Sintered fused silica based composites

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In present work, complex mixtures were designed based on fused SiO_2 , β-SiC and different oxide additives. The addition of Al_2O_3 and mulite - $3Al_2O_3 \cdot 2SiO_2$ influence was investigated in order to obtain high temperature strength, thermal shock resistant and corrosion resistant composites. Thermal treatment was conducted in conventionally electric furnace in air and in argon respectively, in the 800-1250 ^{o}C temperature range. Sintered composites were characterised by bulk density, open porosity, and thermal shock resistance and thermal expansion measurements. The crystalline phase evolution in conjunction with each heat curing procedure was analysed by X-ray diffraction and FTIR spectrometry. Microstructure investigation of sintered samples was carried using scanning and transmission electron microscopy. The relationship between the FTIR spectra and structure of the powders and sintered composites was explained.

1. Introduction

Fused silica offers excellent thermal shock resistance due to its low thermal expansion coefficient (5.5×10^{-7} cm/cm·K, average from 20 °C to 320 °C) .

The chemical bonds between silicon and carbon atoms in SiC are almost 88% covalent, decreasing the atomic diffusivity and making it difficult to achieve high

densification [1-3]. Sintering additives are usually required to obtain high density, such as boron, carbon, aluminium - or their compounds [4]. In these cases, sintering occurs through solid state mechanisms.

Liquid phase sintering, through solution re-precipitation process, also can be employed to densify SiC based ceramics. The main advantage of this approach is the lower temperatures involved. Liquid phase is generally produced by reaction of the additives with SiO_2 present on the SiC surface [2].

Many parameters account for the production of highly dense ceramics, including powder properties such as high specific surface area, the processing technique used to consolidate the powders, and the sintering conditions, *i.e.* atmosphere, temperature and time. The control of sintering conditions is therefore, of fundamental importance. The amount and composition of the liquid phase can be formulated to provide suitable viscosity to make material transport more efficient and, consequently, to improve densification.

Sintering in electric furnace can be more effective due to the presence of a powder bed covering the samples, which helps to maintain the vapour pressure constant and decreases the sample weight loss.

In the present work, the sintering behaviour of silicon carbide-fused silica mixtures (with and without mulite and alumina addition) obtained by casting in metallic moulds of thermoplastic slurries was investigated in air and in argon firing conditions, respectively

The sintered samples were characterised in terms of bulk density, open porosity, and thermal shock resistance, thermal expansion measurements, crystals size and microstructure observation.

2. Experimental

2.1. Raw materials

Powders of fused SiO_2 (China, grade: 98.72 %SiO_2, with mean particle size d_{50} = 12 μm, and density of 2. 20 g/cm^3), Silicon carbide (Norton 600, green sort, grade 98.5% β-SiC, with mean particle size d_{50} = 10 μm and density of 3.20 g/cm^3) calcinated Al_2O_3 (ACS-ICEM, grade: 99.5%) Al_2O_3 with mean particle size d_{50} = 2μm, and density of 3.85 g/cm^3, mulite-$3Al_2O_3 \cdot 2SiO_2$ (ICEM, mean particle size d_{50} = 4μm and density of 2.65 g/cm^3 were used for experimental works. The particle size distribution of the raw material and mixtures was determined by Fischer method [5].

2.2. Characterisation methods

A TUR - 4 diffractometer with Cu K_α radiation ($20^o <$ $2\theta < 70^o$) was used to analyse the developed mineralogical phases. The sintering bulk density was measured by the hydrostatic method.

A Hitachi S 2600 N scanning electron microscope (SEM) incorporating a microanalysis detector for energy dispersive X-rays (EDS) was used to observe the surface microstructure of samples. An infrared grating spectrophotometer (Shimadzu FTIR 8400) was used for pellet spectra over 4000 to 400 cm^{-1} regions. Infrared transmission spectra were obtained from KBr pellets containing powdered sample material. Sample were first dry-grounded and blended with the KBr; 0,75 wt% of samples was ordinarily used. Powder transmission method was used for FTIR spectra.

The powders were mixed by stirring for 1h in several proportions, according to Table 1.

Table1. Composition of powder mixtures used for thermoplastic slurries preparation.

Composition	S0	S1	S2	S3	S4	S5	S6
Fused SiO_2 (%)	100	90	80	70	50	30	40
SiC, (%)	-	10	20	20	20	20	10
Mulite, (%)	-	-	-	10	10	-	10
Al_2O_3 (%)	-	-	-	-	20	50	40
Thermoplastic binder	20 - 23 %						

Procedures

The powder batches was prepared as a thermoplastic slurry in the 70-80 ^{o}C temperature range by adding and heating a mixture of bees wax, paraffin and grease acids from soy and sunflower oils [5], followed by stirring for 1 hour for homogenization. Both processes, stirring and attrition milling, were tested in order to estimate the effects of the particle size distribution and mean particle size of the additives on the sintering behaviour of silicon carbide. For small amounts of additives, attrition mill is not usually recommended due to the high media wear during milling, although it provides better powder homogeneity. All compositions given in Table 1 were calculated without considering the low amount of SiO_2 (1.38 %) which is present in SiC raw material. The obtained thermoplastic slurries, at 70-80°C, were poured into steel moulds as prism with dimensions of 10 x 10 x 60 mm and as crucibles with d = h = 30 mm.

Sintering were performed in air and argon flow respectively, in furnace applying a heating rate of 15 °C/min up to 1250 °C. Samples were kept at this temperature for 1 h. The densities of sintered samples were characterised by using the geometrical and Archimedes methods and for structural feature by SEM+EDS and FTIR methods.

3. Results and discussion

Compactity

The densification results obtained for the S0-S6 samples, sintered at 1250 ^{o}C in air and in argon environment, respectively, in an electric furnace are shown in Fig.1 . Comparing the density after sintering in air, it should be noticed that the sample sintered under argon does not undergo the best densification.

The sintered density data show that samples sintered in air exhibit higher density than the samples sintered in argon in the graphite resistance furnace. In order to remove the organic binder, the samples were covered with a protective powder bed during sintering. When the SiC amount is increased up to 20% (by weight) in compositions S1, S2, the density increases slightly. An addition of 10% mulite (composition S3) leads to a better densification. The use of a mixture of 10% mulite and 20% alumina as addition in composition S4, exhibits a better densification, but the thermal shock resistance is dramatically affected. This behaviour is probably related to the viscosity of the liquid formed, and depends on the solubility of silicon carbide. Concerning this mechanism, the most important parameter are the viscosity and temperature of the liquid [2]. The final density is related to the amount of liquid phase that could recrystallize [4]. The best densification were obtained for the S6 sample in air (1.93 g/cm^3). The evolutions of water adsorption capacity and of open porosity of the S0 - S6 samples sintered at 1250 oC in air and in argon environment respectively are given in Fig 2 and Fig.3.
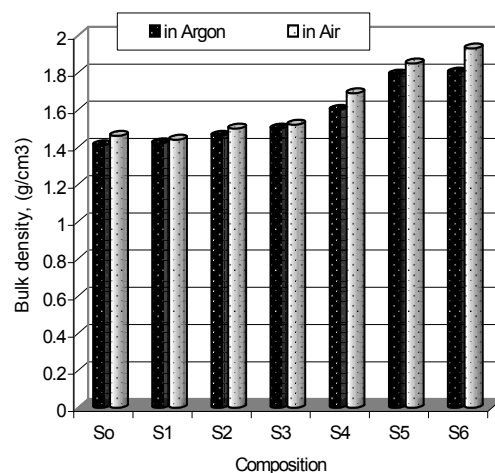

Fig.1 Bulk density of the S0 - S6 samples sintered at 1250 °C in air and in argon environment, respectively
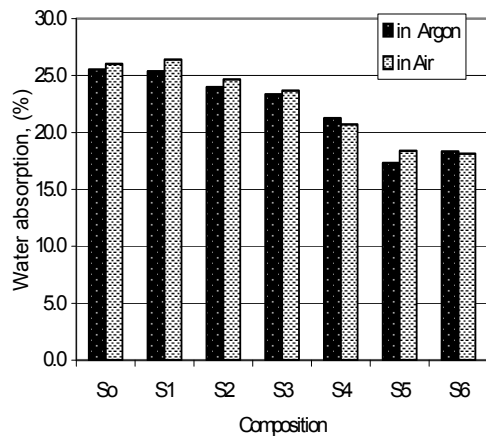
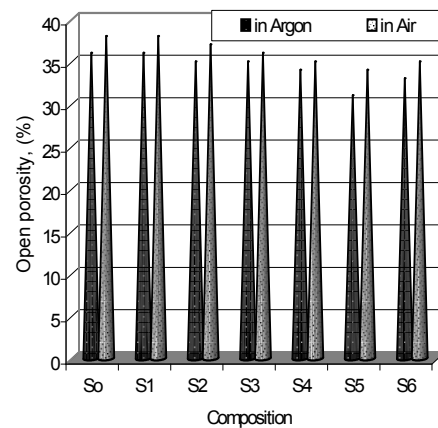*ig.2 Water absorption of the S0 - S6 samples sintered at 1250 ^{o}C in air and in argon environment respectively*

Fig.3 Open porosity of the S0 - S6 samples sintered at 1250 ^{o}C in air and in argon environment respectively

Thermal expansion

The thermal expansion coefficients of composites sintered in air are given in Fig. 4. It can be noticed that the measured values of thermal expansion coefficients are higher than the theoretical values calculated.
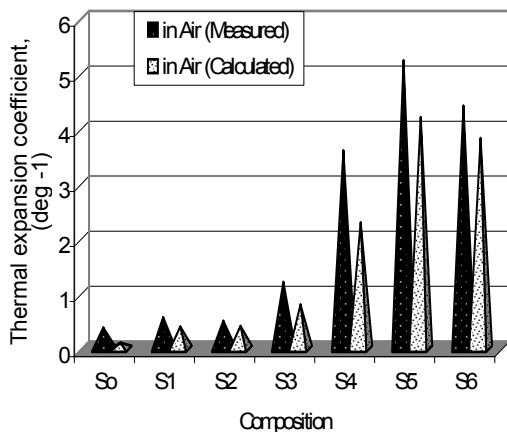

Fig. 4. Thermal expansion of the S0 - S6 samples

Thermal shock resistance

As seen in *Table 2*, an excellent thermal shock resistance (over 35 cycles) was emphasized by the compositions with the highest content of fused silica S0, S1 and S2 and a good thermal resistance (25 cycles) has had the sample S3 (with an addition of 10% mulite).

Table 2. Thermal shock resistance of composites S0 - S6 sintered in air.

Thermal shock resistance (cycles 900 ^{o}C – water)							
	S0	S1	S2	S3	S4	S5	S6
- in air	> 35	> 35	> 35	25	12	4	7

Comparing the results obtained on samples S1, S2, S3 and on the reference sample S0 can be notice their excellent thermal shock resistance. The addition of calcinated alumina affects dramatically the thermal shock resistance of samples S4, S5 and S6.

X-ray diffraction analysis

The mineralogical phases detected by X-ray diffraction on bulk samples S0- S6 are shown in Table 3.

Table 3. The mineralogical phases detected by X-ray diffraction on bulk samples S0- S6.

Sample / Mineralogical phase	S0	S1	S2	S3	S4	S5	S6
3C SiC	-	+	+	+	+	+	+
4H SiC	-	+	+	+	+	+	+
$3Al_2O_3.2SiO_2$ –mulite	-	-	-	-	++	++	+
Al_2O_3	-	-	-	-	+	++	+
SiO_2 - cristobalite	++	++	++	++	+	+	+
Amorphous phase	+++	-	-	-	-	-	-

- not detected; +++ high content, ++ medium content, + low content

Two silicon carbide polytypes are present: 3C and 4H The presence of the 3C polytype indicates that the β--> α transition is not complete. The mulite phase ($3Al_2O_3.2SiO_2$) was not identified by X-ray diffraction as a crystalline secondary phase present in sample S3.

FTIR analysis

The relationship between the FTIR spectra and structure of the sintered composites was investigated. The IR transmission values for the samples S1 - S6 are given in *Table 4*. The IR spectrum of SiO_2 has the most intense

peak around 900 – 1100 cm^{-1}. Shift of the peak positions and the number of peaks can be seen with different polymorph of silica from amorphous silica to quartz. Amorphous silica, for example, has a very intense, broad peak centred at 1095 cm^{-1} and an additional much less intense broad peak at 800 cm^{-1} whilst quartz exhibits an intense broad band around 1100 cm^{-1}.

The sharper bands in 529 – 712 cm^{-1} range should be assigned to the silicon carbide vibrations

Table 4 FTIR Transmittance (T%) of the S1- S6 samples.

Sample	T (%)	Wave number (cm^{-1})	Assignment
S1	67	559	Si-C
	85	705	Si-C
	82	854	Si-O
	36	2994	H-O
	25	3270	H-O
	10	3442	H-O
	15	3522	H-O
S2	95	558	Si-C
	100	712	Si-O
	98	856	Si-O
	87	2976	H-O
	80	3274	H-O
	10	3451	H-O
	15	3528	H-O
S3	88	574	Si-C
	100	796	Al-O
	90	861	Si-O
	70	3277	H-O
	30	3443	H-O
	35	3533	H-O
S4	100	545	Si-C
	90	632	Al-O
	98	888	Si-O
	80	3296	H-O
	50	3441	H-O
	60	3534	H-O
S5	90	544	Si-C
	53	620	Al-O
	60	765	Al-O
	92	979	Si-O
	85	3269	H-O
	60	3449	H-O
	70	3526	H-O
S6	98	526	Si-C
	55	632	Al-O
	65	723	Al-O
	93	968	Si-O
	90	3291	H-O
	68	3449	H-O
	75	3522	H-O

The FTIR spectra of S1, S2 and S3 sample have a similar feature in 400-700 cm^{-1} wave numbers range, assigned with Si-C bond. The 900 – 1100 cm^{-1} is assigned with silicate anions vibrations and the 2900 – 3500 cm^{-1} is assigned with H-O vibrations due to the moisture of environment.

The FTIR spectra of S4, S5 and S6 sample have a similar feature in 600-770 cm^{-1} wave numbers range, assigned with Al-O bond and specific peak in the range 900 – 1100 cm^{-1} assigned with silicate anions vibrations and the 2900 – 3500 cm^{-1} is assigned with H-O vibrations.

4. Conclusions

The use of fused silica with 80-90 % β-SiC, with several proportions of Al$_2$O$_3$ and mulite as additives, was suitable to obtain thermal resistant composite by casting from thermoplastic slurries.

The samples sintered in air, in the presence of powder bed in an electric furnace at 1250 $^{\circ}$C show a lower weight loss and, therefore, higher densification comparatively with the argon environment sintering.

The vitreous silica/silicon carbide composites have proved excellent thermal shock resistance.

X-ray diffraction in conjunction with FTIR transmittance spectra analysis revealed the presence of β-SiC (3C polytype), of the α-SiC (4H polytype), and some amounts of cristobalite.

Acknowledgements

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