# Toughening of silicon carbide-based materials

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**ABSTRACT.** Silicon carbide sintered samples with the same density and different microstructure were obtained through different sintering procedures. The "two-step sintering" method was useful to achieve SiC based-materials characterized by finer microstructure than those obtained with the conventional sintering process. This was demonstrated with both solid-state sintering (with boron and carbon as sintering additives) and liquid-phase sintering (with alumina and yttria as sintering additives). The finer microstructure enhanced the fracture toughness of the materials. The toughening mechanism was different: change in the fracture mode from transgranular to intergranular in the solid-state sintered material and improvement of the crack deflection mechanism in the liquid-phase sintered samples. The highest value of fracture toughness (7 MPa $m^{1/2}$) was reached with a very fine powder produced using waste tires as carbon source and quartz.

**SOMMARIO.** Campioni sinterizzati a base di carburo di silicio aventi pari densità e differente microstruttura sono stati ottenuti variando il ciclo termico di sinterizzazione. Con il metodo "two-step sintering" è stato possibile ottenere materiali aventi una microstruttura più fine rispetto a quella ottenuta con la metodologia classica. Tale affinamento della microstruttura è stato ottenuto sia con la sinterizzazione in fase solida (boro e carbonio come additivi) che con quella in fase liquida (allumina e ittria come additivi). Nei materiali aventi microstruttura più fine è stato riscontrato una aumento della tenacità. Il meccanismo di tenacizzazione è dovuta alla variazione della modalità di frattura, da transgranulare ad intergranulare, nel caso della la sinterizzazione in fase solida ed al meccanismo della crack-deflaction nel caso della sinterizzazione in fase liquida. Inoltre, il valore maggiore di tenacità (7 MPa $m^{1/2}$) è stato ottenuto con una polvere sub-micronica ottenuta utilizzando pneumatici fuori uso come fonte di carbonio e quarzo.

**KEYWORDS.** SiC; Sintering; Fracture toughness; Microstructure.

## INTRODUCTION

Silicon carbide (SiC) is one of the most interesting ceramic material due to its properties like high hardness, low bulk density, high oxidation resistance which make it suitable for a wide range of industrial applications. Sintering of silicon carbide was first performed by Prochazka [1] using boron and carbon through a solid state mechanism (SSiC). This process is normally performed at 2150-2200°C and the densification is enhanced by the reduction of the superficial energy of the grains promoted by boron [2] and the reaction between carbon and the silica film [2-4] located on the SiC particle surface.

SSiC obtained with boron and carbon, which represents the additive system most widely used, normally showed an exaggerated grain growth due to the high sintering temperature needed to reach high sintered density. The coarse microstructure affects the mechanical properties and Snead et al. reported that the highest value of fracture toughness (4 MPa $m^{1/2}$) could be achieved with an average grain size in the range 1-5 μm.

Higher fracture toughness can be reached with the liquid-phase sintering process (LPSiC). Omori et al. developed this process using alumina and yttria as sintering additives. LPSiC is characterized by a finer microstructure than SSiC and higher values of fracture toughness (5-6 MPa $m^{1/2}$) with the toughening mechanism based on the crack deflection.

Several sintering methods have been already tested with SSiC and LPSiC in order to reduce the grain size and to improve the mechanical properties by applying pressure during sintering: hot pressing, hot isostatic pressing and spark plasma sintering [6-10]. In any case, these methods could show limitations in the production costs, product size and shape complexity which can limit the industrial applicability. Two-step pressureless sintering process could be used to overcome the limitations of the pressure-assisted sintering processes in order to obtain toughened SSiC and LPSiC ceramics with fine microstructure.

The two-step sintering method (TSS) proposed by Chen et al. [11] is based on the heating of the sample to a high temperature $T_1$ followed by a rapid cooling down to a lower temperature ($T_2$) and then held at $T_2$ for a long period. The main characteristic of this method is that the grain boundary diffusion of the sample is maintained but the grain boundary migration can be avoided. Therefore, the grain growth associated to the final step of the sintering process is completely suppressed. Several studies focused on this method are available. Chen et al. [11] firstly applied this method in $Y_2O_3$ ceramics, whereas different authors were able to obtain fully densified $BaTiO_3$ [12], ZnO [13-14], $ZrO_2$ [15-18], $Al_2O_3$-$ZrO_2$ [19], $Al_2O_3$ [20-21] and SiC [22] ceramics by using the two-step sintering method. In particular, Lee et al. [22] obtained nanostructured SiC ceramics through a two-step liquid phase sintering process based on hot pressing with alumina, yttria and calcia as sintering aids, but they did not evaluate the effects of the finer microstructure on the mechanical properties. The toughening effects of the TSS method on the SSiC and LPSiC were the scopes of our study. These activities were performed in the frame of the TyGRe project aimed to redirect the waste tire gasification process towards the material recycling, by coupling a second thermal process, dedicated to the synthesis of silicon carbide.

Hence, TSS method was tested with SSiC method using commercial powder, whereas TyGReSiC powder was used to performed the test with LPSiC.

## EXPERIMENTAL PROCEDURE

Commercially available α-SiC (Densitec 15C, Saint Gobain, France) and TyGRe SiC powder (β phase) were used as starting powders. Densitec 15C is a ready-to-press powder with the appropriate amount of organic binder and sintering aids (boron and carbon), whereas TyGReSiC was produced by carbothermal reduction using char and quartz as raw materials and it was mixed with the sintering additives (alumina and yttria) using ethanol as solvent. The main physical and chemical characteristics of the powders are reported in Table 1. The dried powders were used to manufacture discs with diameter 10 mm and thickness 3 mm by uniaxial pressing at 60 MPa followed by cold isostatic pressing at 200 MPa. Sintering was performed in a graphite resistance high temperature furnace in flowing argon at 1 atm. Temperatures of the conventional sintering (CS) and TSS were different on the basis of the sintering mechanism (Tab. 2).

| Powder | Free C [%wt] | O [%wt] | SSA [$m^2/g$] | Al [ppm] |
|---|---|---|---|---|
| Densitec 15C | 0.2 | 0.85 | 15 | 250 |
| TyGReSiC | max 0.5 | 1-2 | n.d. | 1410 |

Table 1: Physical and chemical properties of the SiC powders

| Sintering | Powder | Conventional sintering (CS) | Two-step sintering (TSS) |
|---|---|---|---|
| SSiC | Densitec 15C | 2130°C | 2030°C ($T_1$), 1980°C ($T_2$) |
| LPSiC | TyGReSiC | 1925°C | 1850°C ($T_1$), 1800°C ($T_2$) |

Table 2: Sintering parameters.

Density of the samples was determined by the Archimedes method (ASTM C373). Polished and chemically etched (Murakami's etching) samples were observed using scanning electron microscopy (SEM- LEO 438-VP) and inverted metallurgical microscope (Reichert-Jung, MeF3).
The fracture toughness was calculated by Vickers indentation method on the basis of the equation proposed by Niihara et al. [23]:

$$K_{IC} = 0.203 H a^{1/2} (c / a)^{-3/2} \tag{1}$$

where $H$ is the hardness, $a$ is the impression radius and $c$ is the crack length. Ten indentations were performed with a load of 98 N.

## RESULTS AND DISCUSSION

### *Density and microstructure*

Images of the microstructure of SSiC and LPSiC samples are shown in Figure 1 and 2, respectively. Samples obtained by TSS showed finer microstructure regardless of the sintering mechanism. Microstructure of the TSS-SSiC sample (Figure 1b) is mainly composed of equiaxed grains with some elongated grains with length of 10 μm. TSS-LPSiC microstructure showed very small grains if compared with that of CS-LPSiC. (Figure 2).
The micrographs reported in Figure 2 show an high level of porosity due to the chemical etching that leaches the grain boundary phase. The real lower content of residual porosity in the LPSiC samples can be evaluated from the images reported in Figure 3. Sintered densities of the samples are reported in Table 3. TSS-SSiC and CS-SSiC- showed very similar sintered density, whereas LPSiC sintered density is 98.0% T.D with both processes. These results confirmed that the second step of TSS method performed at lower temperature than CS leads to similar final densification with very limited grain growth.

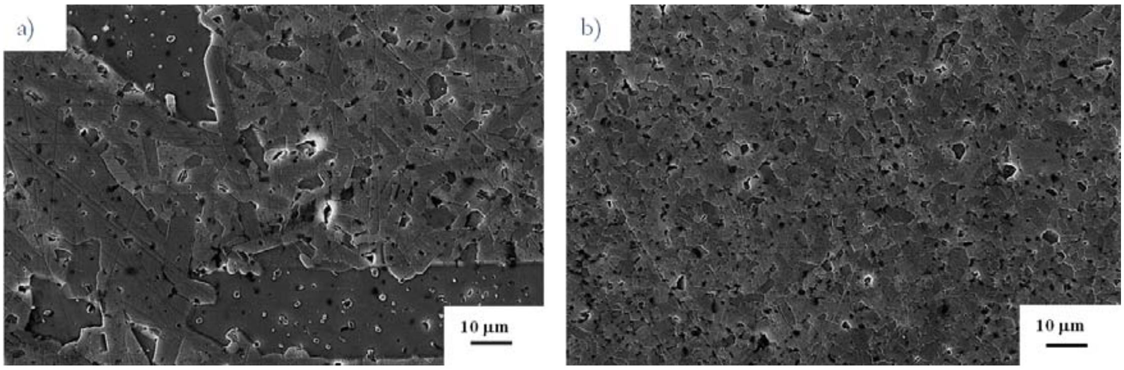

Figure 1: Microstructure of SSiC obtained by a) conventional sintering and b) two-step sintering.

| Powder | Additives | Sintering | Density (%T.D.) |
|---|---|---|---|
| Densitec 15C | B, C | CS-SSiC | 98.6 |
| | | TSS-SSiC | 98.5 |
| TyGReSiC | $Al_2O_3$, $Y_2O_3$ | CS-LPSiC | 98.0 |
| | | TSS-LPSiC | 98.0 |

Table 3: Sintered density obtained with different sintering mechanisms (solid and liquid phase) and processes (conventional and two-step sintering).

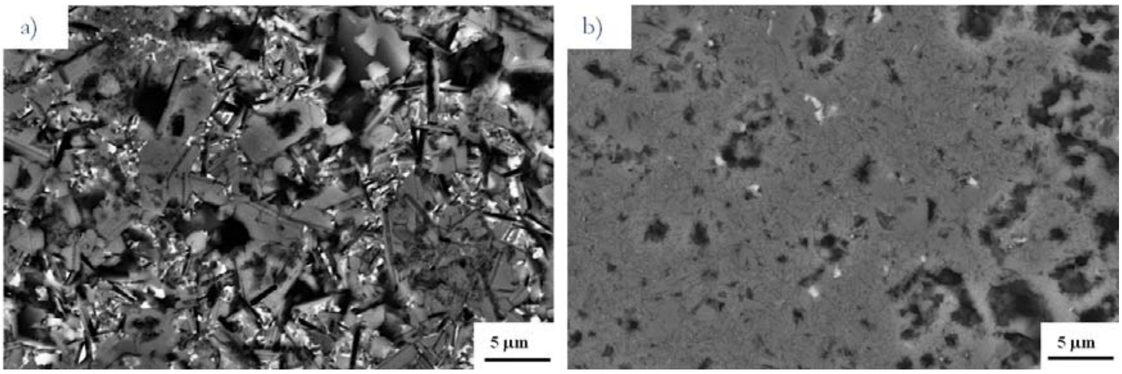

Figure 2: Microstructure of LPSiC obtained by a) conventional sintering and b) two-step sintering. The high level of porosity is due to the leaching of the grain boundary phase.

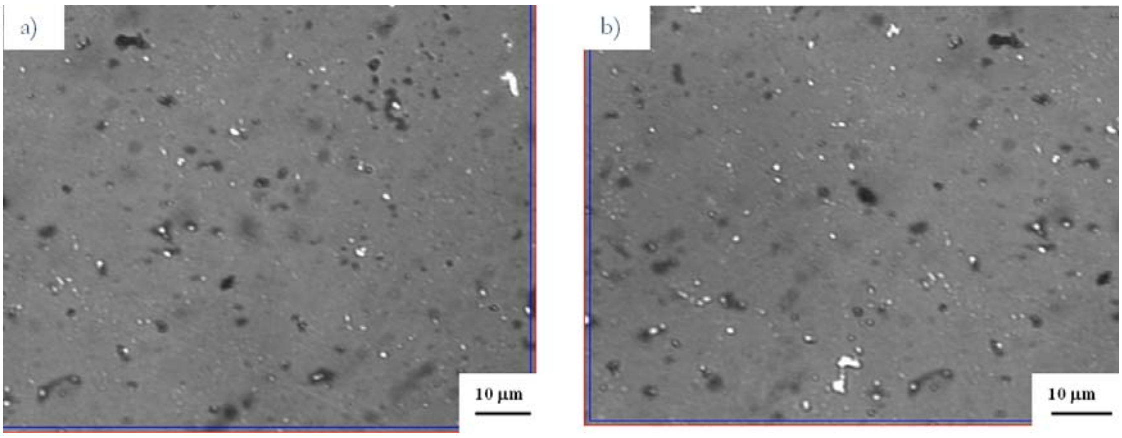

Figure 3: Images of the polished surface of LPSiC obtained by a) conventional sintering and b) two-step sintering.

### *Fracture toughness*

Fracture toughness ($K_{IC}$) values are reported in Table 4. TSS samples always showed higher values of $K_{IC}$, with a more relevant difference in the TyGReSiC.

| Powder | Additives | Sintering | Toughness (MPa m$^{1/2}$) |
|---|---|---|---|
| Densitec 15C | B, C | CS-SSiC | 3.0±0.1 |
| | | TSS-SSiC | 3.4±0.1 |
| TyGRe SiC | $Al_2O_3$, $Y_2O_3$ | CS-LPSiC | 5.6±0.2 |
| | | TSS-LPSiC | 6.6±0.3 |

Table 4: Fracture toughness obtained with different sintering mechanisms (solid and liquid phase) and processes (conventional and two-step sintering).

The toughening mechanisms are different. In the case of SSiC, conventional sintered sample showed typical transgranular fracture mode without any toughening mechanism due to the coarse microstructure (Figure 4a and 5a). On the contrary, the finer microstructure of TSS-SSiC is responsible for the mixed transgranular-intergranular fracture mode with grain bridging and crack deflection toughening mechanism (Figure 4b and 5b) [24].

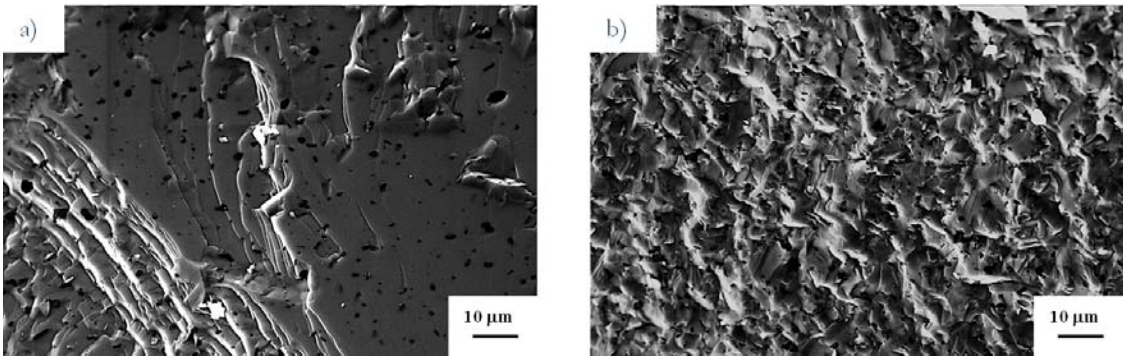

Figure 4: Images of the fracture surfaces of SSiC obtained by a) conventional sintering and b) two-step sintering.

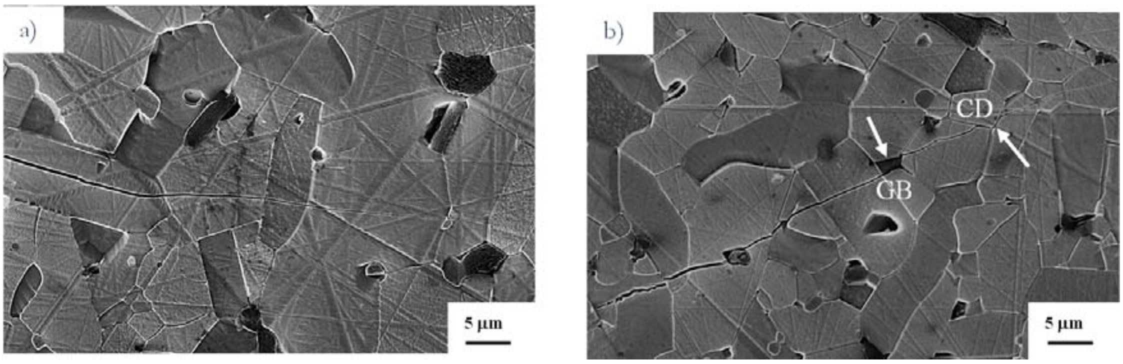

Figure 5: Images of the crack paths of SSiC obtained by a) conventional sintering and b) two-step sintering. Crack deflection (CD) and grain bridging (GB) are indicated by arrows

LPSiC is normally toughened by crack deflection mechanism due to the grain boundary phase composed by yttrium aluminate [25]. TyGReSiC exhibited similar fracture mode, mainly intergranular, (Fig. 6), but the crack deflection mechanism was more evident in the TSS sample having finer microstructure (Fig. 7b).

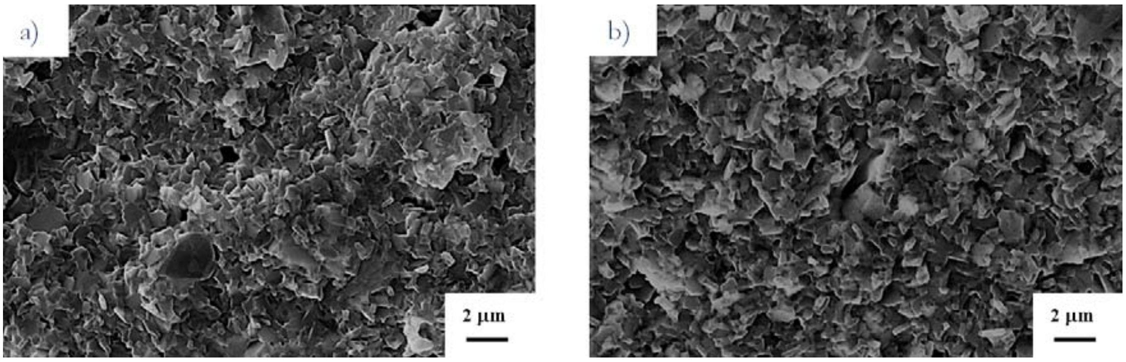

Figure 6: Images of the fracture surfaces of LPSiC obtained by a) conventional sintering and b) two-step sintering.

## CONCLUSIONS

Solid and liquid two-step sintering methods were successfully applied to different SiC powders. SSiC and LPSiC were obtained both below 2000°C with finer microstructure. SSiC showed different fracture mechanism: transgranular in CS-SSiC and mixed transgranular-intergranular in TSS-SSiC. The difference in fracture toughness was not so evident even if grain bridging-crack deflection toughening mechanism was put in evidence in TSS-SiC.
LPSiC was applied to the SiC powder obtained starting from the carbonaceous residue of waste tires. TSS-LPSiC showed the highest fracture toughness due to the enhancement of the crack deflection mechanism.

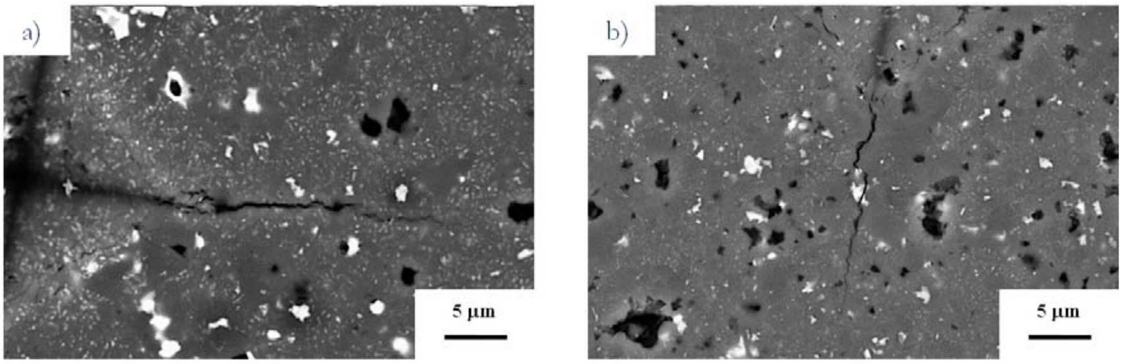

Figure 7. Images of the crack path of LPSiC obtained by a) conventional sintering and b) two-step sintering

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