JOURNAL OF

Ceramic Processing Research

# SiC Nano-materials produced through liquid phase sintering: processing and properties

## D. Sciti\*, J. Vicens<sup>a</sup>, N. Herlin<sup>b</sup>, J. Grabis<sup>c</sup> and A. Bellosi

CNR-ISTEC, Institute of Science and Technology for Ceramics, I-48018 Faenza <sup>a</sup>LERMAT-ISMRA, Laboratoire d'Etudes et de le Recherche sur le Matèriaux, 6 Bd. Maréchal Juin, F-14050 Caen <sup>b</sup>CEA-SACLAY, Laboratoire Francis Perrin (CEA-CNRS URA 2453), Service des Photons, Atomes et Molécules, DSM-CEA Saclay, F-91191 Gif/Yvette cedex <sup>c</sup>Riga Technical University, Institute of Inorganic Chemistry, Miera 34, Salaspils Lv-2169 LATVIA

SiC nano-powders, produced via laser and plasma synthesis were processed to obtain fully dense and nano-sized materials, with a grain size ranging from 80 to 150 nm. Densification was achieved through hot pressing, adding alumina and yttria as sintering aids, as used in conventional liquid phase sintered SiC from commercial powders. Different processing conditions were tested and compared to optimize the process. The densification behaviour was studied. The microstructure was analyzed by scanning and transmission electron microscopy. Vickers hardness, fracture toughness, Young modulus and bending strength were measured on dense samples. Mechanical tests show that, the properties of these nano-materials are comparable to those of sub-micrometre grain-sized SiC materials.

Key words: Nanoceramics, Silicon carbide, Densification behaviour, Microstructure, Mechanical properties.

# Introduction

Recently, the class of nano-phase ceramic materials has attracted a lot of scientific interest as an increase of many relevant properties is expected [1-8].

However, while there are plenty of studies on oxide nano-ceramics and nano-composites, little literature can be found concerning non-oxide nano-ceramics such as silicon carbide, which is considered to be one of the most important structural materials. One possible reason for this lack is that, starting from nano-powders, it is difficult to sinter SiC to full density while maintaining mean grain size dimensions below 100 nm [1-4]. Significant grain growth in fact occurs during sintering such that pressure-assisted sintering systems have to be used in order to overcome microstructural coarsening. By contrast, by pressureless sintering high densities without excessive grain growth were rarely achieved [2, 3].

The aim of this study is to test the liquid phase sintering technique conventionally used for micrometric SiC powders, for the densification of non-commercial nanopowders'. The goal is to obtain dense materials with limited grain growth in respect to the starting powders grain size. It is well known that the final properties of nano- or ultrafine -non-oxide-ceramics are strongly affected by the characteristics of the raw powders (particle morphology, grain size distribution, presence of agglomerates, oxygen content, etc.) and the way they are produced and processed [9]. For this reason, synthesis techniques and features of the nano-powders are described. Different processing procedures are tested and compared.

Once dense materials with fine microstructure are obtained, some relevant mechanical properties are measured and briefly discussed.

#### **Experimental**

#### **Powder Synthesis**

The starting nano-powders, produced by laser synthesis and plasma synthesis, are labelled SiC1, and SiC2 respectively (Table 1).

The laser synthesis method (CEA-Saclay, France) is based on the absorption of laser radiation by a component of a reactive mixture [15]. Energy is transferred by collisions, dissociation occurs and nano-powders are produced in a flame by nucleation and growth. This process is inherently very clean because homogeneous nucleation occurs in a well-defined reaction zone without interaction with the chamber walls. The physical and chemical properties of the particles can be controlled by changing the molecular precursors and the synthesis parameters (laser power, pressure, etc.). The size of the particles can be controlled by changing the residence time in the laser beam [16, 17]. Details of the experimental apparatus are reported elsewhere [16].

<sup>\*</sup>Corresponding author:

Tel : +39-0546-699748 Fax: +39-0546-46381

E-mail: dile@istec.cnr.it

	Specific surface area m <sup>2</sup> /g	d <sub>e</sub> nm	d <sub>cryst</sub> nm	Grain size nm	SiO <sub>2</sub> wt %	Crystalline phases
SiC1	60	30	15	30	~7	β-SiC, Traces of Si, C, SiO
SiC2	36	62	42	10-20 200-400	3-5	$\beta\mbox{-SiC},$ traces of $\alpha\mbox{-SiC},$ 4H and 6H, Si

Table 1. Characteristics of the starting powders.  $d_e$ : average particle size calculated from the specific surface area assuming spherical particles.  $d_{cryst}$ : crystallite size

In the present study, for the production of SiC1, the experimental parameters were chosen in order to obtain grain diameters in the range 25-35 nm. The reactive gas flow was composed of a mixture of  $C_2H_2$  (62 cm<sup>3</sup>/minute) and SiH<sub>4</sub> (120 cm<sup>3</sup>/minute), which results in a powder with a slight excess of carbon.

The plasma technique (PCT, Latvia) allows the production of powders through vaporization of coarse, commercially-available silicon powders (Si  $\geq$  99.6%) and subsequent condensation of products into a radio frequency, inductively-coupled nitrogen plasma (ICP). The formation of SiC is obtained by injection of ammonia and hydrocarbons in to the region of silicon vapours. The particle size, chemical and phase composition, crystallinity of the powder are controlled mainly by: the carbide content, the injection of quenching gas and the gas flow rate during plasma synthesis.

For the production of SiC2, a raw powder of Si with a particle size of 10-40  $\mu$ m was introduced into the plasma tail by the carrier gas (N<sub>2</sub>). The flow rate of the plasma-forming gas was 8 m<sup>3</sup>/h<sup>-1</sup> and the feed rate of the raw powder was 0.9 kg h<sup>-1</sup>. Details of the processing and experimental apparatus are described in Ref. 17.

The powders phase compositions were determined by conventional X-ray powder diffraction analysis. The specific surface area was determined by the BET method.

The crystallite sizes  $d_{cryst.}$  were calculated from the XRD data by using the Scherrer formula. The average particle size  $d_e$  was calculated from the specific surface area assuming that particles have a spherical form. The particles' morphology was determined by TEM analysis.

### **Material Production**

 $Al_2O_3$  (Baikalox CR30) and  $Y_2O_3$  (HC-Starck) were selected as sintering additives since they are the most widely used combination of oxides for liquid phase sintering of SiC [11-14].

The following compositions were prepared. From SiC1:

SiC+7 wt % Al<sub>2</sub>O<sub>3</sub>+3 wt %  $Y_2O_3$ , labelled S73 From SiC2:

SiC+6 wt % Al<sub>2</sub>O<sub>3</sub>+4 wt % Y<sub>2</sub>O<sub>3</sub>, labelled S64

SiC+2.7 wt % Al<sub>2</sub>O<sub>3</sub>+3.5 wt % Y<sub>2</sub>O<sub>3</sub>, labelled S23.

The compositions of S64 and S23 were chosen on the basis of previous work on liquid phase sintered SiC from commercial submicrometre powders [12]. In the



Fig. 1. Powder processing flow chart: ruote A and B.

the isolicinial stage. up/ut <sub>0.85</sub> . defisition fate at feative defisity 0.05. p <sub>1</sub> . that feative defisity)											
Material	Starting powder	route	Amount of sintering aids	Sintering cycle	Densification parameters						
					$T_0$	$ ho_0$	$T_1$	$\rho_{\text{isoth}}$	$d\rho/dt_{0.85}*10^{-4}$	ρ	f
			wt %	°C/min	°C	%	°C	%	$g/cm^3 s^{-1}$	g/cm <sup>3</sup>	%
S73	SiC1	А	10	1860/16	1410	38.9	1700	87.5	28	3.20	100
<b>S</b> 73	SiC1	В	10	1820/20	1060	34.5	1600	84.3	20	3.20	100
S64	SiC2	В	10	1870/20	1510	47.4	1750	82.2	22	3.21	98.9
S23	SiC2	В	6.2	1880/25	1580	47.4	1800	63.1	15	2.91	89.5

**Table 2.** Characteristics of the nano-materials, sintering cycles and densification parameters. (T<sub>0</sub>: Temperature at which densification starts.  $\rho_0$ : relative density at T<sub>0</sub>. T<sub>1</sub>: Temperature at which dissolution/reprecipitation stage starts.  $\rho_{isoth}$ : relative density at the beginning of the isothermal stage.  $d\rho/dt_{0.85}$ : densification rate at relative density 0.85.  $\rho_f$ : final relative density)

case of sample S73, the alumina/yttria ratio was modified because the specific surface area of SiC1 is very high. A higher content of alumina (which has a quite high specific surface area, about  $30 \text{ m}^2/\text{g}$ ) was considered to be more effective for a homogeneous distribution of the sintering aids (and thus liquid phase) around SiC particles.

Two processing routes were tested, as explained in the diagram of Fig. 1. The main differences are the following:

– In route A, SiC and sintering aids were separately dispersed in ethyl alcohol using ultrasonic pulses associated with magnetic stirring, in order to achieve a good dispersion in the liquid medium. The typical time was 30 minutes. Then, the two batches were mixed together and further homogenized for 1 h with ultrasonic dispersion and magnetic stirring. Prior to sintering, uniaxial pressing at 200-400 kg/cm<sup>2</sup> was applied to improve the green density.

– In route B, the powders were dispersed in hexane and organic additives (trioleine and phosphate ester: EHPHOS PS21-A) and then ball milled. Before hot pressing, uniaxial pressing was performed at a lower pressure compared to route A (50 kg/cm<sup>2</sup>).

Water-based systems were not considered, in order to avoid further oxidation of SiC nano-powders. Previous studies carried out on SiC1 showed in fact that after 12 hours in water, the oxygen content strongly increases.

Hot pressing treatment was carried out in a vacuum  $(10^{-3} \text{ torr})$ , with an applied pressure of 30 MPa, at different conditions of temperature and time as indicated in Table 2.

The microstructure of selected samples was analyzed by scanning electron microscopy (SEM) on fracture surface and polished and plasma etched surfaces. Phase analysis was determined by X-ray diffraction. Transmission electron microscopy (TEM) and energy dispersive analysis (EDS) was also carried out. The mean grain size was determined through the equivalent circle method on SEM micrographs of polished and plasma etched surfaces.

On selected samples, the following mechanical properties were measured: Vickers hardness (HV) obtained using a load of 1.0 kg, fracture toughness ( $K_{Ic}$ ) by Direct Crack Measurement (DCM) method with a load of 10 kg, using the formula proposed by Anstis et al. [19], Young's modulus (*E*) by the resonance frequency method on samples  $28 \times 8 \times 0.8$  mm<sup>3</sup>, and strength ( $\sigma$ ) up to 1300°C by 4-pt bend method on  $2 \times 2.5 \times 25$  mm<sup>3</sup> (inner span 10 mm, outer span 20 mm). 5 samples were tested for each temperature.

# **Results and Discussion**

## Characteristics of the starting SiC powders

The characteristics of the starting powders are given in Table 1, TEM micrographs are shown in Fig. 2. Both powders are highly crystallized and have a low degree of agglomeration as confirmed by the comparison between mean grain size and crystallite size. However, SiC2 contains a small amount of  $Si_3N_4$  with a low degree of crystallinity, as revealed by a broad peak in XRD diffraction patterns. Chemical analysis confirmed the presence of a small amount of N (~5 wt %).



**Fig. 2.** TEM images of the starting SiC powders. (a) *SiC1*, 30 nm, (b) HRTEM of *SiC1* showing the silica layer, (c) TEM of *SiC2* showing the presence of 100 nm SiC particles, 10 nm SiNOC particles and graphite lamellae.

Properties	S64	S73 route A		
mgs (µm)	$139 \pm 7$	$78\pm 8$		
HV (GPa)	$21.9\pm0.3$	$21.9\pm0.5$		
$K_{Ic}$ (MPa·m <sup>1/2</sup> )	$3.0 \pm 0.2$	$2.6 \pm 0.2$		
E (GPa)	334	376		

The particles morphology is quite different: in SiC1, particles are spherical in shape and have a narrow size distribution, the mean grain size is 30 nm, Fig. 2a. By contrast SiC2 has a bimodal size distribution, with the coarsest particles in the range 200-400 nm and finest particles in the range 10-20 nm, Fig. 2c. Some graphite particles and very small particles (10 nm) containing a Si-N-O phase were also detected.

In both cases, the high reactivity of particles surface leads to a considerable oxygen uptake, i.e. ~7 wt % and 3-5 wt % for SiC1 and SiC2 respectively, Table 1. In Fig. 2b a HRTEM of a 20 nm particle of SiC1 is shown, revealing a 1 nm thick silica layer on the surface.

#### **Densification behaviour**

Nearly full dense materials were obtained for compositions S64 and S73, with relative densities of about 99% and 100%, respectively. Sample S23 reached a final relative density of 89.5%.

Some parameters indicating the densification behaviour (Table 2) and the sintering curves (Fig. 3) confirm that:

i) The starting relative density was mainly affected by the grain size distribution and specific surface area of the powders. Thus, samples prepared from powder SiC2, namely S64 and S23, showed green densities of 47%, while in the case of S73 the starting density was only 38% after processing route A and 35% after route B. The higher value after route A (no organic



**Fig. 3.** Densification curves showing the increase of relative density in function of: temperature during heating up and soaking time during the isothermal stage.

additives), demonstrates that organic additives were not so effective in improving the particle packing.

ii) The shrinkage behaviour revealed that a total amount of 6.2 wt % of sintering additives is not enough for densification of nano-SiC powders. In the case of sample S23, all densification stages (particle rearrangement, dissolution/diffusion/reprecipitation) are highly retarded in respect with samples containing 10 wt % of sintering aids, due to the low amount of liquid available between SiC particles. The change of slope in the densification curves, which gives an indication of the starting of the dissolution/reprecipitation stage, occurred at a higher temperature in sample S23 (Table 2) compared to sample S64. The densification rate calculated in correspondence of relative density 0.85% is very low.

iii) The sintering rate in material S73 produced from SiC1 is faster, compared to S64. This is related to the viscosity of the liquid phase. In S73, the different  $Al_2O_3/Y_2O_3$  ratio and the higher amount of silica present in the starting *SiC1* compared to *SiC2* must have favoured the formation of a less viscous liquid. This is also confirmed by the estimated temperature for liquid phase formation (Table 2) that is about 50°C lower for mixture S73, compared to S64. By contrast, the presence of some nitrogen in SiC2 must have further contributed to an increase in the viscosity of the liquid phase in samples S64 (and S23).

## Microstructure

Crystalline phases in the dense materials were  $\beta$ -SiC and traces of  $\alpha$ -SiC, and C, as in the starting powders. YAG phase (3Y<sub>2</sub>O<sub>3</sub>·5Al<sub>2</sub>O<sub>3</sub>), which usually forms in SiC materials with alumina and yttria as sintering aids [12] was hardly detected and its amount was estimated to be less than ~1% vol. Most probably, Y<sub>2</sub>O<sub>3</sub> formed amorphous silicatic phases, in addition to the above described crystalline ones.

One interesting feature is that in S73 samples (processed with either route A or B) the high content of silica favoured the formation of mullite rather than YAG. The content of this phase (8-9 vol %) was estimated from the comparison of the relative intensities of diffraction peaks of SiC and mullite in XRD spectra, taking into account the scattering powers of both phases (3.2 for cubic SiC and 0.84 for mullite).

In S64, by contrast, no mullite was detected, despite the large amount of  $SiO_2$  present. Possible explanations for this different behaviour are related to the characteristics of the liquid phase, as already pointed out. The higher content of yttria in mixture S64 and the presence of N in the starting SiC2 powder increased the viscosity of the liquid during sintering of S64 and hindered its devitrification during cooling down from the sintering temperature, according to previous studies concerning the effect of nitrogen on the devitrification of oxide glasses [20].



**Fig. 4.** SEM images of plasma etched microstructures: (a) S73 route A, (b) S73 route B, (c) S64.

The polished surfaces analized by SEM reveal that sample S64 contains a small amount of porosity, S73 route B is dense but it presents some macro- crack- like defects probably due a not optimized removal of the organic binders, while S73 by route A (i.e. processed without organic additives) is fully dense.

After plasma etching, the microstructures are delineated by grain boundary phases. Fig. 4a-c compares the materials S73 (from routes A and B) and S64. SiC grains are mainly separated by a thin grain boundary film, which is the residue of the liquid phase sintering medium. In S64, etched surfaces revealed a core/rim structure in SiC grains, typical of liquid phase sintered SiC [21]. In the core region only Si and C are present. In the outer rim, traces of Al and O were observed. In S73 materials, the core rim structure is less evident.

This difference is related to the grain growth mecha-

nisms during sintering which, in turn, depend on the characteristics of the liquid phase. In fact, the less refractory liquid phase in mixture S73 must have favoured an enhanced degree of dissolution of the original SiC particles (only 30 nm in size) and speeded up the diffusion processes. As a consequence, during sintering and grain growth, the major part of grains grew as SiC containing Al and O, resulting in an homogeneous chemical composition (Fig. 4a and b). The presence of faceted grains, (i.e. atomically smoothed interfaces), confirms that diffusion processes in these materials were faster and the rate-controlling mechanism is the reaction at the interface [14].

On the other hand, in S64, only the finer portion of the SiC particles underwent dissolution. Reprecipitation of SiC from the liquid phase (containing also Al and O) occurred onto the undissolved portion of the larger original particles, resulting in the core-rim structure. The rounded morphology of grains confirms that diffusion is the rate-controlling mechanism during densification.

The mean grain size in S64 is 140 nm and grain size distribution ranges from 50 to 450 nm.

Considerable difference was observed in materials S73, routes A and B.

S73 processed according to route B, underwent coarsening during sintering. The mean grain size increased from 30 nm in the starting powder to 150 nm after hot pressing, with a grain size ranging from 50 to 500 nm. By contrast, S73 processed according to route A, exhibited a mean grain size of 78 nm and limited grain growth (grain size distribution ranged from 35 to 250 nm). Since sintering conditions were roughly the same, (Table 2), it is likely that, for mixture S73 processed according to route B, grain coarsening occurred in the early stages of densification, due to a not optimized powder processing in the green state. The results obtained confirm that route A was more efficient for the production of dense materials starting from a powder with a uniform particle size of 30 nm.

TEM analysis performed in the pockets of intergranular



**Fig. 5.** (a) Bright field image and diffraction pattern (insert) of a portion of intergranular phase containing crystalline mullite in S73. (b) Intergranular phase in S73.



**Fig. 6.** (a) Amorphous intergranular phase in S64, as revealed by the diffraction pattern (insert). (b) HRTEM of an interface between the glass and a SiC crystal viewed along the [110] direction in S64.

phase confirmed the findings of X-ray diffraction analysis. In S73 materials, crystalline pockets of mullite were detected, as shown in the example in Fig. 5a. Glassy Ysilicate phases of variable composition were also found confirming the presence of amorphous phase typical of these systems (Fig. 5b). The mean composition of the glassy phase, estimated through EDS analysis is: O 62.4 at %, Al 6.1 at %, Si 25.3 at % and Y 6.1 at %.

By contrast, in sample S64, the intergranular phase is almost completely glassy (Fig. 6a). The mean composition in this case is slightly different, consistent with the different starting compositions and formation of crystalline/amorphous phases: O 64.2 at %, Al 9.6 at %, Si 16.9 at %, Y 9.2 at %. An example of an interface between the glass and a SiC crystal viewed along the [110] direction is shown in Fig. 6b.

#### **Mechanical properties**

Mechanical properties were tested on S73 route A, (m.g.s. 80 nm) and S64 (m.g.s. 140 nm). Hardness values (Table 3) are quite high, due to the small mean grain size. No difference was observed in the samples tested, despite diverse mean grain sizes. Moreover, the comparison with SiC materials with a mean grain size around 500 nm produced from commercial powders and described in a previous work [12], indicates that there is no increase in hardness with a decrease in the mean grain size, in contrast with the findings of other authors [1, 2]. The reason for this behaviour is under investigation.

The values of fracture toughness (Table 3) suggested a small difference between the materials tested, namely S73 with the finest grain size has a lower toughness compared to S64, which is related to the microstructural features. SEM analysis of the crack path after indentation revealed that the path is almost completely intergranular in S73, while in S64 toughening mechanisms such as transgranular fracture of big grains and some crack bridging phenomena were observed (Fig. 7a, b). The microstructural characteristics of SiC grains



Fig. 7. Final portion of the crack path in: (a) S73 route A, (b) S64.

and intergranular phase in S64 must have provided more effective mechanisms of crack energy dissipation. The behaviour observed in the present work is in agreement with the findings of other studies [2, 8] on similar SiC materials, where toughness decreases with decreasing the mean grain size is explained by a reduced efficiency of crack deflection and crack bridging mechanisms.

Concerning Young's modulus values (Table 3), the better performance of sample S73 is probably related to the large amount of crystalline mullite at the grain boundaries, with a consequent reduction of the residual glassy phase. Amorphous silicate-like phases possess very low values of E, so that even small amounts strongly affect the elastic modulus [22]. In sample S64, in addition to the glassy phase, some porosity is present (1 vol %), which decreases the modulus according to an exponential law [23].

Strength values as a function of the temperature are reported in the plot of Fig. 8 and are compared to values obtained in a previous study for liquid phase



Fig. 8. Strength values vs temperature for S73 route A, S64 and a SiC material from Ref. 12.



Fig. 9. An example of processing defect present on fracture surface of sample S64.

sintered SiC produced from a commercial powder [12]. Sintering additives and the sintering cycle of the reference material are very close to those of the nanomaterials. These results clearly indicate that, despite the different mean grain size, strength values are very close in the range investigated, (except S73 strength at 1300°), i.e. the nano-SiC performance is not better than that of fine-grained SiC produced from a commercial powder.

On the fracture surfaces of the nano-materials, obtained after strength tests, big defects were detected, probably acting as critical flaws. These defects (an example is shown in Fig. 9), are mainly processing flaws, due to inhomogeneous compaction of nano-powders in the green state. The results obtained confirm that in order to benefit from the refined microstructure, the defect size must be in the same size range as the grain size, which requires a further improvement in the processing techniques, particularly concerning powder treatment and forming.

Good strength retention (up to about 600 MPa) is observed at 1000°C for both nano-materials. At 1300 °C the strength considerably decreases, mainly due to softening of the intergranular glassy phases. The relatively good performance of S73 is due to the characteristics of the grain boundary phase and in particular to the smaller amount of glassy phase and the massive crystallization to mullite.

#### Conclusions

Liquid phase sintering was found to be an efficient route for densification of SiC nano-powders allowing one to obtain fully dense materials with limited coarsening. Thus, starting from powders with a mean grain size of 30 nm, dense materials with a mean grain size lower than 100 nm were obtained.

Powder processing before sintering was confirmed to be a crucial step for the characteristics of the final materials. Organic additives were proved to be unnecessary to improve the packing behaviour and, in some cases, the final materials had a worse microstructure than those processed without binders.

The amount of sintering aids and their ratio significantly affected the densification behaviour and characteristics of the intergranular phase. 10 wt % of additives was found to be the appropriate amount for achieving dense materials.

The mechanical properties of the present materials in terms of strength and toughness are very close to the values found for submicrometre grain size materials. Even if dense materials without excessive grain growth are obtained via a liquid phase, a further decrease of grain size is not expected to be beneficial for strength and toughness, unless the limits deriving from processing (defects and glassy phase) are overcome through innovative powder treatment procedures.

### Aknowledgements

This work was carried out in the frame of the EU project BETCT97-0592 – Thematic Network Nanomat.

The authors wish to thank S. Guicciardi and C. Melandri for testing mechanical properties.

#### References

- R. Vaßen and D. Stöver, Mat. Sci. Eng. A 301 (2001) 59-68.
- R. Vaßen and D. Stöver, J. Am. Ceram. Soc. 82[11] (1999) 2585-93.
- R. Vaßen, A. Kaiser, J. Förster, H.P. Buchkremer, and D. Stöver, J. Mat. Sci. 31 (1996) 3623-37.
- R. Vaßen and D. Stöver, J. Mat. Proc. Tech. 92-93 (1999) 77-84.
- M. Mitomo, Y.-W. Kim, and H. Hirotsuru, J. Mat. Res. Vol. 11, No. 7 (1996) 1601-4.
- Y.-W. Kim, M. Mitomo, and H. Hirotsuru, J. Am. Ceram. Soc. 78[11] (1995) 3145-48.
- G.-Dong Zhan, M. Mitomo and Y.-W. Kim, J. Am. Ceram. Soc. 82 [10] (1999) 2924-26.
- Y.-W. Kim and M. Mitomo, J. Am. Ceram. Soc. 82[10] (1999) 2731-36.
- 9. R. A. Andrievski, J. Mat. Sci. 29 (1994) 614-31.
- K. Motzfeldt, Proceedings of the International Conference on Engineering Ceramics 92, Smolenice Castle, Oct. 1992, M. Haviar Ed., Reproprint, Bratislava, 1993, p. 7
- M.A. Mulla and V.D. Krstic, Am. Ceram. Soc. Bull. 70 (1991) 439-443.
- 12. D. Sciti and A. Bellosi, J. Mat. Sci. 35 (2000) 3849-55.
- 13. N.P. Padture, J. Am. Ceram. Soc. 77[2] (1994) 519-523.
- H. Ye, V.V. Pujar, and N.P. Padture, Acta Mater. 47[2] (1999) 481-487.
- W.R. Cannon, S.C. Danforth, J.H. Flint, J.S. Haggerty, and R.M. Marra, J. Am. Ceram. Soc. 65[7] (1982) 324-330.
- M. Cauchetier, O. Croix, and M. Luce, Adv. Ceram. Mater. 3[6] (1998) 548-552.
- P. Tougne, H. Hommel, A.P. Legrand, N. Herlin, M. Luce, and M. Cauchetier, Diamond and related materials 2 (1993) 486.
- J. Grabis, Nanosize Nitride-Based Composite Powders produced by ICP Technique. In: M. Rühle, H. Gleiter

(Ed.), Interface Controlled Materials, EUROMAT 99, vol 9, Wiley-YCH, 2000, p. 267.

- G.R. Anstis, P. Chantikul, B.R. Lawn, and D.B. Marshall, J. Am. Ceram. Soc. 64 (1981) 533-38.
   S. Hampshire, R.A.L. Drew, and K.H. Jack, Physics and
- S. Hampshire, R.A.L. Drew, and K.H. Jack, Physics and chemistry of glasses 26[5] (1985) 182-186.
- 21. L.S. Sigl and H.-J. Kleebe, J. Am. Ceram. Soc. 76[3] (1993) 773-776.
- 22. A. Kelly and N.M. Macmillan, Strong Solids, Clavendom Press, Oxford, 1986, p. 170
- 23. P. Boch and J.C. Glandus, Interceram 3 (1983) 33-40.