 was found to exhibit a decreased in α' content. The addition of 5wt% of silica resulted in the formation of more elongated β-SiAlON grains with aspect ratio varying from 4:1 to 10:1 while α' generally retained it's equiaxed morphology (Figure 3). This reduction is believed to result from the increased liquid content (approximately 12vol%) which retains a significant concentration of Gd and might also promotes α'→β' transformation on post-sinter cooling.

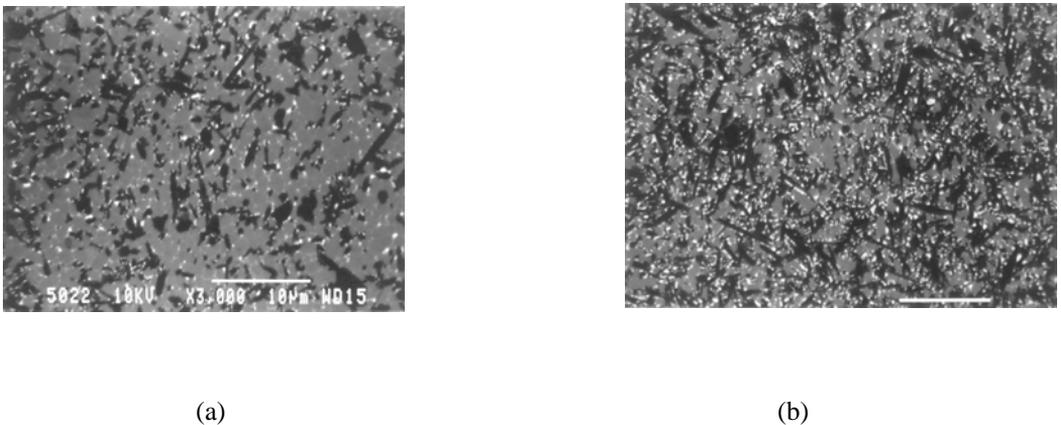|	
(a)	(b)

Figure 3.   The scanning elecron micrographs of as-sintered Gd3 SiAlON with addition of (a) 2 wt% and (b) 5 wt% of SiO_2. The scale bar is equivalent to 10μm.

2. Oxidation test

Figure 4 displays the oxidation curves for materials Gd3 and Gd3/5S, with material Gd3 displaying lower weight gain during oxidation. The linear nature of the plot in Figure 4 indicates that over the first 15h of exposure the oxidation process follows a parabolic relationship with respect to time, which suggests the oxidation process in these systems is diffusion-controlled. However, the rate of weight gain is no longer controlled by a parabolic relationship after 15h exposure.

The back scattered electron image for specimens exposed for a time period of 10h are shown in Figure 5. From the micrographs, three distinct regions can be identified:
(a)   the bulk ceramics
(b)   a zone of ~15μm wide depleted in gadolinium
(c)   an external oxide layer 10 - 60μm wide containing some gadolinium.

In the bulk ceramic zone, no significant microstructural change was observed apart from the crystallisation of the glassy phase. The gadolinium depleted area observed in both samples can be divided into two different zones. Firstly, the zone containing α' and β' phase, but not containing any intergranular phase. The formation of this zone suggests a diffusion of Gd ions from the grain boundaries into the oxidation scale. Secondly, the

outer zone, approximately 5 - 15 μm wide which contains β' phase only. The transformation of α' to β' phase due to the out-diffusion of Gd from the α' phase as well as from grain boundary to the oxide layer has resulted in the formation of β' rich zone.
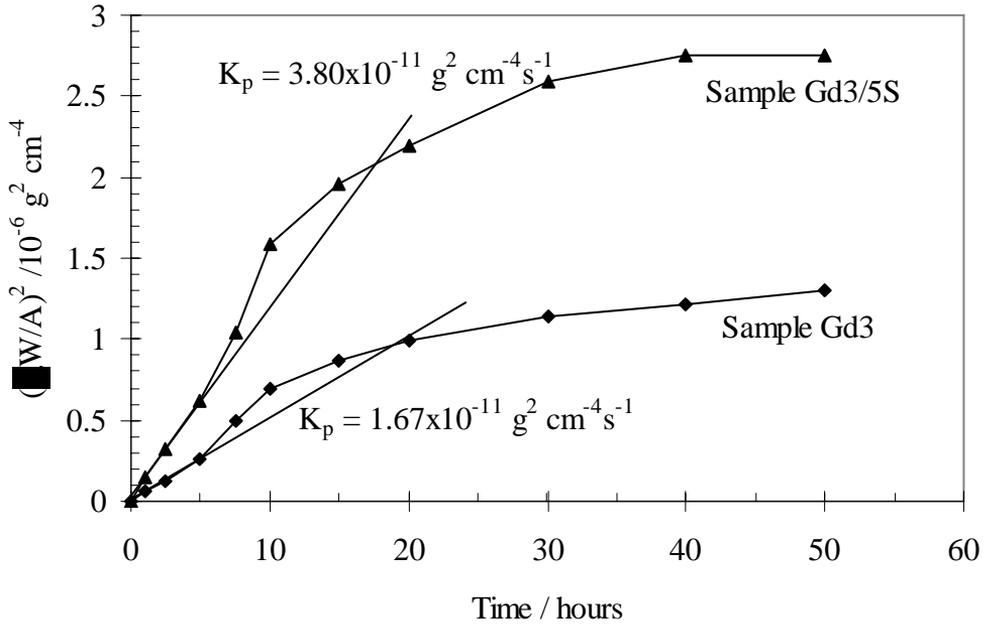

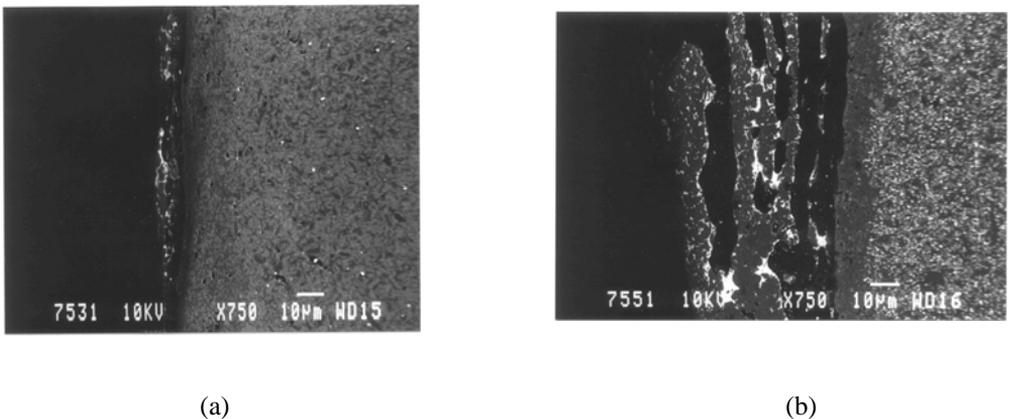Figure 4.   The relationship between weight gain per unit area and time during oxidation of sampels Gd3 and Gd3/5S.

| (a) | (b) |

Figure 5.   The SEM micrographs of (a) Gd3/2S and (b) Gd3/5S cermics after 10h oxidation at 1350°C

After 10 hours exposure in an oxidising environment at 1350°C, the Gd3/5S material developed a thicker oxide scale (30-60μm) compared with the other two materials. The white contrast outer layer of oxide scale contains a high Gd concentration because of

progressive depletion of Gd on the grain boundary as well as from α-SiAlON near to the surface. The oxides scales observed are porous and severely disrupted, due to the fact that gaseous nitrogen is released when silicon nitride based ceramics are oxidised.

Findings from the present work showed that material Gd3 exhibit greater resistance to oxidation at 1350°C compared to material Gd3/5S. The parabolic rate constant obtained for Gd3 (1.85×10^{-11} g^{2}cm^{-4}s^{-1}) is almost half the value observed for material Gd3/5S (3.80×10^{-11} g^{2}cm^{-4}s^{-1}). It is suggested that this is due to much higher α' phase and smaller volume of grain boundary glass phase formed in Gd3. The Gd cation may diffuse out from the α', but the rate of diffusion is slower due to α' stability.

CONCLUSIONS

Evidence for microstructural control was manifested by the variation of $\alpha':\beta'$ phase ratio as a result of starting compositional change. The use of Gd as the stabilising element in the α'/β' is a better choice than Nd or Sm due to the relative ease of the Gd cation in entering the α-SiAlON structure. The oxidation process in the Gd α/β-SiAlON systems is determine by the outward diffusion of the Gd cation from the intergranular phase and α' phase. Gd α/β-SiAlON material which contains ~100 α' exhibit greater resistance to oxidation at 1350°C compared to β'/YAG ceramic.

ACKNOWLEDGEMENT

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