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Pressureless sintered SiAlON with low amounts of sintering aid

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β'-SiAlONs of compositions $Si_{2.6}Al_{0.393}Y_{0.007}O_{0.4}N_{3.6}$ and $Si_{2.6}Al_{0.384}Y_{0.014}O_{0.4}N_{3.6}$ were pressureless sintered from mixtures of Y_2O_3 and separately milled β-Si_3N_4, AlN, and SiO_2. On sintering, the carbon content of these SiAlONs was reduced to negligible levels and their oxygen content was also proportionately reduced, presumably due to reaction of carbon with SiO_2. These SiAlONs had densities in excess of 98% of theoretical, four-point bend strengths of 460 and 155 MN m^{-2} at r.t. and 1400° C, respectively, and 1400° C oxidation rates lower than those reported in the literature for hot-pressed Si_3N_4 and for a similar but stronger SiAlON with 2.5 wt % Y_2O_3. These results indicate that increasing the Y_2O_3 content of SiAlONs increases their strength but decreases their oxidation resistance.

1. Introduction

The demand for ever higher operating temperatures in heat engines has created the need for materials with high oxidation resistance and strength. Silicon carbide- and silicon nitride-base ceramics have properties which make them likely candidates for applications in advanced heat engines, and among the new types of silicon nitride-base ceramics that have received a great deal of attention since they were first reported [1, 2] are the SiAlONs; so-called because they are made up of silicon (Si), aluminium (Al), oxygen (O), and nitrogen (N) atoms. The attention given these SiAlON ceramics stems mainly from the reportedly low thermal expansion, high oxidation resistance, and ease of fabrication by conventional pressureless sintering techniques. In addition, the single phase β'-SiAlONs [3, 4] have an extensive homogeneity range in terms of composition and, consequently, they could well have a corresponding variation in physical properties. This variation in properties might then allow tailoring the composition to the intended application.

The main objective of the present investigation was to produce β'-SiAlONs with high silicon nitride (Si_3N_4) content and low amounts of sintering aid by pressureless sintering methods and to determine the strength and oxidation resistance of the resulting ceramics. Additional objectives were to produce these SiAlONs from β-Si_3N_4 and to use a novel milling approach for their preparation.

In order to carry out these objectives, β-Si_3N_4, aluminium nitride (AlN), and silica (SiO_2) were ball-milled separately; the resulting powders were chemically analysed; and using these analyses as a guide the powders together with small amounts of yttria (Y_2O_3) as a sintering aid were compounded into the desired compositions. Cold-pressed bars of these compositions were sintered in nitrogen. The sintered bars were then used to determine the oxidation resistance, and modulus of rupture as a function of temperature.

2. Materials

The materials used in this investigation were powdered β-Si_3N_4, AlN, SiO_2, and Y_2O_3. These materials are listed and characterized in Table I together with other materials used in processing them.

3. Equipment

Two different types of ball mills were used in this investigation: nickel-lined ball mills of 1500 cm^3 capacity with ~ 3700 g nickel shot (0.63 to 1.27 cm diameter) as milling media, and alumina ball mills of 1400 cm^3 capacity with ~ 1200 g of

TABLE I Characterization of raw materials

Material	Source	Manufacturer designation	Purity	Size	Specific surface area ($m^2\ g^{-1}$)	Chemical analysis		Spectrographic analysis or manufacturer specifications (ppm unless noted otherwise)
						Oxygen (wt %)	Carbon (wt %)	
β-Si_3N_4	Cerac pure	S-1068	99.9%	-325 mesh	1.50	1.70	0.019	Si, major-720 Al-350 Ca-30 Co-60 Cr-70 Cu-60 Fe-30 Ni-200 W
AlN	Atlantic Equipment Engineers	Al 106	99.9%	-325 mesh	1.83	2.96	0.69	Al major-125 B-140 Ca-900 Co-450 Cr-80 Cu-530 Fe-40 Mg-90 Mn-290 Mo-<100 Na-120 Ni-290 Si-190 Ti-<80 V-340 W-<50 Zr
SiO_2	Cerac pure	S-1061	99.9%	-325 mesh	0.92	ND	0.012	Si major-1000 Al-<10 Ca-50 Cr-120 Cu-50 Fe-190 Mg-130 Mn-90 Ti
Y_2O_3	Molycorp	5600	99.99%	NA	8.39	ND	0.144	Y major-130 Al-60 Cr-60 Cu-123 Fe-130 Si
HNO_3	Eastman	13058	Reagent ACS	–	–	ND	ND	Residue on ignition = 3 ppm
Ethanol	IMC Chemical Group	NA	200 proof	–	–	–	–	Residue after evaporation = 0.0012 wt %
n-Heptane	NA	NA	NA	–	–	–	–	98.38–98.49 boiling range. sp.gr. = 0.0683 (20/20)
Silicone oil	Dow Corning	DC-705	NA	–	–	–	–	

NA = not available.
ND = not determined.

1.27 cm diameter alumina balls as milling media. The rest of the equipment used in this investigation (presses, cold-pressing dies, furnaces, tensile testers, analytical equipment, etc.) was standard laboratory equipment.

4. Procedures

The procedures used for the preparation and testing of SiAlON test specimens are outlined in the flow diagram in Fig. 1. These procedures will be briefly described in the order shown in that figure.

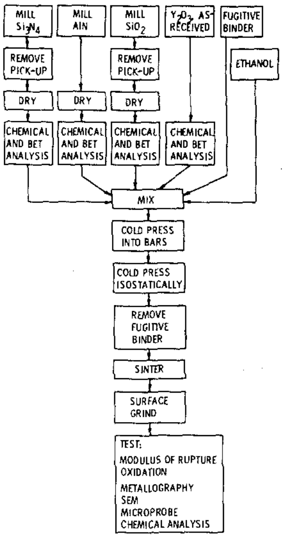

Figure 1 Flow chart for the preparation and testing of SiAlON ceramics.

4.1. Milling

Batches of 200 g of -325 mesh β-Si_3N_4 were milled for 300 h in the nickel-lined ball mills with 500 ml distilled water as milling fluid.

The -325 mesh SiO_2 was also milled in nickel-lined mills. The powder batches were 150 g and 500 ml distilled water were used as milling fluid. Milling time was 130 h.

The -325 mesh AlN was milled in 200 g batches in alumina mills with 500 ml *n*-heptane as milling fluid. Milling time was 100 h.

4.2. Removal of pick-up

During ball milling, materials resulting from the wear of balls and mills (pick-up) contaminate the milled powders. In most cases this pick-up may be detrimental to the properties of the SiAlONs and must be removed from the milled powder.

After separating the slurries of milled β-Si_3N_4 and SiO_2 from the nickel shot by sieving, most of the nickel pick-up in the milled powders was removed magnetically. The slurries were heated, stirred, treated with 100 g concentrated HNO_3, then centrifuged to remove most of the liquid. Distilled water was added to the moist powder cakes and stirred while heating to wash the powders. The water was then removed by centrifuging. The washing–centrifuging procedure was repeated twice more, for each batch. The resulting powder cakes were vacuum dried at about 100° C and pulverized in a Waring blender. The powders were kept in air tight containers until ready for use.

No attempt was made to remove the alumina pick-up (~ 1 wt %) from the AlN milled powders, since SiAlONs can be compounded with alumina. The slurries resulting from milling AlN were dried in a stream of dry nitrogen and then processed the same as the β-Si_3N_4 and SiO_2 milled powders.

It should be noted that the Y_2O_3 powder was not ball-milled because the as-received powder was already quite fine.

4.3. Chemical and BET analyses

The milled and the as-received powders were analysed for oxygen, carbon, and (spectrographically) for trace elements. The chemical analyses of the milled powders and Y_2O_3 were required to calculate the amounts of each of these powders to compound the desired SiAlON. In these calculations, it was assumed that all the carbon in the powders reacted with SiO_2 to form SiO and CO gases [5].

The specific surface areas of the powders were determined by the BET method.

4.4. Mixing

The calculated amounts of milled β-Si_3N_4, milled AlN, milled SiO_2, and as-received Y_2O_3 were weighed in an analytical balance and placed in a polyethylene bottle together with about twice their amount of stainless steel balls, 70 wt % ethanol and 5 wt % silicone oil (as a temporary binder). The powders were mixed for 1 h at 100 rpm. The resulting slurry was dried with constant stirring at about 100° C. After removing the balls by sieving, the resulting powder agglomerates were broken up in a Waring blender.

4.5. Cold-pressing

The powder mixtures were shaped into bars approximately 3.81 cm × 0.92 cm × 0.47 cm in a double acting steel die at a pressure of 207 MN m^{-2} (30×10^3 psi). These bars were then encased in

TABLE II Milling data and characterization of milled materials

Milling data				Characterization of milled powders				
Material	Mill/Media	Milling fluid	Milling time (h)	Post-milling treatment	Specific surface ($m^2 g^{-1}$)	Chemical analysis		
						Oxygen (wt %)	Carbon (wt %)	Other elements (Spectrographic analysis and in ppm, unless noted otherwise)
β-Si_3N_4 (S-1068	Ni/Ni shot	Distilled H_2O	300	Leach, wash, dry	10.14	2.83	0.241	0.1 wt % Al-300 B-130 Be-670 Ca-60 Cr-180 Fe-250 Mg-520 Ni
AlN (AL 106)	Alumina/Alumina	*n*-heptane	100	Dry	8.28	4.8	0.94	<100 B-150 Ca-800 Co-380 Cr-60 Cu-570 Fe-60 Mn-300 Mg-420 Mo-80 Ni-630 Si-80 Ti-<80 V-700 W-<50 Zr
SiO_2 (S-1061)	Ni/Ni shot	Distilled H_2O	130	Leach, wash dry	27.1	ND	0.037	630 Al-130 Ca-70 Cr-110 Cu-80 Fe-210 Mg-900 Ni

TABLE III Characterization of pressureless sintered SiAlONs

Designation	Formulae*	Density ($g cm^{-3}$)	% theoretical density	Chemical analyses		
				Oxygen (wt %)	Carbon (wt %)	Other elements (spectrographic trace analyses) (ppm unless noted otherwise)†
SiAlON A	$Si_{2.6}Al_{0.393}Y_{0.007}O_{0.4}N_{3.6}$	3.13	98.1‡	4.40	0.032	7.3 wt % Al-380 Ca-130 Co-170 Cr-100 Fe-90 Mg-410 Mo-540 Ni-10 Sr-30 Ti-90 W-1.2 wt % Y
SiAlON B	$Si_{2.6}Al_{0.386}Y_{0.014}O_{0.4}N_{3.6}$	3.17	98.8§	4.38	0.030	7.0 wt % Al-80 B-300 Ca-50 Co-130 Cr-100 Fe-80 Mg-40 Mn-210 Ni-<10 Sr-20 Ti-30 W-1 wt % Y

* SiAlON formulae correspond to $Si_{3-x}Al_xO_xN_{4-x}$ [3, 4].

† Estimated accuracy: ± 50%.

‡ Based on a density of 3.19 $g cm^{-3}$ for the hot-pressed SiAlON A composition.

§ Based on a density of 3.21 $g cm^{-3}$ for the hot-pressed SiAlON B composition.

plastic bags, evacuated, sealed and isostatically cold-pressed at 483 MN m^{-2} (70 x 10^3 psi).

4.6. Removing the fugitive binder

The silicone oil binder was removed from the bars by heating them in flowing nitrogen at 450° C for ~ 1 h.

4.7. Sintering

The bars were placed in a tungsten boat and sintering was carried out in a furnace with graphite heating elements. The bars were sintered for 4 h at 1760 ± 20° C in a stagnant nitrogen atmosphere at 34.5 kN m^{-2} (5 psi) gauge pressure. The temperature was controlled and monitered with W versus W–26Re thermocouples.

The sintered specimens were surface ground into test bars 0.635 cm x 0.318 cm x ~2.54 cm and the edges bevelled 0.12 mm. The bars used for oxidation tests were further polished to a mirror finish on a 10 μm diamond lap; these bars were 0.630 cm x 0.315 cm x 1.5 cm.

4.8. Testing

The ground bars were used to determine the four-point modulus of rupture (MOR) as a function of temperature up to 1400° C in air. The silicon carbide (SiC) MOR fixture used had a bottom span of 1.905 cm ($\frac{3}{4}$ in.) and a top span of 0.953 cm ($\frac{3}{8}$ in.). A SiC muffle furnace mounted on an Instron tensile tester was used to heat up the bars and fixture to the test temperature. The bars were bend tested at a cross-head speed of 0.051 cm min^{-1} (0.020 in. min^{-1}).

Oxidation tests were carried out in air at 1400° C. During the tests, the bars were held in a platinum crucible having two side holes and a loosely fitting cover, so as to allow access of air to the SiAlON bars. At various time intervals, the bars were cooled and weighed in an analytical balance with microgram sensitivity. From the weighing data, weight gains as a function of time were determined.

The densities of the sintered SiAlONs were determined by water immersion. Chemical, X-ray, scanning electron microscopy (SEM), microprobe, and optical microscopy analyses of the sintered and ground SiAlONs were carried out.

4.9. Auxiliary experiment

To compare densities, the two SiAlON compositions made by pressureless sintering were also made by hot-pressing. These materials were hot-pressed in a graphite die at 1750 ± 25° C and 27.6 MN m^{-2} (4000 psi) for 1 h in flowing nitrogen. These materials were assumed to be 100% dense.

5. Results and discussion

5.1. SiAlONs investigated

The two SiAlON compositions used in this investigation were compounded from the finely milled Si_3N_4, AlN, and SiO_2 powders chemically characterized in Table II, and small amounts of Y_2O_3 (Table I) as sintering aid. These two SiAlONs (SiAlONs A and B, Table III) were compounded with 0.56 and 1.11 wt% Y_2O_3, respectively, and their compositions were calculated to fall within the β' homogeneity range defined by the equation $Si_{6-z}Al_zO_zN_{8-z}$ [3, 4]. However, in this work the equivalent equation $Si_{3-x}Al_xO_xN_{4-x}$ will be used for ease of comparison with other SiAlON compositions published in the literature [6, 7]. In this work $x = 0.4$. This value of x was chosen, in part, because the resulting SiAlONs have relatively high Si_3N_4 and this allows more meaningful comparisons with data for hot-pressed Si_3N_4 and for SiAlONs with high Si_3N_4 published in the literature. A somewhat lower value of x could have been obtained with the Si_3N_4 and AlN powders described in Table III. However, other milling runs yielded Si_3N_4 and AlN powders with higher oxygen contents and a value of x smaller than about 0.4 would have prevented reproducibility of SiAlON compositions in future work.

As will be shown later, Y_2O_3 is detrimental to the oxidation resistance of SiAlONs and for this reason Y_2O_3 additions were made as small as possible. The minimum Y_2O_3 additions were determined by sinterability. Thus, the same SiAlONs with less than about 0.25 wt% Y_2O_3 could not be pressureless sintered significantly and the same SiAlON without Y_2O_3 additions could not be consolidated to more than 2.63 g cm^{-3} even after hot-pressing at 1750° C and 27.6 MN m^{-2} (4000 psi) for 1 h in a nitrogen atmosphere. SiAlONs with 2.5 and higher wt% Y_2O_3 additions have been reported in the literature [6] and this will allow comparing the gross effects of Y_2O_3 on modulus of rupture and oxidation resistance.

5.2. Modulus of rupture (MOR)

The four point MOR plots of SiAlONs A and B as a function of temperature are shown in Fig. 2. The number of bars tested and the range of MOR values are also indicated in this figure. Both SiAlONs A and B have about the same MOR at r.t.

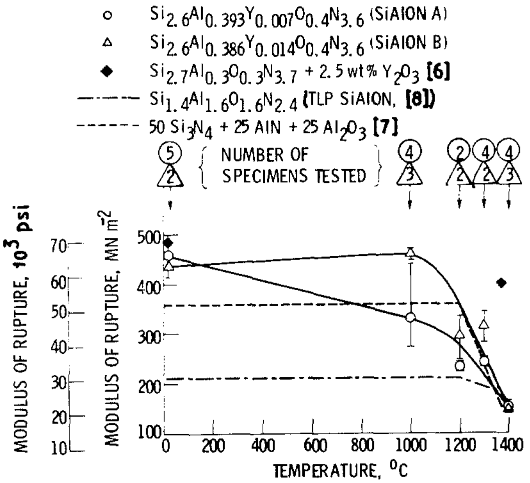

Figure 2 Four-point modulus of rupture of various SiAlONs as a function of temperature.

(415 to 500 MN m^{-2}) and at 1400° C (140 to 165 MN m^{-2}). At intermediate temperatures SiAlON A has generally lower MOR than SiAlON B. Both of these SiAlONs show an accelerated drop in strength with temperature beyond the 1000 to 1200° C range. This drop in strength with temperature beyond 1000 to 1200° C is common to most of the SiAlONs reported in the literature.

For comparison purposes, the MORs versus temperature reported in the literature for other SiAlONs are also plotted in Fig. 2. At 1400° C the two SiAlONs from [7] and [8] have about the same MOR as SiAlONs A and B. The SiAlON with 2.5 wt% Y_2O_3 from [6] has higher MOR at 1400° C. At lower temperatures, SiAlONs A and B have generally higher MOR than the two SiAlONs from [7] and [8]. Other SiAlONs with higher MORs in the r.t. to 1400° C range have been reported [9], but these were three-point MORs and the compositions were not defined. For these reasons, further comparisons would be meaningless. The MORs of SiAlONs A and B could probably be improved. The processing variables (sintering time and temperature, particle size of powders, composition, etc.) have not been optimized and there is considerable room for improvement in other properties as well as in MOR.

5.3. Oxidation

The weight increases with time on oxidizing SiAlONs A and B in air at 1400° C are plotted in Fig. 3. For comparison purposes, the 1400° C oxidation behaviour for hot-pressed Si_3N_4 [10] and for two SialONs [6, 8] are also plotted in this figure. The SiAlONs from the present investigation have better oxidation resistance than hot-pressed Si_3N_4 [10] and much better oxidation resistance than the SiAlON with 2.5 wt% Y_2O_3 [6]. It is assumed that the improved oxidation resistance of SiAlONs A and B, when compared with the 2.5% Y_2O_3 SiAlONs, may be due to their lower Y_2O_3 content. In addition, SiAlONs with 2.5 and 5 wt% Y_2O_3 [6] have generally higher strengths and much lower oxidation resistance than the 0.56 and 1.11 wt% Y_2O_3 SiAlONs from the present investigation. Thus, it appears that increasing Y_2O_3 additions increase the strength of SiAlONs at the expense of their oxidation resistance.

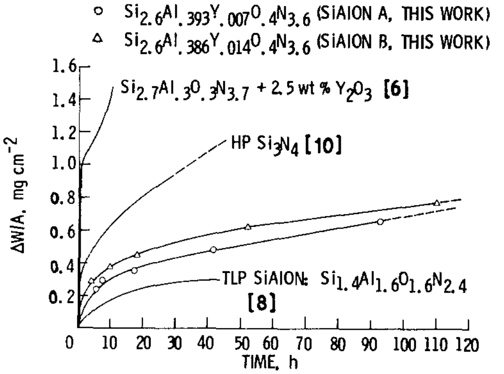

Figure 3 Weight gain of various Si_3N_4-base ceramics oxidized at 1400° C.

The transient liquid phase (TLP) SiAlON [8] has a higher oxidation resistance than the SiAlONs from this investigation. However, Al increases the oxidation resistance of SiAlONs [11] and the TLP SiAlON has a much higher Al content than the SiAlONs from this investigation. Therefore, SiAlONs with higher Al content made by the methods of the present investigation can be expected to have improved oxidation resistance.

X-ray diffraction analyses of the oxidized layers of SiAlONs A and B show α-cristobalite (strong), β-Si_3N_4 (medium), and mullite (weak). The β-Si_3N_4 may have been unoxidized SiAlON scraped off the surface on taking the X-ray sample.

5.4. Microstructures

The optical photomicrographs of SiAlONs A and B are similar and they show small amounts of a light grey phase, smaller amounts of (dark looking) holes or pull-outs, and very small amounts of a bright, metallic-looking phase in a fairly uniform matrix.

Scanning electron microscopy (SEM) photomicrographs of SiAlONs A and B are very similar and they show equi-axed grains about 1.1 μm average diameter.

Electron microprobe analyses of SiAlONs A and B showed that the light grey spots seen in the optical photomicrographs have higher Al, Fe, Ca, and Mg, and lower Si and Y than the matrix. In addition, X-ray diffraction of these SiAlONs shows only the β' phase. From this it is surmised that the light grey spots are glass. Electron microprobe analysis showed that the bright, metallic looking spots are richer in Fe (and possibly richer in Ca) than the matrix. This bright phase may be an Fe (Ca)-Si alloy or intermetallic compound but the amount of this phase is too small for identification by X-ray diffraction. Electron microprobe scans of the matrix of SiAlONs A or B showed that its composition is essentially constant.

5.5. Chemical and surface area analyses and implications

In Table I are shown the chemical analyses of the as-received powders and in Table II that of some of the same powders after milling. Table II also includes some milling and processing data.

Comparison of Tables I and II shows that after milling and leaching the Ni content of Si_3N_4 increased by about 500 ppm and that of the SiO_2 by about 900 ppm. From the weight loss of balls and mill it was calculated that the AlN picked up 1.0 wt % alumina.

From the chemical analyses of the milled powders and Y_2O_3, only the elements Si, Al, Y, O, N, and C were taken into account for computing the amounts of powders required for compounding the SiAlONs. For computing purposes, spectrograhically determined impurities other than Si or Al were regarded as part of the major metallic element (Al, Si, or Y) in the powder.

Comparison of Tables I and II also shows that the specific surface area of Si_3N_4 was increased 6.75 times by milling. Those of the AlN and SiO_2 were increased by 4.5 and 29.5 times, respectively. The large specific surface areas of the milled powders and Y_2O_3 would account for the relatively small amounts of sintering aid (Y_2O_3) required to effect pressureless sintering of SiAlONs A and B to over 98% of their theoretical density. It is noteworthy that the 0.56 wt % Y_2O_3 used in SiAlON A is equivalent (in number of covalent bonds) to about 0.19 wt % MgO. This will give an idea of the very small amounts of additives (or impurities) that can bring about densification of SiAlONs made from fine powders and of the importance of using high purity raw materials.

As already stated in Section 4.3, excess SiO_2 was used for compounding SiAlONs A and B to allow for its loss by reaction with C to form CO and SiO gases during sintering. The analyses of sintered SiAlONs (Table III) show very low residual carbon and, within the cumulative inaccuracies of the chemical analyses, the oxygen content is that corresponding to that in the SiAlON formulae. Therefore, the assumed reaction of SiO_2 and C is probably correct.

6. Conclusions

The main objective of the present investigation was to produce β'-SiAlONs with high Si_3N_4 by pressureless sintering a mixture of separately milled β-Si_3N_4, AlN, and SiO_2 with very small amounts of Y_2O_3 as sintering aid. The results and conclusions can be summarized as follows:

(1) β'-SiAlONs of compositions $Si_{2.6}Al_{0.393}Y_{0.007}O_{0.4}N_{3.6}$ (SiAlON A) and $Si_{2.6}Al_{0.386}Y_{0.014}O_{0.4}N_{3.6}$ (SiAlON B), and densities of 3.13 and 3.17 g cm^{-3}, respectively, were made by pressureless sintering at 1760° C, for 4 h in stagnant N_2. It is concluded from these results that very small amounts of additives (or impurities) are required to effect pressureless sintering of mixtures of very fine Si_3N_4, and AlN, and SiO_2 powders.

(2) The four-point modulus of rupture (MOR) of SiAlONs A and B range from about 460 MN m^{-2} at room temperature to 155 MN m^{-2} at 1400° C. Although SiAlONs with higher strengths have been reported in the literature, their compositions were either undisclosed or, if disclosed, their oxidation resistance was lower than that of the SiAlONs produced in this investigation.

(3) The SiAlONs from this investigation gain weight at a rate of about 0.004 mg cm^{-2} h^{-1} after being oxidized in air for 35 h at 1400° C. By comparison, under similar conditions, published results show that hot-pressed Si_3N_4 oxidizes at a rate of 0.013 mg cm^{-2} h^{-1}; a SiAlON with 2.5 wt % Y_2O_3 oxidizes at $\sim$0.043 mg cm^{-2} h^{-1}; and a SiAlON with a much higher Al content (known to increase oxidation resistance) oxidizes at 0.0011 mg cm^{-2} h^{-1}. It is concluded that the oxidation resistance of the SiAlONs produced by the methods of this investigation may be increased by increasing their aluminium content.

(4) After pressureless sintering SiAlONs A and

B their carbon content was reduced to negligible levels and their oxygen content was lowered to the values to be expected had the carbon originally present in the starting powders reacted with SiO_2 to form CO and SiO gases. From this it is concluded that excess SiO_2 must be used on compounding β'-SiAlONs to compensate for losses due to reaction with carbon.

(5) From the results of this investigation when compared with data for other SiAlONs published in the literature it is concluded that increasing amounts of Y_2O_3 additions increase the strength of SiAlONs at the expense of their oxidation resistance.

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