

LIQUID -PHASE SINTERED SILICON CARBIDE BASED CERAMICS WITH AlN-Y₂O₃ AND AlN-La₂O₃ ADDITIVES

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ABSTRACT

Microstructure development and phase formation processes during sintering of silicon carbide based materials with 10 vol.% of AlN - Y₂O₃, or AlN - La₂O₃ sintering additives were investigated. Densification of the materials occurred by liquid-phase sintering mechanism. Ratio of α - and β -SiC powders in the initial mixtures was a variable parameter. Shrinkage behavior during sintering was shown to strongly depend both on the combination of sintering additives and on the sintering atmosphere used. Kinetics of β -SiC to α -SiC phase transformation under conditions of post-sintering heat treatment at 1900-1950°C was studied, the degree of transformation determined by quantitative x-ray analysis. Evolution of microstructure resulting from β to α phase transformation was followed up by scanning electron microscopy. Transformation-controlled grain growth mechanism similar to the one observed for silicon nitride based ceramics was established. Possibility of in-situ platelet reinforced dense SiC-based ceramics fabrication by means of sintering was shown.

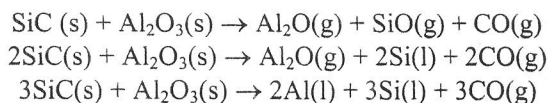
Key words: silicon carbide, ceramics, sintering, phase formation, post-sintering heat treatment, phase transformation, microstructure.

INTRODUCTION

Silicon carbide is considered to be an important structural ceramic material because of a promising combination of properties, such as high oxidation resistance, good mechanical properties retained to high temperatures, high wear resistance, good thermal shock resistance due to high thermal conductivity, etc. All these properties are inherent to silicon carbide due to highly covalent bonding. The latter, however, causes complications with sintering of SiC-based ceramics to high densities, which disadvantage is characteristic for all non-oxide covalent compounds, such as Si₃N₄ and AlN.

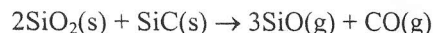
Unlike the aforementioned compounds, which tend to decompose severely at high temperatures, silicon carbide can be densified by solid-state sintering process at high temperatures of about 2100°C with the aid of B and C [1], which dramatically improve the shrinkage kinetics. However, thus sintered materials have poor or,

at the best, moderate mechanical properties (flexural strength of 300-450 MPa and fracture toughness of 2.5-4 MPa·m^{-1/2}). Liquid-phase sintering of SiC can be achieved at much lower temperatures (1800-1900°C) [2, 3] with the aid of metal oxides, such as Al₂O₃, Y₂O₃, and other rare-earth oxides [4-8]. The densification of SiC by liquid-phase sintering lately draws more attention because the materials processed by this method exhibit superior mechanical properties. The liquid phase sintering of SiC is somewhat similar to the same process for Si₃N₄. The oxide sintering aids react with SiO₂, which is always present at the surface of SiC particles, forming an oxide melt and enhancing densification. However, oxides interact with SiC with massive gaseous products formation leading to high weight loss and porosity [9, 10]. It is known that alumina may interact with silicon carbide according to the following reactions [4]:



These reactions occur more actively with the increase of alumina content and the temperature of sintering. These reactions can be to some extent suppressed by the application of the high external partial pressure of CO and/or application of reactive powder beds [4]. However, such an approach is not completely effective and enables to achieve the final density not higher than 98% of theoretical density. Moreover, such techniques are costly and do not guarantee the reproducibility of materials properties.

Additional weight loss during liquid phase sintering of SiC occurs due to the reaction between SiC and SiO₂ surface films:



It is therefore obvious that an alternative combination of sintering additives, which will eliminate or reduce the above mentioned effects determined for densification, will be the best possible solution. As it was suggested by Chia *et al* [11], aluminum nitride, AlN, in combination with yttria, Y₂O₃, may present a solution. However, this possibility was not investigated in detail and only a limited amount of information is available [11, 12]. Which is of additional interest, due to certain structural similarities SiC and AlN produce solid

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solutions and formation of mixed crystalline structures was observed [13-17].

By analogy with silicon nitride, it seems to be possible to tailor the microstructure and the structure-sensitive properties of silicon carbide based ceramics by varying α - to β -SiC ratio in the initial mixtures. If α -SiC is used as a starting powder, the final material is characterized by fine homogeneous microstructure with uniaxial grains [5, 18], which results in moderate fracture toughness. Additions of β -SiC in combination with some specially developed thermal treatment leads to in-situ platelet reinforced material formation with improved mechanical properties [5, 7, 19].

In the present work sintering behavior and microstructure development of $\alpha\beta$ -SiC-AlN- Y_2O_3 and $\alpha\beta$ -SiC-AlN- La_2O_3 materials under conditions of pressureless sintering were investigated. The Y_2O_3 for La_2O_3 substitution was investigated for possible sinterability improvement due to lower refractoriness of La_2O_3 - based oxynitride systems as well as lower eutectic formation in relevant oxide systems [20]. Influence of RE sintering additive type on sinterability, phase and structure formation were studied.

EXPERIMENTAL

Mixtures were prepared from high-purity powders of α -SiC (UF-15, H. C. Starck, Goslar, Germany), β -SiC (B10, H. C. Stark, Goslar, Germany), AlN (H. C. Starck, Germany, grade C), Y_2O_3 (>99.98 % purity, Aldrich Chemical Company, USA), or La_2O_3 (>99.9% purity, Sigma-Aldrich Co., Switzerland) by attrition milling with alumina milling media in isopropyl alcohol for 4 hours at 500 RPM. The total amount of sintering aids was kept constant at 10 vol.%. The ratio of α -SiC/ β -SiC was a variable parameter, the content of α -SiC chosen as 5wt% and 10 wt% relative to the amount of β -SiC. The ratio AlN/ Y_2O_3 was kept constant at 3:2, the proportion chosen from the AlN - Y_2O_3 phase diagram [21]. The ratio AlN/ La_2O_3 was kept at the same value in anticipation of similarities between these two oxides behavior, the exact phase relationships in AlN- La_2O_3 system being unknown until present time.

The slurry obtained after attrition milling was separated from the milling media by passing through a ASTM 325 sieve and subsequently dried in a vacuum rotaevaporator. Samples of the mixture were taken for granulometric analysis and specific surface determination. The former was performed by means of laser granulometry (Granulometer 1064, CILAS, France), while the latter was accomplished by BET (ASAP 2000, Micrometrics Instrument Corp., USA). The process of drying was then completed in a drying box (48 hours, 65°C). Finally, the powder was passed through a ASTM 100 sieve to crush soft conglomerates.

Green bodies in the form of cylindrical pellets 20 mm in diameter and 25 mm height were prepared by consequent uniaxial pressing at 100 MPa, and cold

isostatic pressing at 200 MPa. Dilatometric experiments were accomplished in a high temperature dilatometer (DIL 402 E/7, Netzsch GmbH, Germany) with a graphite resistance furnace. Sintering was accomplished in a gas-pressure furnace (Thermal Technologies, Santa Barbara, USA) with a graphite heating element.

Post sintering heat treatment (annealing) was carried out in the same furnace that was used for sintering. The sintered samples were subsequently annealed at temperatures 1900°C and 1950°C in nitrogen under normal pressure for up to 16 hours in order to achieve maximal degree of β -SiC to α -SiC phase transformation. Kinetics of the phase transformation was followed up by quantitative XRD analysis.

Sintered and annealed samples were characterized for weight loss, density, phase composition and microstructure. Density was determined by Archimedes method. Evolution of phase composition and phase transformation kinetics were studied by X-ray diffraction (XRD) on a Siemens D-6000 diffractometer (Ni-filtered $CuK\alpha$ radiation, range of detection 10-80° 2 θ). Microstructure was studied by scanning electron microscopy (SEM) on a Phillips XL-30 and on a JEOL-JXA-6400 electron microscopes with EDS, analyzing attachment. Samples for microstructure investigation were prepared by standard ceramographic procedure of multistep grinding and polishing with subsequent chemical etching with Murakami's reagent (10 g of NaOH and 10 g of $K_3Fe(CN)_6$ in 40 ml H_2O at 110°C) for structural elements revelation.

RESULTS AND DISCUSSION

The nominal formulation of the prepared mixtures together with some of their granulometric characteristics are presented in Table 1.

Table 1. Characteristics of the powder mixtures

Material	α -SiC wt. %	β -SiC wt. %	Y_2O_3 wt. %	La_2O_3 wt. %	AlN wt. %	Specific surface area m ² /g
SiC5	4.31	81.75	10.96	-	2.98	13.4
SiC10	8.61	77.45	10.96	-	2.98	12.9
SiL5	4.13	78.42	-	14.68	2.77	13.2
SiL10	8.26	74.29	-	14.68	2.77	13.1

The prepared mixtures were of submicron fineness, and had a narrow grain size distribution ($d_{10} = <0.1 \mu m$, $d_{50} = 0.38-0.40 \mu m$, $d_{90} = 0.99-1.05 \mu m$), the values of these parameters being very close for all mixtures prepared. Therefore, a favorable sintering behavior was expected.

The results of the dilatometric investigations of the densification behavior of the prepared compositions under different sintering atmosphere - flowing nitrogen and flowing argon - are presented in Fig. 1. As it can be

seen, the behavior of SiC and SiL groups of compositions is strikingly different both in terms of linear shrinkage and shrinkage rate depending on the sintering atmosphere. The influence of the α -SiC content in the initial mixture has only a slight effect on the overall shrinkage behavior causing a minor diminishing in shrinkage rate. However, if the Y_2O_3 is substituted for La_2O_3 , the shrinkage behavior changes dramatically. The linear shrinkage in this case is rather low in Ar atmosphere (Fig. 1. (a)), and substantially higher in N_2 (Fig. 1. (b)), compared with the one exhibited by Y_2O_3 doped mixtures, thus making the sintering behavior in regard of the atmosphere of sintering of these two groups of compositions inverse. It must be also noted that in Ar atmosphere the beginning of shrinkage for La_2O_3 doped mixtures is shifted about a $100^\circ C$ towards higher temperatures, while in N_2 by atmosphere shrinkage for both groups of mixtures starts at about the same temperature of $1600^\circ C$.

Even more differences have been observed with regard of shrinkage rate (Fig. 1. (c) and (d)) of the studied compositions. If while sintering in Ar the difference in shrinkage rate basically is limited to the

value of the rate for La_2O_3 doped compositions being sufficiently lower, and the maximum being shifted by $200^\circ C$ towards higher temperatures, the sintering in N_2 provides a much more complicated picture. It can be seen that the materials doped with La_2O_3 exhibit four peaks on the shrinkage rate curves, while the Y_2O_3 doped ones have only two. Such behavior suggest a rather complex sequence of phase formation on heating in the former group of materials because every minimum on the shrinkage rate curve corresponds to a crystalline phase formation, which hinders densification. Only after a temperature higher than the melting point of this phase is reached the densification proceeds.

As it was mentioned before, the exact phase relationships in the AlN- La_2O_3 are not known, and the molar ratio of the components was kept identical to the one in the case of AlN- Y_2O_3 system in anticipation of close similarity of the phase relationships in both systems. However, it is now obvious that in the case of La_2O_3 the phase relations are rather different, and in order to optimize both composition of the additives and

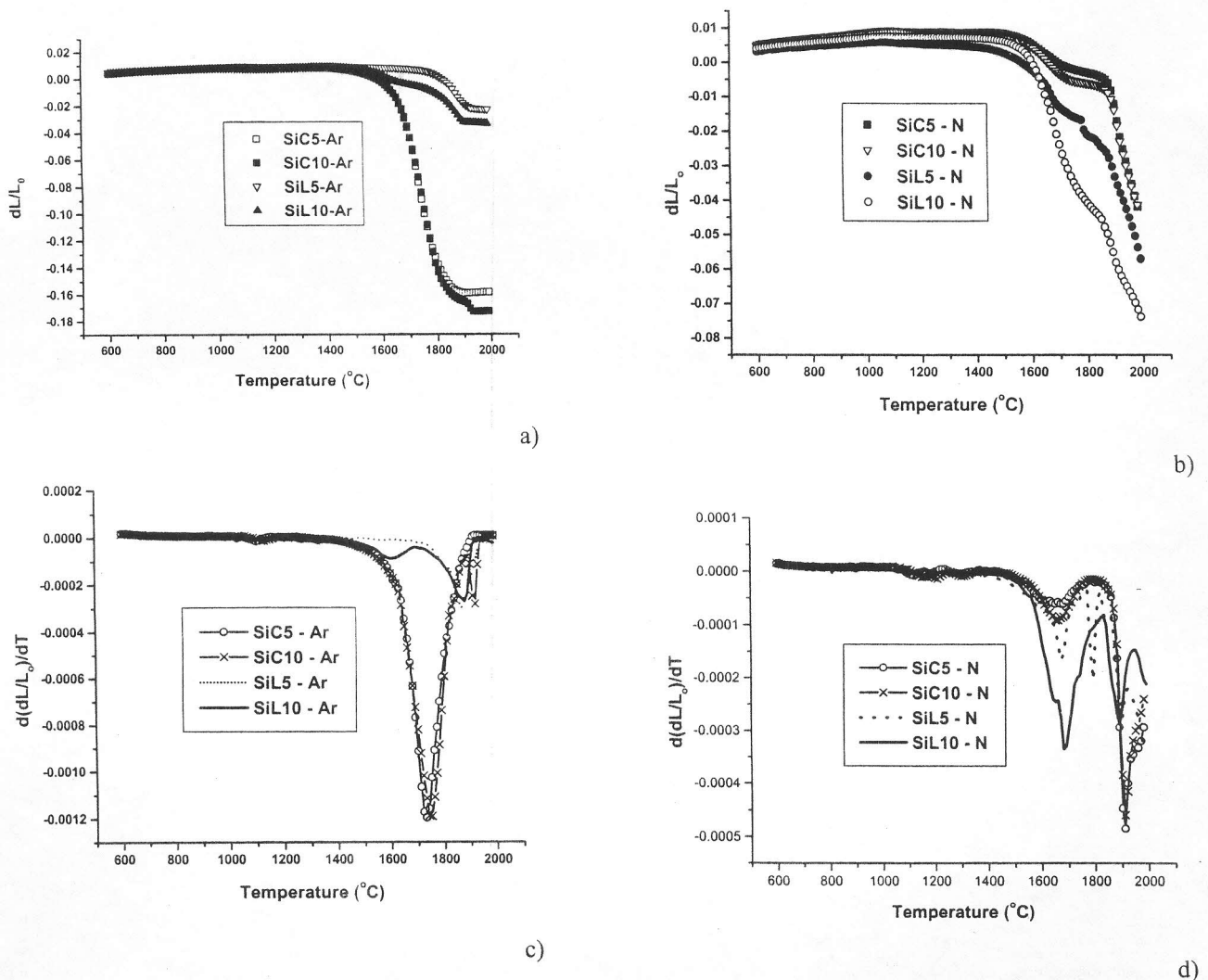


Fig. 1. Dilatometric measurements: (a) and (b) - linear shrinkage in Ar and N_2 , respectively; (c) and (d) - shrinkage rate in Ar and N_2 , respectively.

the sintering procedure further research is necessary, which is the next step in the course of the present research.

In the case of the Y_2O_3 doped materials, the first of the observed peaks on the shrinkage rate curve while sintering in N_2 is tentatively attributed to initial and limited liquid phase formation with participation of surface oxides, SiO_2 and Al_2O_3 present on SiC and AlN powder particles, respectively, with Y_2O_3 . The phase precipitating at about $1700^\circ C$ and subsequently melting at about $1850^\circ C$ was not identified until now.

It should be also mentioned that with the increase of the α -SiC content from 5 to 10 wt.% in the initial mixture the number of peaks on the shrinkage rate curve of La_2O_3 curve diminishes and approximates the curve of the Y_2O_3 doped material with the same α -SiC content.

Based on the results of the dilatometric investigations the time-temperature sintering schedule for furnace sintering was developed as presented in Fig. 2. The results of the furnace sintering of the prepared compositions in nitrogen and argon are presented in Table 2.

Table 2. Green density, sintered density and weight loss after furnace sintering of SiC5 and SiC10 compositions.

Compo sition	Atmos phere of sintering	Green density % td	Apparent density g/cm ³	Relative density % td	Weight loss %
SiC5	Nitrogen	55.1	2.90	86.83	2.70
	Argon	55.2	3.25	97.31	3.21
SiC10	Nitrogen	55.1	2.86	85.63	2.54
	Argon	55.1	3.24	97.01	2.99
SiL5	Nitrogen	55.2	3.29	94.61	0.94
	Argon	55.1	2.71	77.92	2.13
SiL10	Nitrogen	55.1	3.28	94.30	1.39
	Argon	55.2	2.62	75.32	2.48

As it can be seen, although the weight loss in the case of SiL series is lower than for SiC series, the former materials densify poorly under conditions of sintering used. In order to optimize the La_2O_3 doped materials it is necessary to develop a special sintering schedule based on the further phase formation sequence investigation which are under way.

Severe overlapping of the reflexes of β -SiC due to the polytypism of SiC makes the quantitative phase analysis extremely difficult. However, the existing three well defined α -SiC reflexes ($6H$ -polytype) enable to quantitatively evaluate the extent of the phase transformation by normalizing the sum of the $(111)_{3C}$ and $(006)_{6H}$ reflexes intensities. Using this approach a calibration curve can be obtained using the inner standard technique, i. e., a series of powder mixtures of β -SiC with fixed α -SiC additions was analyzed by XRD, and the ratio between the relevant reflexes intensities was determined. Thus obtained curve was subsequently used for the extent of phase transformation during post sintering heat treatment determination.

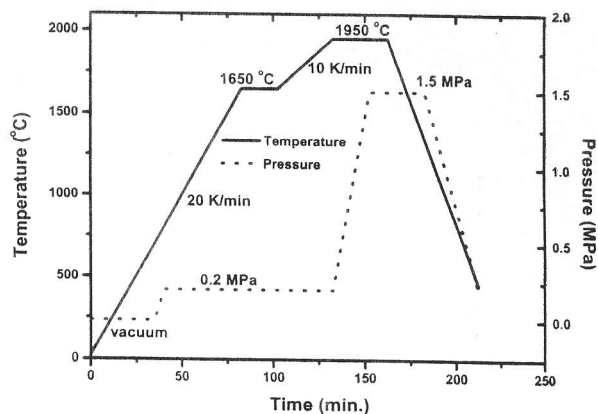


Fig. 2. Time-temperature-gas pressure sintering schedule.

The results of post sintering heat treatment and of the β -SiC to α -SiC phase transformation kinetics are presented in Fig. 3. As it can be seen, the β -SiC to α -SiC phase transformation occurs more readily with the La_2O_3 additions, while Y_2O_3 containing materials exhibit a somewhat sluggish behavior. At present time, only a tentative explanation is possible attributing such behavior to better conditions for diffusion provided by the secondary phases formed in La_2O_3 doped materials. However, further more detailed investigation of the processes involved is necessary.

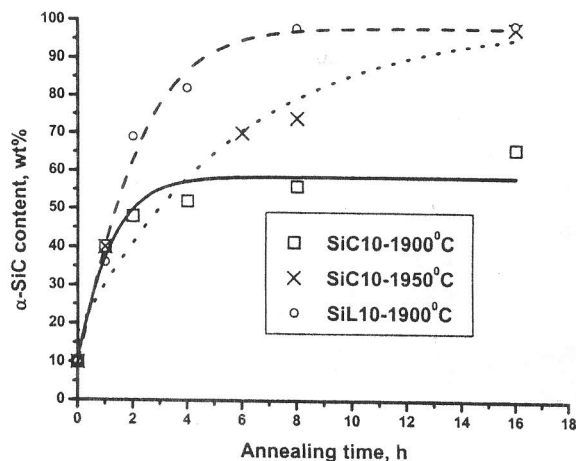


Fig. 3. Kinetics of β -SiC to α -SiC transformation under conditions of isothermal annealing in N_2 .

The microstructure of the as-sintered and thermally treated SiC-AlN- Y_2O_3 material are presented on Fig. 4. If the as-sintered sample has a fine uniaxial grain morphology, the annealed material exhibits microstructure with elongated grain morphology as a result of the β -SiC to α -SiC transformation. The grain growth occurred as well, thus providing evidence of transformation controlled grain growth mechanism.

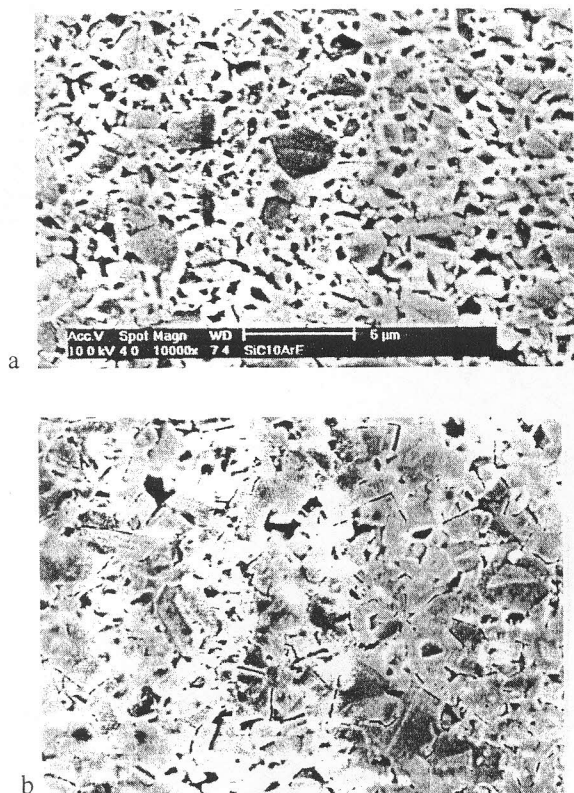


Fig. 4. Microstructures of the (a) as-sintered and (b) annealed (8 hours, N_2 atmosphere) SiC-AlN- Y_2O_3 chemically etched samples.

CONCLUSIONS

Silicon carbide can be sintered up to high densities by means of liquid phase sintering under low gas pressure with AlN- Y_2O_3 and AlN- La_2O_3 sintering additives. As-sintered materials exhibited fine-grained homogeneous microstructure.

Densification behavior of materials with Y_2O_3 and La_2O_3 additions is shown to be inverse: While the former materials densify better in Ar, the latter show better sinterability in N_2 . Moreover, the densification of La_2O_3 doped materials has a complex nature most probably due to a complex phase formation sequence on heating. This phenomena needs further investigation.

Transformation controlled grain growth during post sintering heat treatment of the developed materials was established. A high degree or even a complete β -SiC to α -SiC transformation was achieved by such techniques in reasonably short time intervals. The kinetics of the phase transformation was shown to depend on the composition of sintering additives, the use of less refractory RE dopants accelerating the process. Thus, the possibility of in-situ platelet reinforced SiC ceramics was shown.

Further research aimed at the optimization of both composition and processing of the materials under development is necessary.

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