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SiC–Si_3N_4 Bonded Materials by the Nitridation of SiC and Talc

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Abstract: Silicon carbide-based materials are used in many applications due to their good thermo-mechanical properties at high temperatures. The nitrogenous bond formed from nitriding reactions of silicate minerals seems to be an interesting method to obtain these materials. In this work, the reaction of SiC with talc and N_2 atmosphere is studied. Pellets and/or bars of SiC–talc mixtures were reacted within the range 1395–1650°C. Reaction products were studied through XRD, textural properties, bending strength and microscopy. Reactions and mechanisms for this system are proposed. Silicon nitride is formed as principal bond phase. During reaction, volatilization of Mg takes place, where its loss is favoured at high temperatures and high N_2 flow rates. A loss of SiO(g) is also observed. Mechanical strength has a linear relation with the bond phase content. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

INTRODUCTION

Currently, silicon carbide-based materials are used in many applications due to their good thermo-mechanical properties at high temperatures.[1] The mechanical properties of this ceramic material are limited by the behaviour of the bond phase.[2] Originally, SiC materials were bonded with an alumino-silicate matrix. Then, an oxynitride matrix was developed, and more recently nitride and sialon-bonded materials have evolved.[3,4] The nitrogenous bond formed from nitriding reactions of silicate minerals seems to be a very interesting method of fabrication.[5]

A general method to fabricate these materials is by the reaction between SiC and a mineral at high temperatures (1395–1650°C) in a N_2 flow. SiC acts as a reducing agent for the mineral with simultaneous replacement of oxygen by nitrogen. Most reactions and mechanisms that take place in the SiC–Clay–N_2 system are similar to the carbonitriding reaction in the C–Clay–N_2 system.[6–10] Morrison *et al.*[11] reported *in situ* formation of β'-SiAlON in SiC materials without discussing their mechanical properties. In previous work, Mazzoni *et al.*[12] studied the formation of nitride bonding in the SiC–Clay–N_2 system.

In this work the reactions in the SiC–talc–N_2 system were studied within the temperature range of 1395–1650°C. Reactions and mechanisms for this system are proposed. Nitride containing phases formed were analysed by XRD. In addition porosity, microstructure and mechanical properties are related to the compounds and quantity of the bond phase formed.

MATERIALS AND METHODS

The SiC used was of high grade (green in colour provided by Fabril Casale SAIC, Argentina) and its chemical analysis is shown in Table 1. The talc mineral [$Mg_3Si_4O_{10}(OH)_2$] is from Carmelo Department (República Oriental del Uruguay) and its chemical composition is also given in Table 1. X-ray diffraction analysis of the samples did not reveal the presence of impurity phases.

The main study was performed with fine grain size SiC. The granulometry was: 40% minus 45 μm,

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Table 1. Chemical analyses of SiC and talc

%	SiC	Talc
SiC	>98.5	—
SiO_2	<1	59.83
C	<1	—
Si	<0.1	—
CaO	<0.1	0.33
MgO	<0.1	31.87
Fe_2O_3	<0.3	0.14
TiO_2	—	0.07
Na_2O+K_2O	—	1.37
LOI (Loss on ignition)	—	5.01

20% minus 25 μm, and 40% minus 10 μm. The SiC was dried and mixed with talc in an oscillating mill (Herzog HSM 100). Talc was used in a percentage of 5, 10, 15 and 20 wt% in the mix. The mixtures so obtained were moulded into bars (5.0×0.8×0.8 cm^3), pressed (uniaxially) at 100 MPa or into pellets (dia. = 1.14 cm×height = 1.0–1.5 cm) pressed (uniaxially) at 39 MPa. In both cases, polyvinyl alcohol was used as temporary binder (0.25 wt%).

Bars and/or pellets were reacted in a vertical alumina reactor with nitrogen flow. The nitrogen gas used contained less than 5 ppm of O_2 and H_2O. Temperature was controlled with a Pt–Pt Rh (10%) thermocouple.

The reactor was heated by a SiC furnace. A $MoSi_2$ furnace was used to reach higher temperatures. Reaction temperatures used were within the range 1395–1600°C and the reaction time was 3 h. The N_2 flow used was 1.5 to 3.0 L min^{-1} (linear rate = 3–6 cm s^{-1}). Other experiments were carried out with a higher N_2 flow (5 L min^{-1}).

Mechanical properties of the bars were measured by the modulus of rupture (MOR) three-point bending test using a T22K tensile testing machine manufactured by J. J. Instrument (span: 4.0 cm; v = 2.0 mm min^{-1}).

Samples were observed by means of a scanning electron microscope Philips 505 and electron probe micro analysis (EPMA). Porosities and densities were determined with the Archimedes method. Porosities were also determined by Hg intrusion using a Carlo Erba equipment.

Crystalline phases formed in the reaction were analysed qualitatively and quantitatively using a Philips 1140/00 Diffractometer (Cu–K_α). In quantitative (XRD) analyses the following patterns were used: (a) β–Si_3N_4 provided by Aldrich Chemical Company Inc., Milwaukee, WI 53233, USA; (b) α-Si_3N_4 provided by Toyo Soda Inc., USA. Thermodynamic calculations were made using JANAF tables.[13]

RESULTS AND DISCUSSION

The most important study was performed with the reaction of fine SiC with talc in percentages of 5, 10, 15 and 20%. The SiC–talc bars were analysed by XRD after their corresponding reactions using the above mentioned conditions of temperature and N_2 flow rate. In all the bars the principal bonding phase was Si_3N_4 in α and β forms. In some samples traces of silicon oxynitride (Si_2N_2O) and cristobalite (SiO_2) were detected.

Crystalline phases of Mg such as $MgSiO_3$ or phases of the Si–N–Mg system were not observed. Analyses by XRD did not show the presence of significant quantities of glasses resulting from vitreous or other impurities in the talc. The chemical analysis of samples by means of EPMA confirmed the loss of magnesium during the reaction.

Figure 1 shows the MgO content as a function of temperature for samples made using 20% talc. This behaviour is representative of the results obtained with different talc contents. The decrease of the Mg content in the samples is influenced by the N_2 flow and by the temperature during the reaction.

It is known that reducing gases produce large losses of Mg(g) at high temperatures (1630°C) by evapouration.[14] The decrease of Mg content with the temperature was observed by Yoshiyuki Sugahara *et al.*[15] during montmorillonite carbonitriding. The same authors[16] performed the carbonitriding of antigorite (42.4% of MgO) (reaction with C and N_2) and they detected the presence of $MgSiN_2$ as an intermediate phase prior to Si_3N_4 formation. These authors observed that magnesium silicate formed during the control stage was gradually reduced to volatile SiO and Mg.

In our work, the reducing agent is SiC which produces a reducing atmosphere (CO and SiO). Since the magnesium loss was observed and is corroborated by previous studies and also by the fact

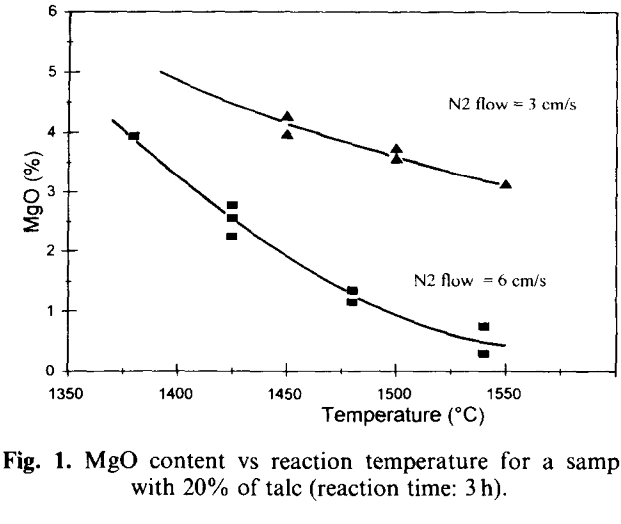

Fig. 1. MgO content vs reaction temperature for a sample with 20% of talc (reaction time: 3 h).

that Mg^{2+} cannot be incorporated in the Si_3N_4 lattice, the following reactions are proposed.

$$\underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} \rightarrow 3\,MgSiO_3 + SiO_2 + H_2O \qquad (1)$$

$$MgSiO_3 + SiC \rightarrow Mg(g) + 2\,SiO(g) + CO \qquad (2)$$
$$\ln K2_{1427°C} = -23.52$$

$$3\,SiC + 3\,SiO + 4\,N_2 \rightarrow 2\,Si_3N_4 + 3\,CO \qquad (3)$$
$$\ln K3_{1427°C} = 17.73$$

$$[\text{Sum } 3.(2) + 2.(3)]\,9\,SiC + 3\,MgSiO_3 + 8\,N_2 \rightarrow 4\,Si_3N_4 + 3\,Mg(g) + 9\,CO \qquad (4)$$

Reaction (1) describes the thermal decomposition of talc. This reaction occurs during the heating of samples ($\simeq$1100°C). Therefore, when reaching the temperatures between 1250 and 1575°C without soaking time a mixture of SiC, $MgSiO_3$ and SiO_2 is present.

In order to explain the Mg loss observed during treatment, reaction (2) is proposed. This reaction strongly depends on low SiO(g) and CO(g) partial pressures because the N_2 flow causes removal of these gases which favours this reaction. It is well known that Mg vapourises at high temperatures, and this vapourisation is enhanced when a reducing atmosphere is present. Volatility diagrams[17] can predict the vapour pressures of various gaseous species involved in the high temperature reaction. For MgO these diagrams were constructed and then used mainly for studying the volatilisation and dense magnesia layer formation in magnesia-carbon refractories.[14,18] In our system, it is very difficult to know the real partial pressure of the gases that intervenes because the reaction takes place in an open system (no equilibrium) and, as Fig. 1 indicates, magnesium vapourisation causes complete loss of Mg with increasing temperature and N_2 flow rate. The equilibrium partial pressure of Mg(g) using reaction (2) would be 2.8×10^{-2} Pa; this pressure is greater than the $P_{Mg} = 1\times10^{-4}$ Pa using the magnesia volatility diagram[17] at 1427°C, with one Po_2 of 1×10^{-2} to 5×10^{-1} Pa (5 ppm O_2 in N_2). Under reduction conditions the P_{Mg} increases and is near to the one calculated from reaction (2).

Reaction (3) is thermodynamically favoured ($\Delta G^0_{1427} = -126$ kJ mol^{-1}) and is the principal reaction to form Si_3N_4. In reactions (2) and (3) SiC acts as a reducing agent which results in Mg(g) loss. Reaction (4) is the sum of reactions (2) and (3) and represents the global reaction proposed. The Si_3N_4 is formed mainly from SiO gas resulting from talc decomposition.

Silica from talc reacts according to the following reactions:

$$SiO_2 + 2\,SiC + 2\,N_2 \rightarrow Si_3N_4 + 2\,CO(g) \qquad (5)$$
$$\ln K5_{1427°C} = -1.39$$

$$SiO_2 + SiC + N_2 \rightarrow Si_2N_2O + CO(g) \qquad (6)$$
$$\ln K6_{1427°C} = 4.35$$

$$SiO_2 + SiC \rightarrow 3\,SiO(g) + CO(g) \qquad (7)$$
$$\ln K7_{1427°C} = -20.35$$

$$3\,SiO(g) + 3\,CO(g) + 2\,N_2 \rightarrow Si_3N_4 + 3\,CO_2(g) \qquad (8)$$
$$\ln K8_{1427°C} = -9.60$$

Reaction (5) must be considered ($\Delta G^0_{1427°C} = 136$ kJ mol^{-1}) due to the low P_{CO} in this system. Silicon oxynitride was detected in some samples since reaction (6) is thermodynamically favoured ($\Delta G^0_{1427°C} = -29$ kJ mol^{-1}).

Reaction (7) participates in the mechanism used to obtain SiC in the SiO_2–C-system,[19] and also occurs in the clay–SiC–N_2 system.[12]

Reaction (8) was proposed by Zhang[20] as the principal reaction in the formation of Si_3N_4. In order that reaction (8) may occur, sufficiently high P_{SiO} and P_{CO} are required because it is not thermodynamically favoured ($\Delta G^0_{1427°C} = 136.6$ kJ mol^{-1}).

In reactions with SiC that form small amounts of nitrogen-containing phases, reactions (2) and (7) are believed to be the most important. These reactions produce a large weight loss (Mg(g) + SiO(g) + CO(g)) without formation of Si_3N_4 and without the presence of crystalline phases such as $MgSiO_3$.

Other reactions which may be considered by taking into account thermodynamic data are:

$$3\,SiC + 2\,N_2 \rightarrow Si_3N_4 + 3\,C \qquad \ln K9_{1427°C} = 1.47 \qquad (9)$$

$$3\,SiO + 3\,C + 2\,N_2 \rightarrow Si_3N_4 + 3\,CO \qquad (10)$$
$$\ln K10_{1427°C} 14.50$$

Reaction (9) may occur ($\Delta G^0 = -20.9$ kJ mol^{-1}) and C formation leads to reaction (10)

($\Delta G^0_{1427°C} = -239\,kJ\,mol^{-1}$). These reactions are unlikely since little Si_3N_4 is formed; also taking into account that free carbon (C) introduced by SiC (chemical analysis) is less than 1 wt%.

Samples show significant quantities of Si_3N_4 which may arise from reactions (3), (5), and (8). Reaction (5) does not justify all the Si_3N_4 present since the amount of SiO_2 coming from reaction (1) is small.

Reactions (5) and (8) are similar to the ones formed in the carbonitriding reaction of clays to prepare β′-Sialons[6–10] or to the ones corresponding to the SiC–clay–N_2 system.[12] These reactions are the result of the reaction of an oxide product (mullite, SiO_2, etc.) with SiC (reducer) permitting the incorporation of N_2 to form nitrides.

The Si_3N_4 formed is a mixture of α and β (more α than β phase) and as the amount of Si_3N_4 increases the quantity of α phase becomes greater. Figure 2 shows the quantities of α and β measured (XRD) in the bars and or/pellets after reaction. Nevertheless there is not a precise relation between these two phases.

It is known[20,21] that the formation of silicon nitride by reduction of SiO_2 produces α-Si_3N_4 (i.e. SiO formation) since the mechanism of the reaction is through the vapour phase. In our work it is possible to propose that most of the reaction to form silicon nitride occurs in the vapour phase, generating a greater quantity of α-Si_3N_4.

The formation of β-Si_3N_4 and little amounts of Si_2N_2O can be explained through the presence of liquid phases. The presence of liquid phases favours the formation of β-Si_3N_4. This fact was verified by Siddiqi and Hendry.[21] Impurities present are also known to play an important role in determining the phases formed and their effect cannot be explained entirely by equilibrium thermodynamics.

The theoretical weight loss (WL) of the SiC–talc–N_2 samples (considering that the reaction products are Si_3N_4, Mg(g), CO and H_2O) is 1.57; 3.14; 4.71 and 6.28 wt% for 5, 10, 15 and 20 wt% of talc content. The WL depends on temperature, reaction time, and N_2 flow; the values measured in the reacted bars were: 0.2 to 2.6% (talc 5%); 1.0 to 5.4% (talc 10%); 1.8 to 7.3% (talc 15%) and 4.0 to 10.0% (talc 20%). The WL increases with temperature at a high N_2 flow rate. The WL measured cannot be related with the degree of nitridation or $Mg_{(g)}$ loss because there are reactions that cause weight losses without Si_3N_4 formation (reactions 2 and 7) and Mg(g) loss (reaction 7). Also the SiO(g) loss must be considered. SiO(g) loss was verified by SiO_2 deposition in the reactor exit (white needles).

Samples obtained from SiC–talc reaction (fine SiC) have relatively low bulk densities within the range 2.17–2.22 g cm^{-3}. These values are similar to those obtained in reacted SiC–SiAlON from SiC–clay–N_2 reaction. Kurosaki Refractories offers one SiC–Si_3N_4 brick (CRD–BFNS) with a bulk density of 2.05 g cm^{-3} and an open porosity of 35.1%; this material has a good resistance to thermal spalling and alkali corrosion. Open porosity (Archimedes method) varied between 29 and 33%. Figure 3 shows the pore volume distribution as a function of the pore radius using Hg porosimetry. Pore sizes are in a narrow range for the four talc contents. The main difference is that the pore radius increase with talc content and for the sample of 5% of talc they are near to 0.25 μm. For 20% of talc the pore radii are 0.7 μm. It is clear that when a large quantity of Si_3N_4 is formed it acts as a matrix and reduces the pore size. The total pore volume (Hg method) did not show major differences with respect to talc content. The apparent specific gravity of the samples was between 3.17 and 3.23 indicating that there is no closed porosity. The

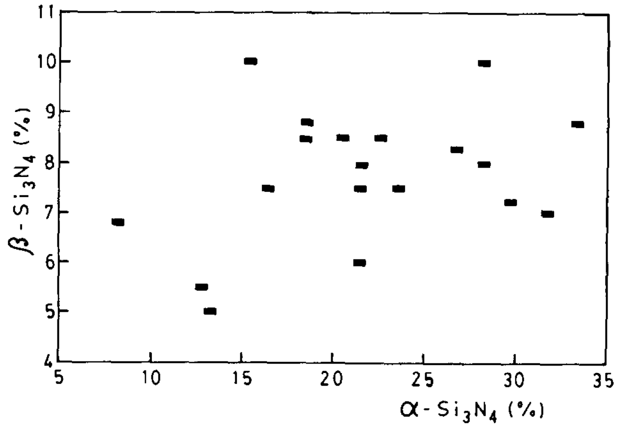

Fig. 2. β-Si_3N_4 vs α-Si_3N_4 content in the reacted samples (XRD).

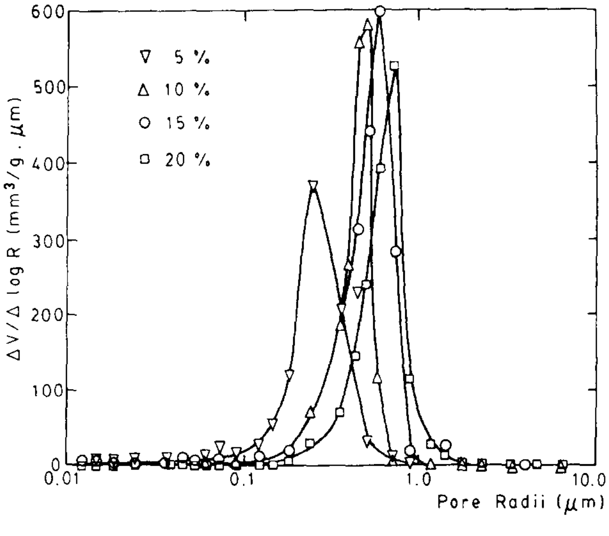

Fig. 3. Pore volume distribution vs pore radii for 5, 10, 15 and 20% of talc content.

presence of open porosity is in agreement with the high gaseous exchange that occurs during the reaction (evolution of CO, Mg and SiO and incorporation of N_2).

Figure 4 shows the variation of the modulus of rupture (MOR) as a function of the total Si_3N_4 ($\alpha + \beta$) using samples with different proportions of talc (5 to 20%) and exposed to different reaction conditions. It is possible to state that the mechanical strength increases with silicon nitride content. Quantitative contents of total Si_3N_4 vary from 13 to 40%, of α-Si_3N_4: 5 to 30% and of β-Si_3N_4: 6 to 17%. The expected theoretical contents based on the talc content were between 9.5 and 39.5% of Si_3N_4 (total).

Some tests were carried out using SiC with a granulometric distribution (Furnas type) from mesh 12 (ASTM) and talc was used in the fine fraction (−325). Samples were prepared using a talc content of 5 to 20 wt% in the mixture. Reaction products formed did not show the quantity of nitrogenous phases (α and/or β-Si_3N_4) expected according to the original talc content. A large weight loss of the bars occurred due to the SiO(g) loss. These results are consistent with the reactivities observed in the SiC–clay system.[12] In this system the coarse grains greater than 100 mesh (ASTM) did not react with talc and did not form nitrogenous phases even under conditions of high temperature (1650°C). In the SiC–talc system using a SiC with a Furnas distribution, the talc reacts only with the fine fraction (lesser than 100 mesh) of the SiC with consequent smaller quantities of α and β-Si_3N_4 formed. In these samples there are greater quantities of vitreous phases. Magnesium and other impurities formed this glassy phase but the presence of crystalline magnesium silicate was not observed. A decrease of magnesium content was observed. A small decrease in SiC content (XRD) was also observed produced mainly by SiO(g) and Mg(g) losses (reaction (2)).

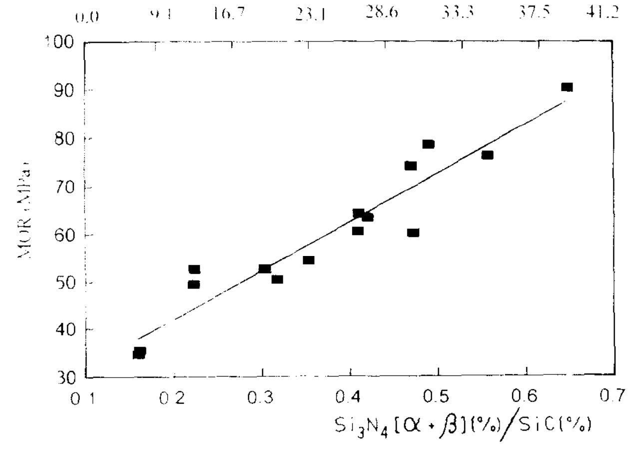

Fig. 4. Modulus of rupture (MOR) vs total ($\alpha + \beta$) Si_3N_4 content.

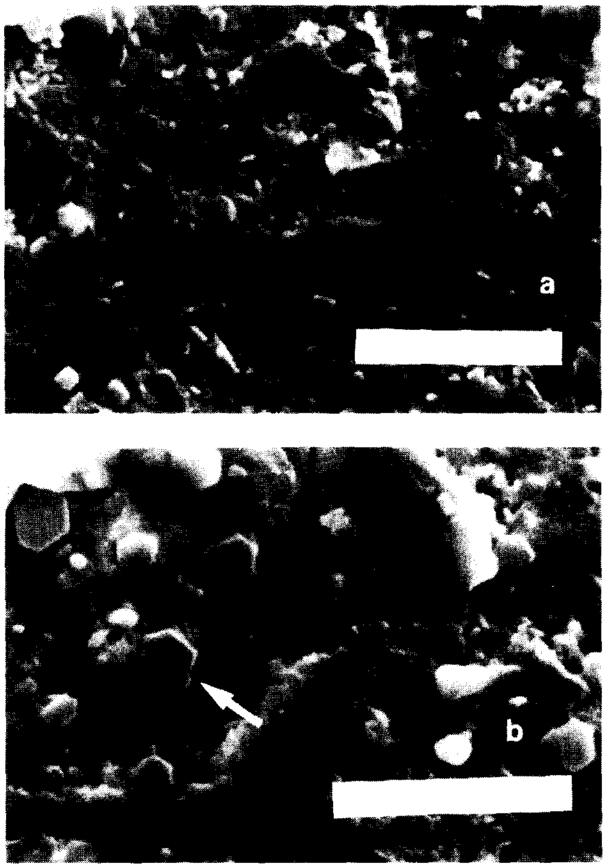

Fig. 5. (a) SEM micrograph showing the reaction product with high Si_3N_4 content (talc 20%, 1630°C) (scale bar = 10 μm); (b) SEM of the SiC–Si_3N_4 product showing hexagonal grains of Si_3N_4 (scale bar = 10 μm).

Figure 5(a) shows the reaction products obtained after reaction with talc at 1630°C (N_2 flow = 6 cm s^{-1}). This sample has a high content of silicon nitride ($\simeq$ 38%) and was etched with HF. The SiC grains are contained in the nitride matrix and cannot be easily identified; Mg was not detected in this sample using EPMA.

Figure 5(b) shows a sample with a high content of α-Si_3N_4. The well defined hexagonal crystalline grains are Si_3N_4 particles (EPMA).

CONCLUSIONS

1. The SiC talc reaction in flowing N_2 at 1390 to 1650°C produces α and β silicon nitride as the principal bonding phase. During reaction, volatilisation of Mg takes place, its loss is favoured using high temperatures and high N_2 flow rates.
2. The α-Si_3N_4 content was always higher than that of the β-form and their relative quantities occur over a narrow range.

3. During reaction, $MgSiO_3$ and SiO_2, resulting from decomposition of talc, reacted to form Si_3N_4 and a loss of SiO(g) was observed.
4. The porosity of the SiC–Si_3N_4 bars was mainly open due to the significant gaseous exchange during the formation of the Si_3N_4 matrix.
5. The mechanical strength (MOR) exhibits a linear relation with the bond phase content.
6. The materials obtained by this method are not of high density. Market offers refractories with similar characteristics when good resistance to thermal spalling is required.

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