

# Pressureless sintering of $\beta$ -SiAlON ceramic compositions using fluorine and oxide additive system

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## Abstract

SiAlONs are silicon aluminium oxynitride ceramic materials with a range of technically important applications, from cutting tools to specialised refractories and the properties of SiAlONs can be tailored for specific purposes. In this study, different  $\beta$ -SiAlON compositions were prepared using fluoride ( $\text{MgF}_2$  as fluorine source plus  $\text{Y}_2\text{O}_3$ ) and oxide ( $\text{MgO}$  plus  $\text{Y}_2\text{O}_3$ ). These compositions were pressureless sintered under nitrogen atmosphere in the range of 1450–1750 °C for 0.5–2.5 h for comparison of densification behaviour and mechanical properties. Densities of samples were measured and analyses of result products were carried out using SEM and XRD. The F-doped sintered  $\beta$ -SiAlON ceramics showed better densities and less pore micrographs especially at lower temperatures compared with the fluorine free samples. Full densifications were achieved for  $\beta$ -SiAlON ceramics with fluoride addition at 1700 °C for 60 min. Consequently, fluorine addition to additive system has a good effect on mechanical properties and densification behaviour.

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**Keywords:**  $\text{Si}_3\text{N}_4$ ; SiAlON; Sintering; Microstructure-final; Fluoride

## 1. Introduction

Silicon nitride ceramics are a family of materials that have received increasingly keen interest for high performance engineering applications due to the fact that they generally possess high mechanical properties, excellent wear and refractory properties for applications ranging from metal cutting tools to gas turbine blades, good anti-oxidation and thermal shock behaviour up to high temperatures.<sup>1–3</sup> Si–Al–O–N is the most fundamental system upon which another metal atom may be added in the designing and fabrication of most useful nitride materials.<sup>4,5</sup>

Self diffusivity in silicon nitride is quite low and species only become sufficiently mobile for sintering at temperatures where the decomposition of silicon nitride commences (>1850 °C) Thus, alternative approaches have been developed by the use of densification additives to create the conditions for liquid phase sintering either with or without applied pressure to assist the process.<sup>6</sup> The densification of  $\text{Si}_3\text{N}_4$  and SiAlON can be

achieved by using oxide additives such as yttria, alumina, and magnesia. In addition, fluorides such as  $\text{MgF}_2$  and  $\text{CaF}_2$  have been investigated for densification of  $\text{Si}_3\text{N}_4$  and SiAlONs.<sup>7,8</sup> Several studies have been reported on the use of fluorine in silicon nitride based ceramics to control composition, oxidation, and optical properties.<sup>9–11</sup> Fluorine as a non-bridging anion in glasses acts as a powerful network disrupter which substitutes for bridging oxygen ions. Fluorine reduces glass transition temperature, viscosity and refractive index, aids crystallisation and increases the potential for phase separation<sup>12</sup> while nitrogen increases  $T_g$  and viscosity in oxyfluoronitride glasses.<sup>13</sup> For these reasons, fluorine additives may be useful sintering aids for silicon nitride based ceramics.

The overall aim of this study is to investigate the sintering of SiAlON ceramics using combinations of oxides and fluorides in order to reduce the melting temperature of the liquid phase formed.

## 2. Experimental

High purity starting powders,  $\alpha$ - $\text{Si}_3\text{N}_4$  (99.9% UBE, Industries, Japan), MgO (BDH Chemicals),  $\text{Al}_2\text{O}_3$  (ALCOA) A17,  $\text{Y}_2\text{O}_3$ , AlN (H.C. Starck-Berlin),  $\text{MgF}_2$  (Sigma–Aldrich) were mixed in appropriate proportions and ball milled with silicon

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Table 1  
Prepared compositions for sintering studies.

Code	Compositions
M1	$\beta$ -SiAlON ( $z=1$ ) + %7 Y <sub>2</sub> O <sub>3</sub> + %3 MgO
MF1	$\beta$ -SiAlON ( $z=1$ ) + %7 Y <sub>2</sub> O <sub>3</sub> + %4.65 MgF <sub>2</sub>

nitride milling balls in isopropyl alcohol for 24 h to ensure homogeneous mixing. Prepared compositions are shown in Table 1. The balls were removed and the slurries firstly dried in a rotary evaporator and then dried at 100 °C in a standard oven during 4 h, and subsequently sieved through a 300 mesh sieve screen. The sieved powder was then uniaxially pressed at a pressure of 30 MPa in a die to produce a compact with dimensions 18 mm diameter  $\times$  18 mm height. After compaction, the samples were further isostatically cold pressed at 250 MPa. Before sintering, samples were embedded in a BN powder bed. Samples were heated at a heating rate of 800 °C/h to temperatures in the range of 1450–1700 °C for 30–150 min in a graphite resistance furnace under a constant flow of 0.1 MPa N<sub>2</sub> (99.9% purity) to protect both samples and carbon furnace from detrimental effect of air. The sintered densities were measured using an Archimedes method. The phases in the sintered products were analyzed by X-ray diffraction instrument (Rigaku, XRD D/MAX/2200/PC, Japan) using CuK $\alpha$  radiation and identified by X'Pert High-Score Report program. The microstructures were examined by scanning electron microscopy (SEM JEOL, JSM-6700F, Japan). Microhardness was measured using a standard Vickers indentation technique with a load of 1 kgf.

### 3. Results and discussion

#### 3.1. Densification behaviour

Table 2 shows the effect of time and temperature on densification behaviour of M1 and MF1 compositions sintered in the range of 1450–1750 °C. It can be seen that for both compositions, containing magnesium oxide or magnesium fluoride,

Table 2  
Effect of time and temperature on densification behaviour of M1 and MF1 compositions sintered under the above mentioned sintering conditions.

Code	Temp (°C)	30 min		60 min		90 min		120 min		150 min	
		Density (g/cm <sup>3</sup> )	R.D. (%)	Density (g/cm <sup>3</sup> )	R.D. (%)	Density (g/cm <sup>3</sup> )	R.D. (%)	Density (g/cm <sup>3</sup> )	R.D. (%)	Density (g/cm <sup>3</sup> )	R.D. (%)
M1	1450 °C	2.920	88.7	2.990	90.8	3.034	92.2	3.050	92.7	3.049	92.7
MF1	1450 °C	2.960	89.9	3.079	93.6	3.093	94.0	3.090	93.4	3.087	93.8
M1	1500 °C	2.953	89.7	3.084	93.7	3.068	93.25	3.074	93.4	3.065	93.1
MF1	1500 °C	3.002	91.2	3.107	94.4	3.124	94.9	3.126	95.0	3.112	94.5
M1	1550 °C	3.020	91.8	3.101	94.2	3.125	94.9	3.143	95.5	3.141	95.4
MF1	1550 °C	3.050	92.7	3.125	95.0	3.149	95.7	3.149	95.7	3.136	95.3
M1	1600 °C	3.096	94.1	3.13	95.1	3.152	95.8	3.164	96.2	3.165	96.2
MF1	1600 °C	3.142	95.5	3.196	97.1	3.207	97.5	3.200	97.2	3.165	96.2
M1	1650 °C	3.080	93.6	3.134	95.2	3.223	97.9	3.242	98.5	3.245	98.6
MF1	1650 °C	3.183	96.7	3.149	95.7	3.280	99.7	3.256	98.9	3.285	99.8
M1	1700 °C	3.22	97.9	3.26	99	3.29	100	3.25	98.8	3.20	97.3
MF1	1700 °C	3.25	98.8	3.29	100	3.29	100	3.24	98.5	3.19	97.0
M1	1750 °C	3.26	99.1	3.23	98.2	3.20	97.3	3.15	95.7		
MF1	1750 °C	3.25	98.8	3.18	96.6	3.16	96.0	3.11	94.5		

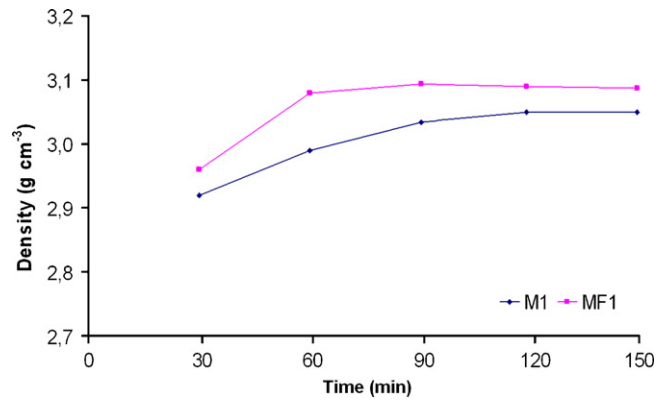


Fig. 1. Density as a function of time for M1 and MF1 compositions sintered at 1450 °C.

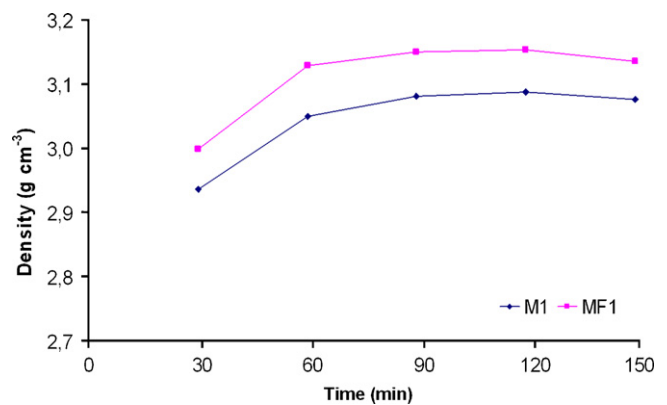


Fig. 2. Density as a function of time for M1 and MF1 compositions sintered at 1500 °C.

the density increased with sintering temperature. Density as a function of time for both compositions is shown in Figs. 1–7 corresponding to increasing temperature. Full densification with a density of  $\sim 3.29$  g/cm<sup>3</sup> (100% R.D.) was achieved for the sample composed of  $\beta$ -SiAlON ( $z=1$ ) + Y<sub>2</sub>O<sub>3</sub> + MgF<sub>2</sub> sintered at 1700 °C for 60 min. The lowest density of 2.92 g/cm<sup>3</sup>

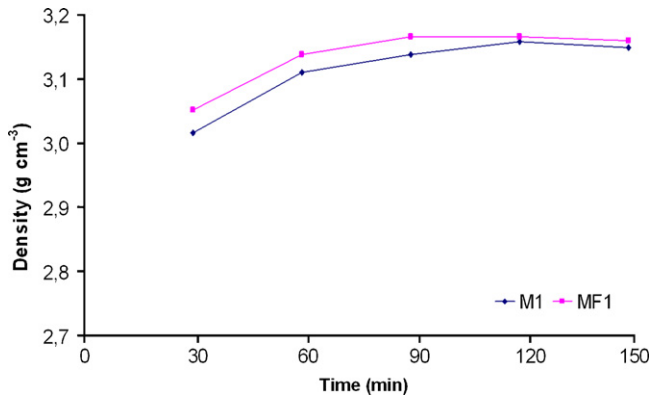


Fig. 3. Density as a function of time for M1 and MF1 compositions sintered at 1550 °C.

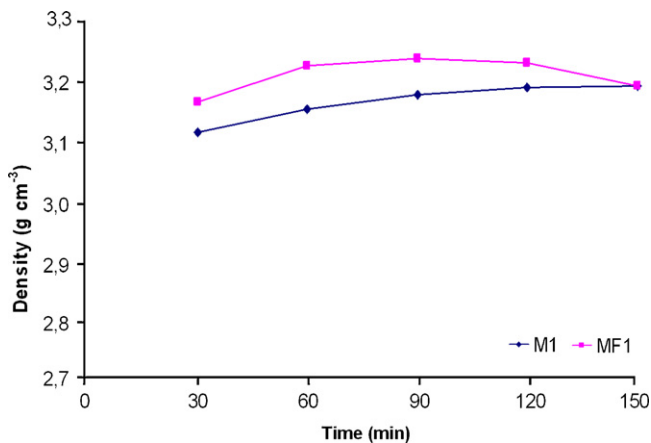


Fig. 4. Density as a function of time for M1 and MF1 compositions sintered at 1600 °C.

(88.7% R.D.) was seen for a sample composed of  $\beta$ -SiAlON ( $z = 1$ ) +  $Y_2O_3$  + MgO sintered at 1450 °C for 30 min. As seen in Figs. 1–5 especially at lower temperatures (1450–1650 °C),  $MgF_2$  doped samples attained higher densification levels compared with MgO doped samples. At higher sintering temperatures and times (1750 °C – 90 min) increasing temperature results in less porous samples. Generally, just a small decrease in

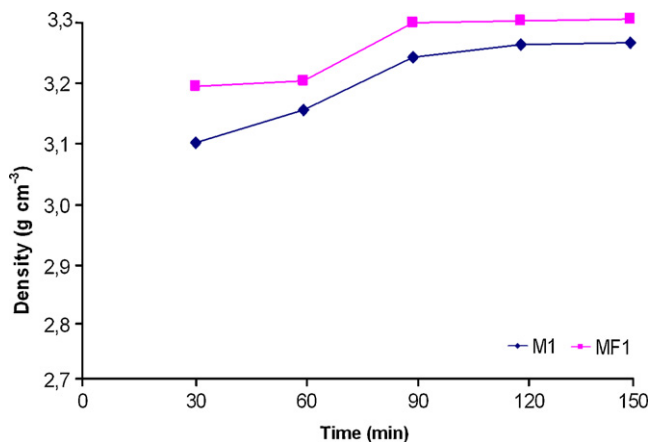


Fig. 5. Density as a function of time for M1 and MF1 compositions sintered at 1650 °C.

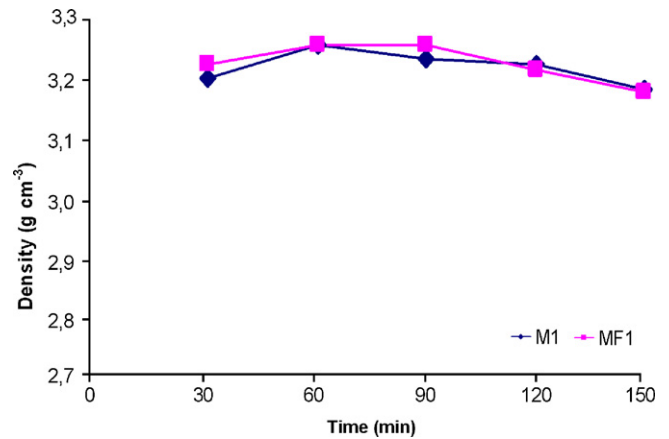


Fig. 6. Density as a function of time for M1 and MF1 compositions sintered at 1700 °C.

density is observed with increasing dwell time for both MgO and  $MgF_2$ . This may be due to volatilisation of the Mg-containing additive.

When the densification behaviour of fluoride added samples are compared with that of fluoride-free samples, the fluoride added samples show better densification results. This is due to addition of fluoride in glass system that causes a reduction in the glass transition temperature ( $T_g$ ) and the viscosity of the glass as the fluorine content of the glasses increases and aids crystallisation.<sup>14</sup> In addition to this, fluorine replacement of one  $O^{2-}$  by two  $F^{-1}$  ions should lead to a greater molar volume.<sup>15</sup> Therefore, viscosities of the glasses with  $MgF_2$  are lower than that of the glasses with MgO. The glass with  $MgF_2$  having greater molar volume provides more effectively sintering by promoting liquid phase. Hereby, when comparing with fluoride and without fluoride compositions as to densification rate, the composition with fluoride commences to densify in earlier stage.

### 3.2. X-ray analysis

After sintering, the resulting samples were analyzed to identify their phase compositions via X-Ray diffraction. As shown in Table 3, at lower temperatures the dominant phase is  $\alpha$ - $Si_3N_4$ .

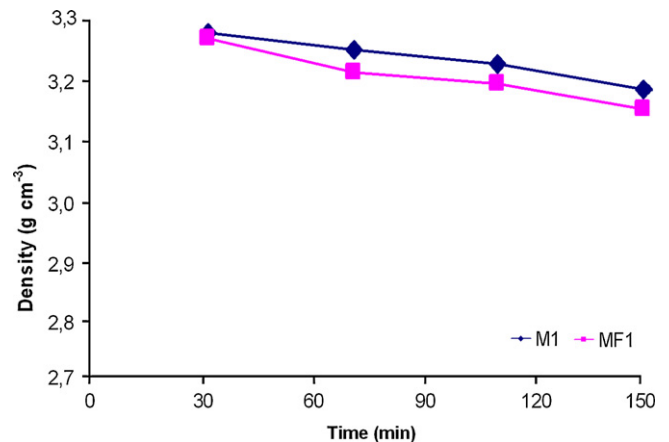


Fig. 7. Density as a function of time for M1 and MF1 compositions sintered at 1750 °C.

Table 3  
X-Ray analysis of the sintered M1 and MF1 samples for 90 min at various temperatures.

Temp. (°C)	M1		MF1	
	% $\beta/(\alpha + \beta)$	Other phases	% $\beta/(\alpha + \beta)$	Other phases
1450	7	SiO <sub>2</sub> , O'-SiAlON	8	SiO <sub>2</sub> , O'-SiAlON
1500	10	SiO <sub>2</sub> , Mg <sub>2</sub> SiO <sub>4</sub>	12	SiO <sub>2</sub> , Mg <sub>2</sub> SiO <sub>4</sub>
1550	12	Al <sub>5</sub> Y <sub>3</sub> O <sub>12</sub>	17	Al <sub>5</sub> Y <sub>3</sub> O <sub>12</sub>
1600	20	Al <sub>6</sub> Si <sub>2</sub> O <sub>13</sub>	23	Al <sub>6</sub> Si <sub>2</sub> O <sub>13</sub>
1650	42	SiAlO <sub>2</sub>	47	–
1700	52	–	58	–
1750	97	–	100	–

The transformation  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>  $\rightarrow$   $\beta$ -SiAlON commences above 1500 °C and increases with increasing temperature. However, small amounts of other phases are present up to 1700 °C. Full transformation was achieved above 1700 °C. In general fluoride doped samples gave slightly faster transformation than oxide doped samples. It reveals that fluorine doping supports to  $\alpha \Rightarrow \beta$ -Si<sub>3</sub>N<sub>4</sub> transformation more than that of single oxide addition.

### 3.3. Microstructural analysis via SEM

Microstructural studies were carried out using scanning electron microscopy. Typical microstructures for pressureless

sintered materials are given in Figs. 8–11. The M1 materials include some heterogeneities of a pore-clustered nature indicative of absence of sintering additive in these regions. This kind of heterogeneity is not visible in the MF1 materials. Both M1 and MF1  $\beta$ -SiAlON ( $z = 1$ ) compositions sintered at 1600 °C for 90 min gave very similar micrographs. Figs. 8 and 9 show that densification has just started at low temperatures with maximum density of  $\sim 97.5\%$  R.D. achieved. However, at a temperature of 1700 °C for 60 min magnesium fluoride containing samples give fully dense microstructures and magnesium oxide containing samples show very little porosity with maximum density of 99% R.D.

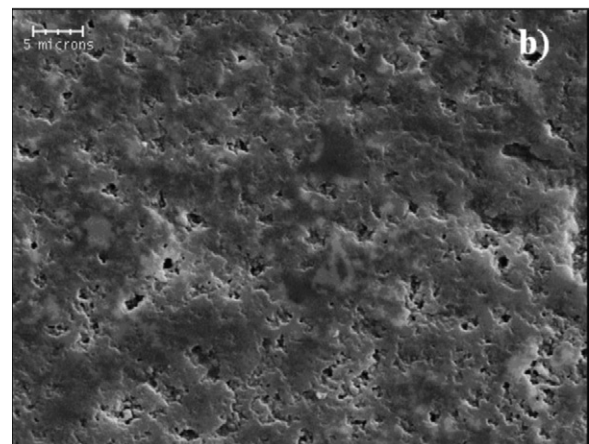
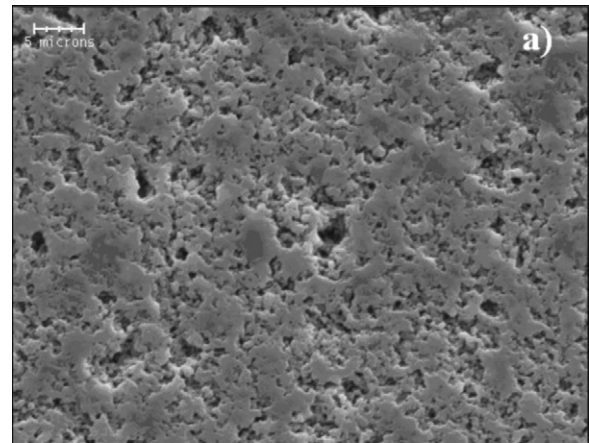
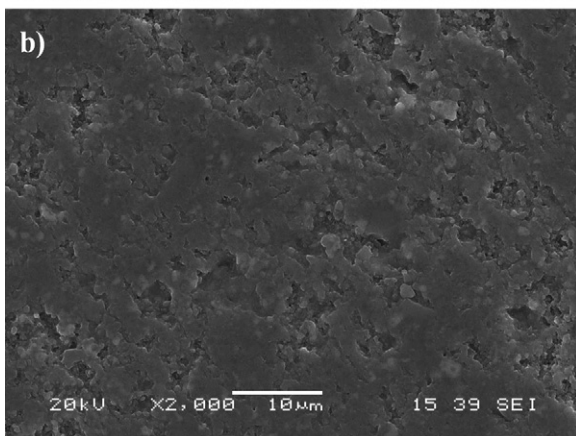
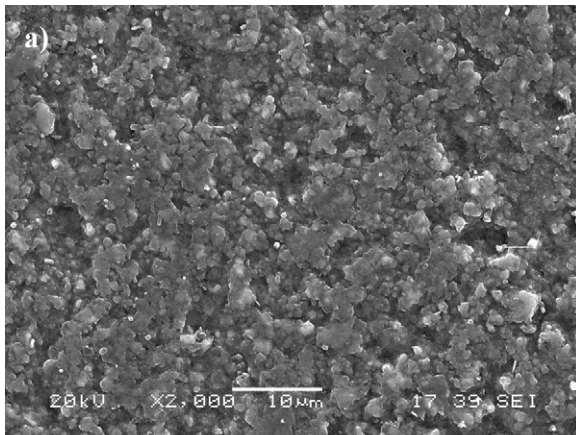


Fig. 8. SEM micrographs of samples run at 1450 °C for 90 min (a) M1, (b) MF1 compositions.

Fig. 9. SEM micrographs of samples run at 1600 °C for 90 min (a) M1, (b) MF1 compositions.

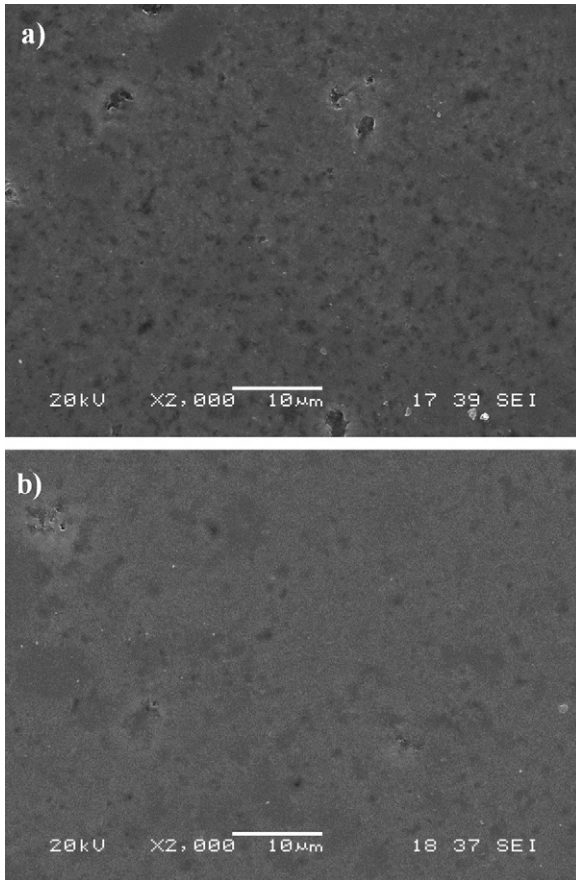


Fig. 10. SEM micrographs of samples run at 1650 °C for 90 min (a) M1, (b) MF1 compositions.

### 3.4. Hardness measurement

Results for microhardness are shown in Table 4 for all sintering temperatures. From the values obtained it can be seen that an increase in microhardness is observed in samples of the same composition, when the sintering temperature is raised as might be expected since density is also increasing with sintering temperature. Also, higher values of microhardness are observed in samples with MgF<sub>2</sub> additives as opposed to MgO additives under the same sintering conditions from 1450 °C to ~1700 °C. After that, the slightly reduction of hardness for samples with MgF<sub>2</sub> additives can be explained by losing of fluoride at high temperatures. Subsequent changes or improvements in the

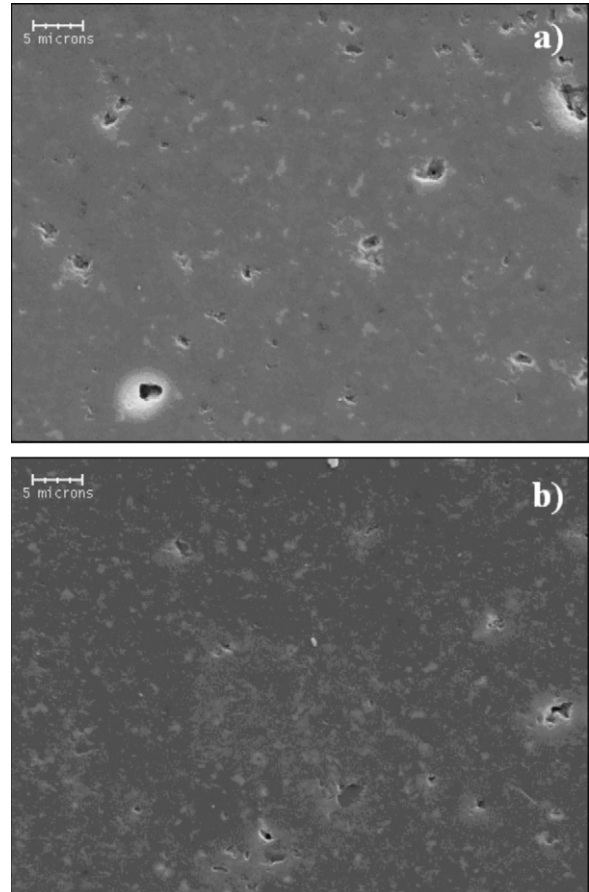


Fig. 11. SEM micrographs of samples run at 1700 °C for 90 min (a) M1, (b) MF1 compositions.

sintering method could produce less porous samples which would be expected to yield much higher microhardness and density. In general, the MgF<sub>2</sub> containing samples had slightly lower microhardness values above 1700 °C than those with MgO, which may be indicative of the type of glass produced using the fluoride additive.

The lowest average hardness value was seen for the composition  $\beta$ -SiAlON ( $z = 1$ ) + Y<sub>2</sub>O<sub>3</sub> + MgO, sintered at 1450 °C (129 GPa HV). The highest microhardness value was for the composition with  $\beta$ -SiAlON ( $z = 1$ ) + Y<sub>2</sub>O<sub>3</sub> + MgO at 1750 °C (21 GPa HV). However, as with density, especially at lower temperatures, MgF<sub>2</sub> additive gives a higher microhardness for the  $\beta$ -SiAlON composition up to 1600 °C. Fig. 12 shows the clear

Table 4  
Hardness values of M1 and MF1 samples run at 1450–1750 °C for 90 min.

Temp. (°C)	M1		MF1	
	Hv 1 (GPa) $\pm 0.2$	K <sub>1c</sub> (MPa m <sup>1/2</sup> ) $\pm 0.3$	Hv 1 (GPa) $\pm 0.2$	K <sub>1c</sub> (MPa m <sup>1/2</sup> ) $\pm 0.3$
1750	21	6.5	20.0	6.9
1700	20.9	6.0	20.3	6.3
1650	17.2	4.7	17.8	5.2
1600	12	4.4	14.4	5.0
1550	8.5	4.2	10.8	4.9
1500	3.9	–	5.6	–
1450	1.8	–	2	–

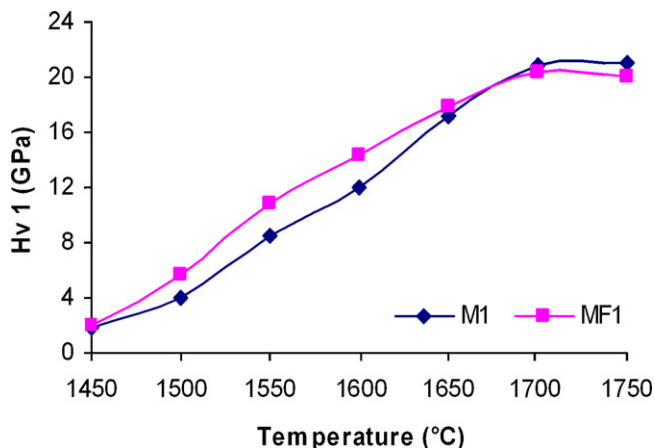


Fig. 12. Microhardness as a function of sintering temperature for M1 and MF1 samples.

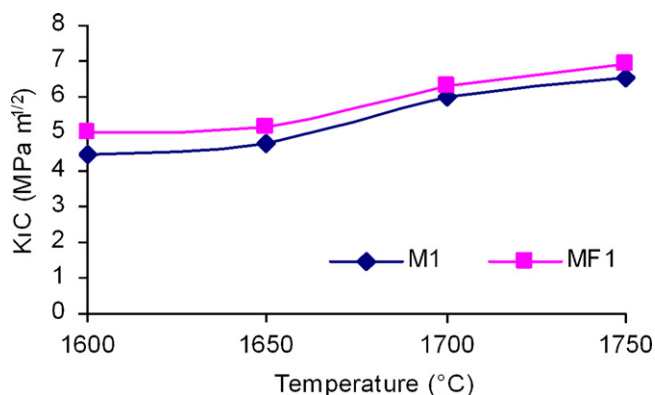


Fig. 13. Fracture toughness as a function of sintering temperature for M1 and MF1 samples.

difference between samples with fluoride and without fluoride in hardness. This is due to the relatively better densification behaviour of the  $\text{MgF}_2$  doped  $\beta$ -SiAlON composition.

In addition to this, the samples with  $\text{MgF}_2$  show higher indentation fracture toughness values at all temperatures. The highest  $K_{1c}$  of  $6.9 \text{ MPa m}^{1/2}$  was obtained for the  $\text{MgF}_2$  doped sample at  $1750^\circ\text{C}$ . Fig. 13 shows the increase in fracture toughness with sintering temperature (in parallel with density increase) and higher  $K_{1c}$  values for the fluoride containing samples.

Çalışkan has reported that fluoride addition to liquid phase supports to increase aspect ratio of silicon nitride grains.<sup>16</sup> Microstructures having grains with higher aspect ratios is known to have better fracture toughness due to toughening mechanism provided by the bridging of elongated grains.<sup>17</sup> The higher fracture toughness of  $\text{MgF}_2$  added samples compared to that of  $\text{MgO}$  added samples is due to these higher aspect ratios. Remaining untransformed  $\alpha$  grains in  $\beta$  matrix have an influence on hardness owing to the fact that the hardness of single crystal  $\alpha$ - $\text{Si}_3\text{N}_4$  is considerably higher than that of single crystal  $\beta$ - $\text{Si}_3\text{N}_4$  and  $\beta$ -SiAlON.<sup>18</sup>

#### 4. Conclusions

The densification of a  $\beta$ -SiAlON composition ( $z = 1$ ) by pressureless sintering by doping with oxide ( $\text{Y}_2\text{O}_3 + \text{MgO}$ ) or oxide

and fluoride ( $\text{Y}_2\text{O}_3 + \text{MgF}_2$ ) additives produced samples with between 86.7% and 100% theoretical density. The density of the samples was seen to increase with increasing sintering temperature. At all temperatures fluoride containing samples gave higher  $\beta$ -SiAlON transformation. However, at lower temperatures  $\text{MgF}_2$  doped  $\beta$ -SiAlON ceramics have higher density and hardness than  $\beta$ -SiAlON doped with  $\text{MgO}$ , showing that fluoride additions result in faster densification but density and hardness values of  $\text{MgF}_2$  and  $\text{MgO}$  doped  $\beta$ -SiAlON ceramics at higher temperatures are similar. This reveals that with  $\text{MgF}_2$  additive there is a greater degree of sintering at lower temperatures.

The fluorine addition to M–Si–Al–O–N glasses leads to a reduction in the melting temperature.<sup>13</sup> Because fluorine plays the role of a powerful network modifier and thus effectively lowers the melting temperature of the sintering liquid, so sintering of  $\beta$ -SiAlON ceramics using combinations of  $\text{Y}_2\text{O}_3$  and  $\text{MgF}_2$  leads to better densification at lower temperatures. This is also the case for the microhardness which evolved in the same manner as density with increase in temperature.

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