Sintering of Silicon Carbide Ceramics
With Additives Based On the (Y_2O_3-Al_2O_3-SiO_2) System

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Abstract. The sintering behavior of silicon carbide using alumina, silica and yttria as additives was investigated. Powders containing 90 vol. % SiC and 10 vol. % additives (keeping $1Y_2O_3$:$1Al_2O_3$ molar ratio) were sintered at 1950ºC/1h, in a dilatometer or a graphite resistance furnace. Thermal treatments were also done from 1500ºC/1h up to 1800ºC/1h, in order to evaluate the formation of transient crystalline secondary phases. The sintered samples were characterized through XRD, SEM and TEM analysis. The results showed that sintering behaviour is clearly related to the additive composition investigated, as demonstrated by linear shrinkages and linear shrinkages rate curves. Temperatures of particle rearrangment, solution-reprecipitation of SiC grains, as well as secondary crystalline phase(s) formation and dissolution could be revealed after dilatometric analysis. These temperatures are in good agreement with XRD results. Microstructural observations through SEM and TEM analysis are also related to the sintering behaviour.

Introduction

Silicon carbide based ceramics are promising in structural applications due to a whole of properties including high temperature strength, low density, excellent thermal shock and wear resistance[1]. Hence, silicon carbide can be applied in automotive heat engines, cutting tools, heat exchange, mechanical seals, etc.

In order to achieve high densification, sintering of silicon carbide ceramics occurs through solid state [2-4] or via liquid phase [5-6], depending on the additives employed. During liquid phase sintering, there are some reactions of additives with silica present on the silicon carbide particles surface [7-8] which induce the liquid formation, with a subsequent solution reprecipitation process. The main advantage of a liquid phase sintering compared to a solid state sintering is the lower temperatures for sintering.

Knowledge of the sintering behaviour is desirable in order to produce materials with suitable microstructure and properties, to be used in several applications. Sintering of silicon carbide ceramics can be conducted in a dilatometer or in a graphite resistance furnace. The sintering behaviour of a powder compact during heating can be described trough dilatometric experiments based on the shrinkage values at each temperature step. The shrinkage depends on the initial length and the compact length at each step. The measurements can also provide the temperatures of maximum shrinkage. However, sintering conducted in dilatometer spend longer periods to reach equilibrium conditions, due to the continuous gas flow employed during experiments, which leads to variable pressure within the system. Another disadvantage of this sintering is the greater weight loss involved.

In spite of the absence of the parameters control during sintering, sintering in graphite resistance furnace can be more effective due to the presence of a powder bed covering the samples, which helps maintain the vapour pressure constant and decrease the sample weight loss. Moreover, several samples can be simultaneous sintered.

It is well known that sintering additives based on the SiO_2-Al_2O_3-RE_2O_3 system (RE = Y, rare earth) can be used to obtain high density silicon carbide ceramics via liquid phase sintering [9-10]. The amount and composition of the liquid phase should be formulated to provide suitable viscosity to make material transport more efficient and, consequently, to improve densification [11-13]. In the present work, sintering behaviour of SiC using SiO_2-Al_2O_3-Y_2O_3 as additives was investigated and can be related to the formation of different crystalline phases upon heating.

Experimental Procedure

The oxide additives silica (SiO_2, Fluka), yttria (Y_2O_3, Sigma Aldrich) and alumina (Al_2O_3, A-16 SG Alcoa), in several proportions were mixed in attritor (Szegvari Attritor System, Union Process) with 90 vol % silicon carbide (SiC, BF 17, H. C. Starck, 91.1% β-SiC). Mixtures 1, 2 and 3 are prepared with a constant Y_2O_3 / Al_2O_3 molar ratio and containing 60, 33 and 20 mol % SiO_2, respectively.
Mixtures were dried in Rotoevaporator (WB 2000, Heidolph) and the powders were uniaxially and cold isostatically pressed (200 MPa, National Forge). Two samples of each composition were pressed to obtain estimates of the experimental error. Sintering was carried out in dilatometer (DIL, 402, Netzch) and in graphite resistance furnace (Astro 1000, 4560, FP 20, Thermal Technology Inc.) both at 1950ºC/ 1 h, keeping a heating rate of 15ºC/min, using argon dynamic flux. Powder beds of silicon carbide mixed with oxide additives (mixture 1) were used during sintering in graphite resistance furnace in order to avoid oxide evaporation and SiC decomposition.
Densities before and after sintering, as well as weight loss during sintering, were evaluated for each sample. Final sample densities values are expressed in terms of theoretical density, which varies depending on the composition of additives presented in the mixture, and were calculated according to the mixture's rule [14].
Thermal treatments were also done in graphite resistance furnace from 1500ºC/1h up to 1800ºC/1h, in order to evaluate the formation / dissolution of transient crystalline secondary phases according to the temperature employed.
X-ray diffraction patterns were obtained for each sample in each thermal treatment / sintering temperature, using Cu $_{kα}$ (Dmax 2000, Rigaku).
Microstructure of polished and polished / plasma etched cross sections samples were observed through scanning electron microscope (SEM, XL 30, Philips). Samples were prepared through a conventional way. Microstructure of sample 3 was also observed trough transmission electron microscope (MET, 200C, JEM, Jeol).

Results and Discussion

Sintering behaviour

Linear shrinkages for all samples after dilatometric experiments are shown in Fig. 1a. It can be seen that at 1950 ºC there is no shrinkage, thus the densification process is hindered for all samples at such temperature.
The respectively linear shrinkage rates are presented in Fig. 1b, which helps the investigation of the sintering kinetics involved in the densification process of silicon carbide. The sintering behaviour is clearly related to the additive composition investigated. Four peaks can be clearly observed. T1 is related to the particle rearrangment and the first liquid formation. T2 is related to solution-reprecipitation of silicon carbide grains (SRSiC), which is hindered through a secondary crystalline phase(s) formation (T3). When the temperature is increased, these phases are dissolved and the main SRSiC occurs (T4).
Samples 2 and 3 present three peaks of maximum shrinkage rate (T1, T2, T4) and one peak of minimum, related to the decrease of shrinkage rate (T3), as indicated in Table I. However, sample 1 present only one peak of maximum shrinkage rate due to SRSiC process. This composition is located in the glass-forming region [11], and, consequently, has no secondary crystalline phases,
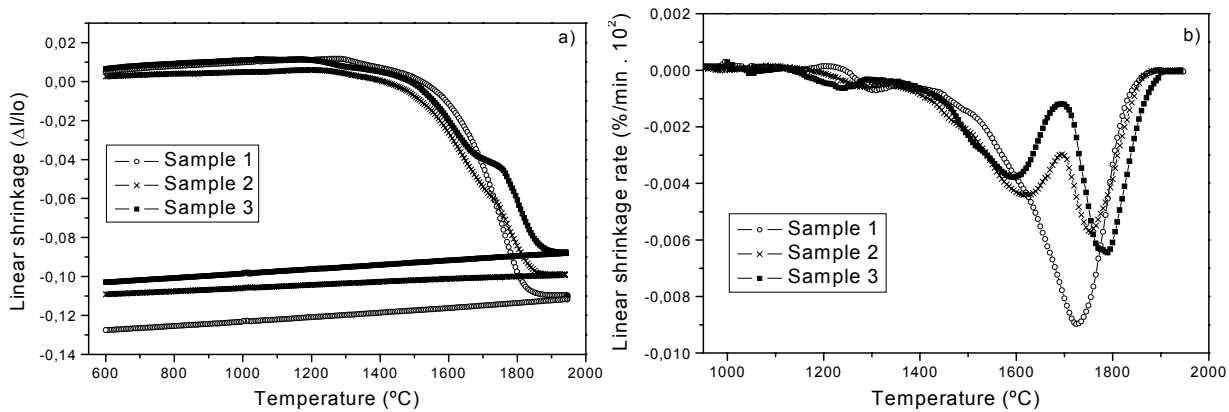
Figure 1: Dilatometric results for silicon carbide samples sintered at 1950ºC/1h:
a) linear shrinkage; b) linear shrinkage rate

which are an obstacle to the SRSiC process. This process occurs at lower temperatures if compared to the other samples.

Densification results of samples sintered in graphite resistance furnace at 1950ºC/1h are also shown in Table I. Although higher densities of all samples were achieved (more than 90% td), sample 1 (located in glass forming region) presents lower density as compared with the other ones, probably due to an effect of the estimative of the theoretical density through mixture rules.

Table I: Maximum (T1, T2 and T4) and minimum (T3) temperatures of linear shrinkage rate and densification results of silicon carbide ceramics samples sintered at 1950ºC/1h.

Sample	Temperatures of maximum and minimum peaks after experiments in dilatometer (ºC)				Densification results after sintering in graphite resistance furnace	
	T1	T2	T3	T4	Density (% t. d.)	Weight loss (%)
1	1310	-	-	1725	90.37 ± 0.710	7.76 ± 0.047
2	1295	1595	1700	1800	95.43 ± 0.322	6.45 ± 0.152
3	1240	1595	1695	1790	95.14 ± 0.461	4.60 ± 0.149

Microstructural observations

X-ray diffraction patterns of bulk samples, thermal treated at different temperatures are shown in Fig. 2. α and β-SiC polytypes were present in all samples, independent of the composition or the temperature applied in thermal treatment/sintering, as major crystalline phases. The crystalline secondary phases in each thermal treatment temperature, for different composition of additives, are shown in Table II. No secondary crystalline phases were identified in sample 1 up to 1700ºC. However, at higher temperatures, YAG and $Y_4Al_2O_9$ were identified, as predicted by Al_2O_3-Y_2O_3 phase diagram. These data are in good agreement with dilatometric results. Up to 1700ºC, the crystalline secondary phases identified in sample 2 were $Y_{4,67}(SiO_4)_3O$, YAG, $Y_4Al_2O_9$ and $Y_2Si_2O_7$ varying with temperature. At higher temperatures, $Y_2Al_2O_6$ and $Y_4Al_2O_9$ were identified. According to Al_2O_3-Y_2O_3 and SiO_2-Y_2O_3 binary equilibrium system at composition 3, YAG and $Y_2Si_2O_7$ are stable up to 1835ºC and 1775ºC, respectively. These data are in good agreement with observed crystalline phases.

These results showed that the crystalline phases detected after x-ray experiments are in good accordance to the predicted phases. Although Y_2O_3/Al_2O_3 molar ratio is constant in all samples, there are clearly alterations in transient secondary crystalline phases formation / dissolution, which can be observed more carefully through x-ray diffraction analysis. These results can be related to dilatometric experiments data.
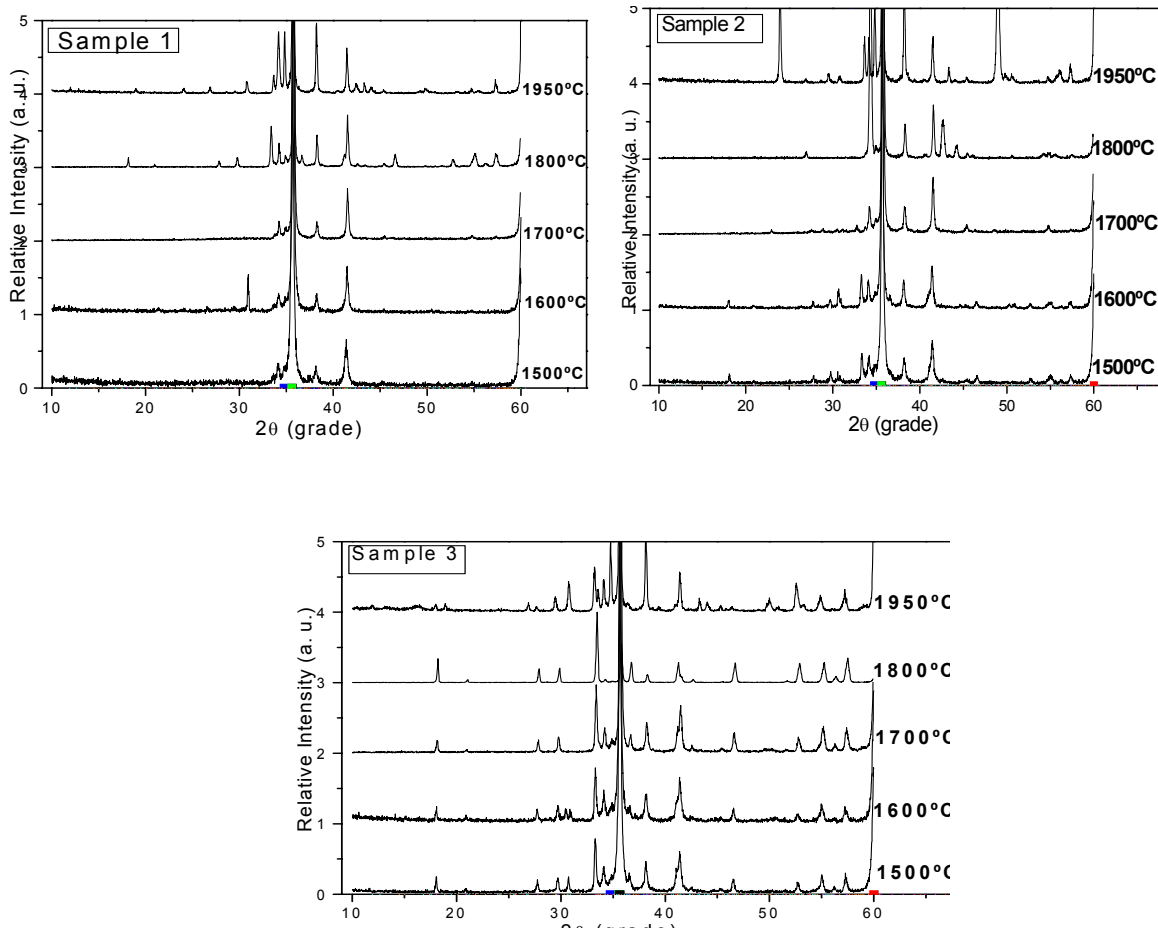
Figure 2: X-ray diffraction patterns of several silicon carbide samples treated at different temperatures:

a) Sample 1 (60% SiO_2); b): Sample 2 (33% SiO_2); c): Sample 3 (20% SiO_2)

Table II: Crystalline secondary phases identified in several silicon carbide samples by XDR analysis according to several temperatures

Sample	1500º/1h	1600º/1h	1700º/1h	1800º/1h	1950º/1h
1	-	-	-	YAG	$Y_4Al_2O_9$
2	$Y_4Al_2O_9$ +YAG+ $Y_{4.67}(SiO_4)_3O$	$Y_{4.67}(SiO_4)_3O$	$Y_2Si_2O_7$	$Y_2Al_2O_6$	$Y_2Al_2O_6$ + $Y_4Al_2O_9$
3	YAG	YAG+ $Y_2Si_2O_7$	YAG	YAG	YAG + $Y_4Al_2O_9$

The secondary phase observed in MEV appears to be well distributed in all samples, indicating good mixture homogeneity (Fig. 3, left). The morphology of silicon carbide grains could be revealed after plasma etching (Fig. 3, right), with a normal distribution in all sintered samples. No secondary or abnormal grain growth was observed.

The microstructure of sample 3 was also observed in MET (Fig. 4). This microsctructure is representative of silicon carbide ceramics sintered via liquid phase using additives based on the SiO_2-Al_2O_3-RE_2O_3 system. The morphology of silicon carbide grains can be observed, as well as twin grains which indicates the β−α-SiC phase transformation. The secondary phases in grain boundaries are continuous and crystallize in wide regions. The low contact angles in triple points indicate a good wettability when related to silicon carbide grains.
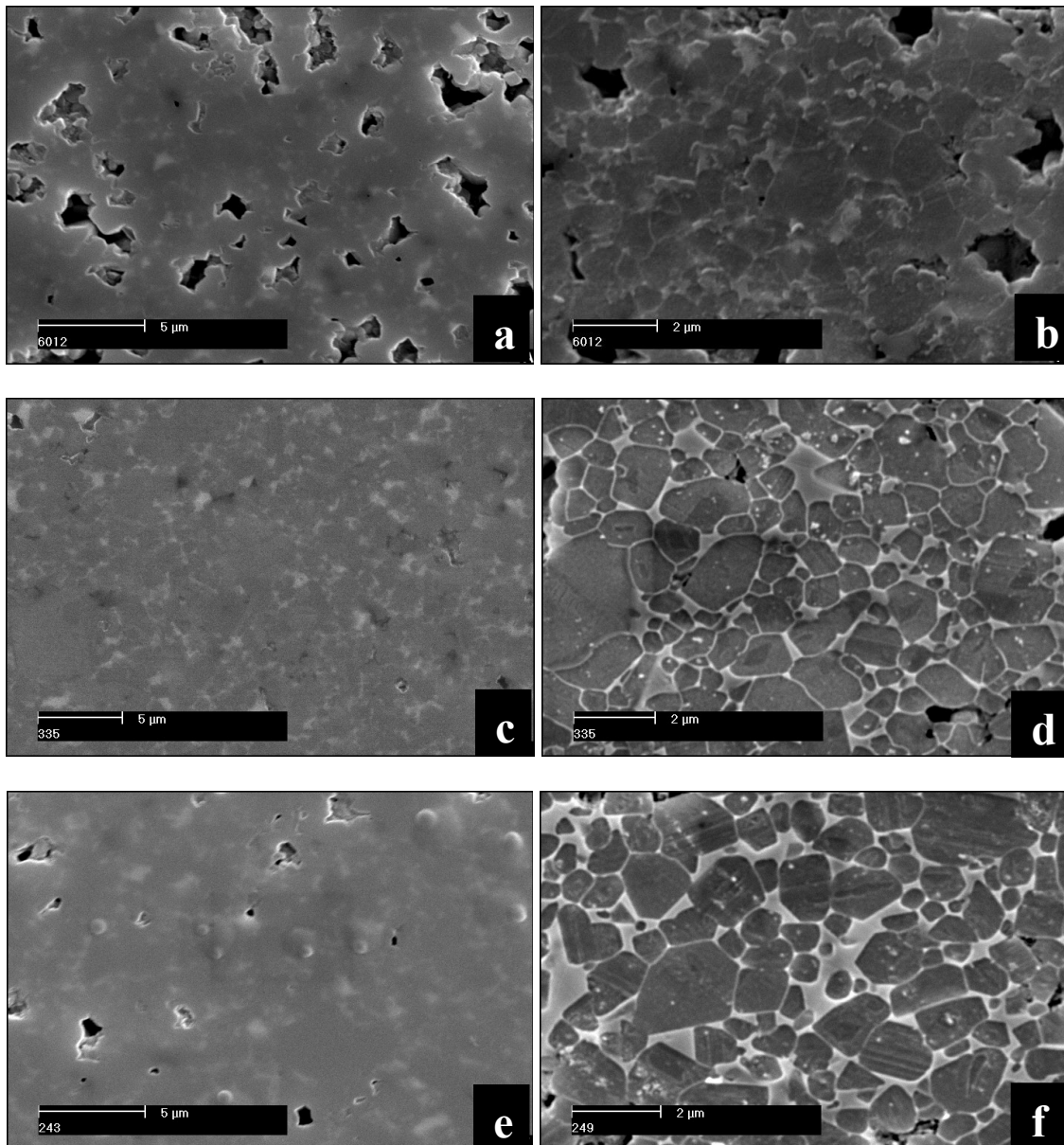
Figure 3: SEM micrographs of polished (left) and polished / etched (right) silicon carbide ceramics sintered at 1950ºC/1h with (SiO_2-Y_2O_3-Al_2O_3) additive system:
a) and b):Sample 1 (60% SiO_2); c) and d): Sample 2 (33% SiO_2); e) and f): Sample 3 (20% SiO_2).
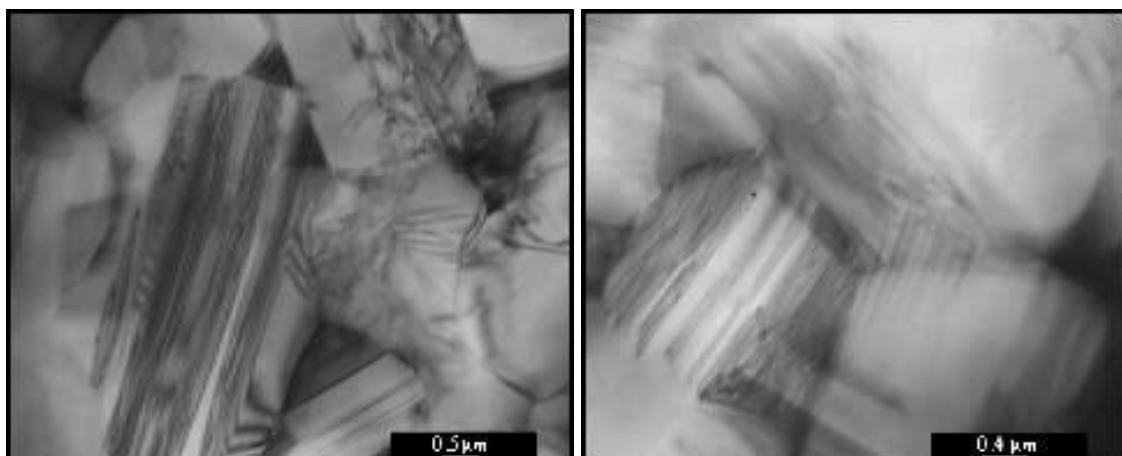

Figure 4: TEM micrographs of silicon carbide ceramic (Sample 3) sintered at 1950ºC/1h with (SiO_2-Y_2O_3-Al_2O_3) additive system.

Conclusions

The composition and the sintering temperature have a great effect in the viscosity of the formed liquid phase, if the secondary phase is amorphous or crystalline with different stoichiometry. The dilatometric results support the x-ray diffraction analysis; the temperature at which the crystalline phases are formed is the same as the temperature in which the linear shrinkage rate shows inflection points.

Summary

Silicon carbide is one of the most important structural ceramics materials, which can be applied in abrasives, refractories, automotive engine components, cutting tools and many other applications. Sintering of silicon carbide can occur in the presence of oxide additives, which forms a liquid phase at sintering temperatures.

In this work, liquid phase pressureless sintering of silicon carbide based ceramics was investigated using different compositions based on (Y_2O_3-Al_2O_3-SiO_2) system. 10 mol % of additives (among several compositions) were mixed with silicon carbide, dried and cold isostatically pressed. Samples were sintered in a graphite resistance furnace at 1950ºC/1h. Final density and weight loss during sintering were estimated. Secondary crystalline phases were determined through x-ray diffraction. Microstructures of sintered materials were observed by scanning and transmission electron microscopy. Dilatometric experiments were useful to understand the liquid sintering process of silicon carbide, which is dependent on crystalline secondary transient phases that are formed and/or dissolved at different temperatures. The secondary phases identified during sintering change with composition and have a significant influence on final density and weight loss, changing the microstructure of the sintered material.

Acknowledgements

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