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ScienceDirect

Ceramics International 36 (2010) 9–14

CERAMICS INTERNATIONAL

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Spontaneous infiltrations of compound systems of Y_2O_3, Sm_2O_3, RE_2O_3, Al_2O_3 and AlN in SiC ceramics

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Received 2 March 2009; received in revised form 17 April 2009; accepted 24 May 2009
Available online 22 July 2009

Abstract

Silicon carbide ceramics (SiC) are used in different applications in the engineering area due to the excellent properties, mainly in high temperatures. They are usually obtained by liquid-phase sintering enabling to form volatile products and, consequently, defects. The present work aims at studying the obtention of SiC ceramics by spontaneous infiltration using a eutectic composition of the Al_2O_3/Y_2O_3, AlN/Y_2O_3, Al_2O_3/Sm_2O_3, AlN/Sm_2O_3, Al_2O_3/RE_2O_3 and AlN/RE_2O_3 systems. RE_2O_3 is the concentrate of the rare-earth oxide obtained from Xenotime ore. Infiltration tests were carried out in argon atmosphere, graphite crucibles, in several temperatures near the melting point of each system, varying from 2.5 to 60 min. It was observed that Al_2O_3/Y_2O_3, Al_2O_3/Sm_2O_3, AlN/Sm_2O_3 and Al_2O_3/RE_2O_3 systems do not infiltrate appropriately and the AlN/Y_2O_3 and AlN/RE_2O_3 systems infiltrated spontaneously more than 20 mm; however, the first one presented a higher degree of infiltration, approximately 97%.

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Keywords: D. SiC; Spontaneous infiltration; Rare-earth oxides

1. Introduction

Silicon carbide is an inorganic chemical substance with density of about 3.20 g/cm^3, which presents two crystalline phases: β-SiC stable until 2000 °C and α-SiC stable until 2300 °C; SiC is decomposed [1,2] in silicon and carbon above this temperature. Due to SiC covalent character, the ceramics are normally obtained by liquid-phase sintering, using additives in large reasonable quantities. Although these ceramics presented many properties for several structural applications [2–11], they are obtained in high temperatures and for long time of sintering, occurring chemical reactions that generate volatile products and, consequently, formation of secondary porosity decreasing its mechanical resistance [4,12–15]. An alternative for the production of these ceramics in lower time and temperature could be obtained by infiltration of liquid in SiC compacts.

The infiltration rate depends on the relation among the viscous forces, capillarity and hydrostatics represented by Poiseuille equation [16–21]. The difference of the pressure system is related to the superficial tension of the liquid, contact angle in which the liquid would wet the solid, density of the liquid, height of the liquid in the capillary and static middle radio of pores (R_S). Considering that the static radio (R_D) is equal to the geometric radio of pores (experimentally verified), that the hydrodynamic radius also depends on the pore tortuosity and the hydrostatic pressure can be neglected at the first moment of the infiltration process, the height of infiltration (h) can be represented by Washburn's equation, as follows:

$$h^2 = \frac{r\cos\theta}{2\eta}\cdot t \tag{1}$$

where $r = R_D^2/R_S$, η is the liquid viscosity, θ is the contact angle, and t is the time. A parameter r can be determined by BET (Brunauer, Emmett and Teller) and scanning electronic microscopy (SEM) and the contact angle can be obtained by the sessile drop method [16–20,22–27], but viscosity is still tough to be determined in systems melting over 1500 °C.

In the practice, a liquid infiltration in a compact, at high temperatures, is normally measured by the infiltration degree (f), which is defined as the volume percentage of original pores filled up with liquid, as shown in the following equation [28]. The infiltration degree depends on the density of infiltrated (ρ_s),

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doi:10.1016/j.ceramint.2009.05.041

Table 1
Composition (wt.%), contact angle (θ) and melting temperature (T_m) of additive systems.

Ref.	Code	Composition (% mass)					$\theta_{eq.}$ (°)	T_m (°C)
		Al_2O_3	Y_2O_3	RE_2O_3	Sm_2O_3	AlN		
[26]	AY	64.35	35.65	–	–	–	~0	1790
[24]	NY	–	87.96	–	–	12.04	~0	1840
[25]	ARE	60	–	40	–	–	~10	1780
[27]	NRE	–	–	90.00	–	10.00	~5	1830
[26]	AS	51.86	–	–	48.14	–	~10	1755
–	NS	–	–	–	80	20	~10	1850

of the relative density of the green compact (d), and the density of the additive (ρ_a). The temperature of the infiltration should be chosen according to the melting point and wetness results [29,30].

$$f = \frac{\rho_S - 3,2d}{\rho_a(1-d)} \qquad (2)$$

The infiltration may occur through a direct or indirect method. The spontaneous and indirect method promotes more advantages, because it presents a bigger infiltration degree besides being a continuous and unidirectional process [3,28]. Using this method, the liquid infiltrates until reaching the equilibrium (h_{eq}).

This work aims at studying the viability and obtention of SiC ceramics by spontaneous infiltration of Y_2O_3/AlN, Y_2O_3/Al_2O_3, RE_2O_3/AlN, RE_2O_3/Al_2O_3, Sm_2O_3/AlN and Sm_2O_3/Al_2O_3 systems in shorter time and temperature compared to the liquid-phase sintering.

2. Experimental

The following materials were used: β-SiC (H.C. Starck, type BF-12), Sm_2O_3 from Indústrias Nucleares do Brasil–INB, Y_2O_3 (H.C. Starck, type GRADE C fine), Al_2O_3 (Baikalox, type CR6, AS 250 KC, AlN (H.C. Starck, type GRADE C fine), RE_2O_3 rare-earth oxides produced in DEMAR/EEL/USP from xenotima ore with 90% of composition constituted by Y_2O_3, Yb_2O_3, Er_2O_3, Dy_2O_3 and Ho_2O_3 [25].

Table 1 presents codes of powder mixes, their respective compositions (which were chosen according to their smaller contact angles, $\theta_{eq.}$) and the melting temperature (obtained according to the Standard DIN 51730). This data was obtained based on previous studies [24–27].

The additives were mixed in attrition mill for 1 h at 1000 rpm, in isopropyl alcohol, dried in rotative evaporator at 80 °C and pressed as cylinder up to 20 mm in diameter in a uniaxial press at 30 MPa and isostatic press at 300 MPa. Compacts were pre-sintered at 1500 °C, for 30 min in a graphite resistance furnace type ASTRO to acquire enough mechanical resistance for machining, Fig. 1(a). The samples were submitted to porosimetry analysis in a Porosimeter by Quantachrome – model Autoscan 33, with the aim of determining the size and distribution of pores taking on a mathematical model of cylindrical pores. This format of SiC substrate is predetermined by a spontaneous indirect infiltration test with unidirectional flow.

The SiC sample was placed on an additive disc inside in a graphite crucible, Fig. 1(b), and heated in a graphite resistance furnace up to the melting temperature of the respective additives. After the liquid formation, isotherms were recorded from 2.5 to 60 min, followed by cooling at 30 °C/min, Fig. 1(c). After infiltration, samples were cut in a longitudinal section and analyzed which concerns to microstructure (SEM) and chemical composition by energy dispersive spectroscopy (EDS). Some parts of the infiltrated region were cut, grinded and sieved (400 mesh) and submitted to an analysis of density using Multivolume Pycnometer 1305 from Micromeritis in order to evaluate the infiltration degree using Eq. (2). The calculation of infiltration degree was done only to samples that obtained better results.

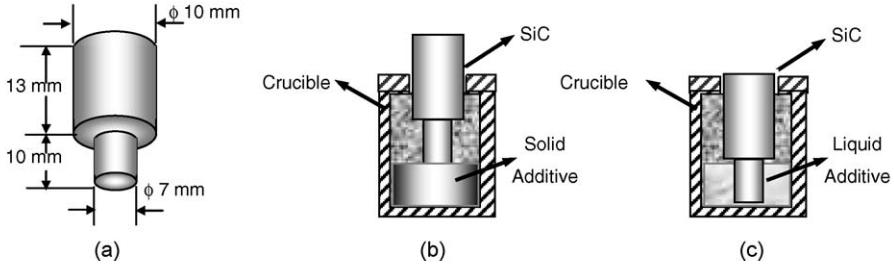

Fig. 1. Samples schematic design for infiltration tests: (a) SiC machined substrate, (b) SiC substrate/crucible/additive before the additive melting and (c) after additive melting.

3. Results and discussion

3.1. Characterization of SiC compacts

The relative density of compacted SiC substrate was approximately 54 T.D.%. According to results of porosimetry analysis, Fig. 2(a), the porosity of compacted and pre-sintered SiC were 0.202 and 0.234 $\text{cm}^3\,\text{g}^{-1}$, respectively; similar amounts confirming that the heating did not modify the porosity value. The median size of pores from the samples was 125 nm.

The fracture surface of the pre-sintered SiC substrate, Fig. 2(b), analyzed by SEM, presented characteristics of green samples, irregular particles with a median size of 0.5 μm. Opposite to the liquid-phase sintering, it is interesting that the substrate presents irregular and heterogeneous particles so that the additive can infiltrate the porosity of the compacts formed by this kind of morphology.

3.2. Infiltration tests in SiC substrate

All systems containing Al_2O_3, presented low height of infiltration in SiC, in temperatures approached to melting of the respective systems as shown in Fig. 3(a). From these systems, AY presented higher infiltration, with logarithmic kinetics behavior, demonstrating that infiltration is faster in the beginning until the system equilibrates in approximately 60 min, limiting around 12 mm of infiltration in the SiC compact. By increasing the temperature, it is observed that the height of infiltration also increases considering one single system. This indicates that the infiltration mechanism is influenced by the system viscosity according to Eq. (1). Rising to 100 °C above melting temperature, system ARE presents a high infiltration near to equilibrium.

For systems containing AlN, Fig. 3(b), the height of infiltration increases with the time and, the infiltration kinetics presents a logarithmic behavior, as shown to YN system. In these systems, the height of infiltration was lower for higher temperatures than the melting of the respective systems. In temperatures approaching the melting point the mechanism of infiltration is influenced by viscosity and the following systems infiltrated almost completely, except to NS system, which only infiltrates a little under any condition. With temperatures above melting point, the mechanism of infiltration is influenced by reactions occurring in the systems: (i) evaporation of AlN dislocates the composition to oxide compounds and in the formation of more stable products that alter the viscosity of the system, reducing the height of infiltration; (ii) the high temperature can also promote the solution-precipitation process and, consequently, microstructural modifications (in this case, the infiltration depends not only on the viscosity but also the mobility of atoms to delaying the advance of infiltration); (iii)

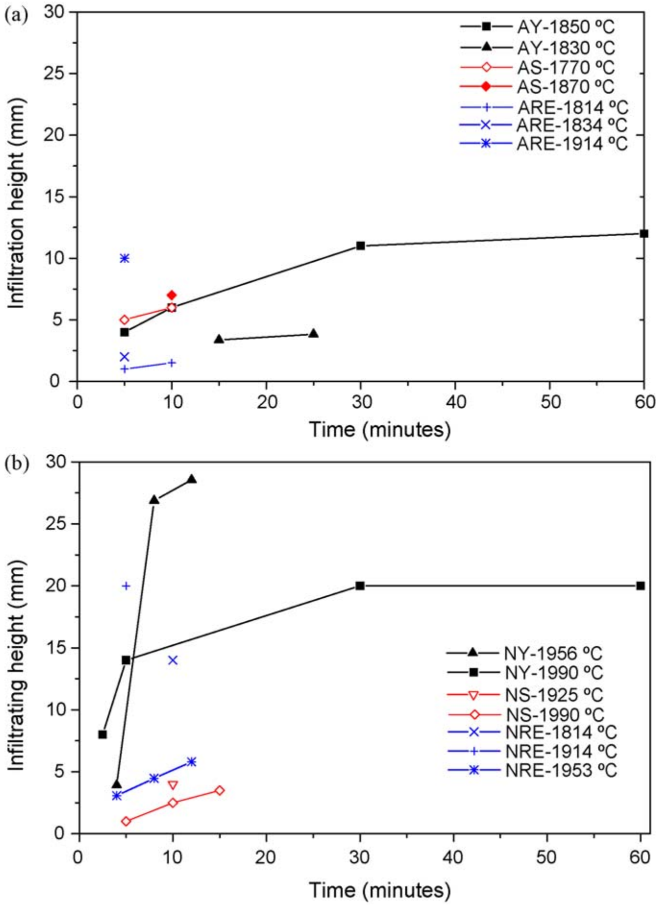

Fig. 3. Height of infiltration according to time and temperature for compacts of SiC infiltrated in (a) AY, AS and ARE, and (b) NY, NS and NRE systems.

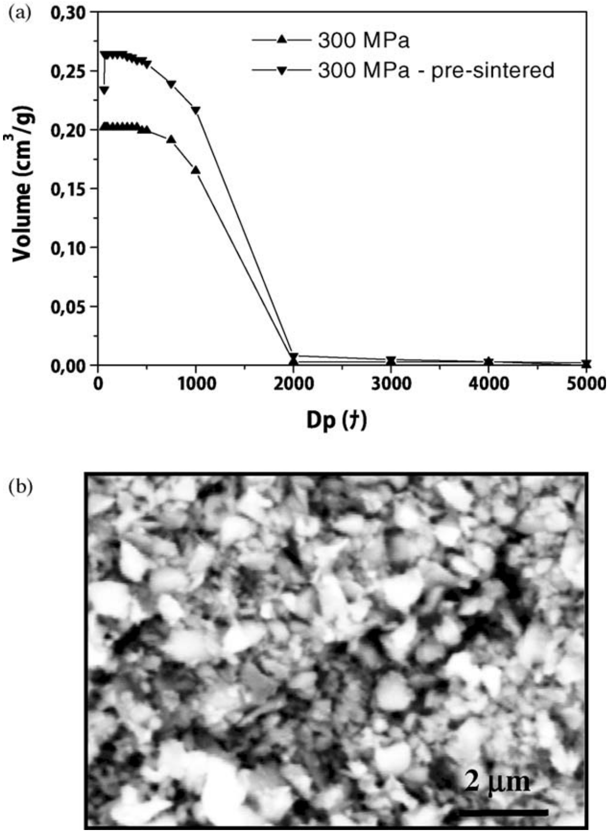

Fig. 2. (a) Porosity of SiC compact, (b) micrography (SEM) of the fracture surface of SiC substrate.

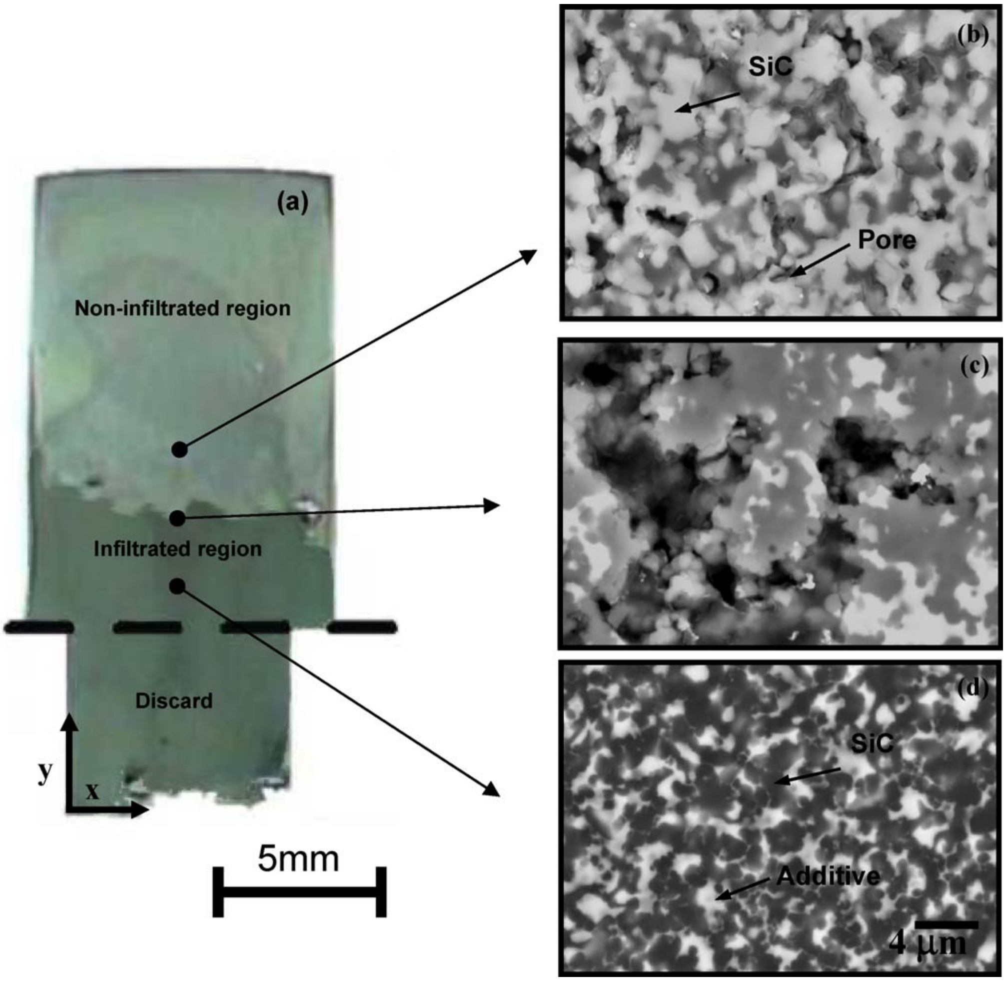

Fig. 4. (a) Image taken with a CCD camera of a longitudinal cut of SiC substrate infiltrated in AY for 5 min, and microstructural variation obtained with SEM (b–d).

the elevation of temperature can close some SiC pores, reducing the advance of infiltration. To study these hypotheses, crystalline phases were determined by the additive/SiC systems and the microstructural modifications of all samples were also analyzed, longitudinally or transversally. As there are many systems, some with more representative results are shown herein.

Fig. 4 shows a photograph from SiC infiltrated with AY for 5 min and the main longitudinal microstructure of the sample.

Micrography of Fig. 4(b) refers to SiC substrate without additive, compact microstructural characteristic, rounded morphology than the pre-sintered compact shown in Fig. 2(b); (c) an intermediate region composed of infiltrated and non-infiltrated SiC; and (d) refers to the additive infiltration, where there are SiC grains (dark gray) involved by additives (white), where no process of solubilization or precipitation occurred because the morphology of SiC grains was similar to the ones presented in (b), only with the additive liquid involving SiC.

Some advances of infiltration (4 mm) can be observed in AY additive infiltrated in the SiC substrate, for 5 min. It is important to mention that the progress for each sample was confirmed by the mapping performed by EDS, with steps of 0.5 mm; this is approximately 450 points for all the sample, where the compounded variation of elements, Si, C, Al, Y and O, was evaluated. The elements of Si and C were present in the whole sample as expected, because the substrate is from SiC. The elements Y, Al and O are present only in the infiltrated regions.

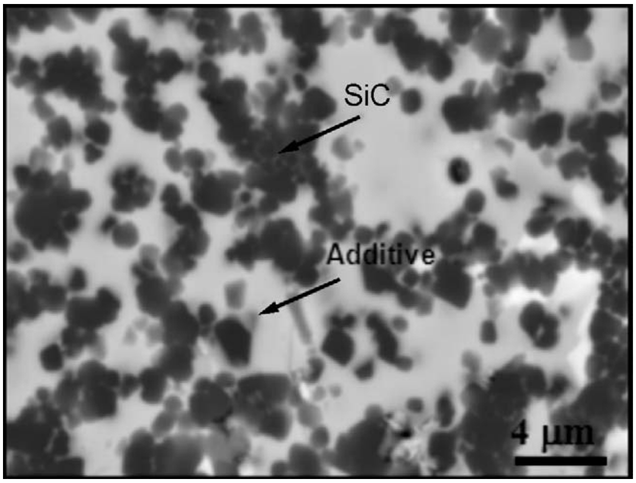

Fig. 5. Microstructure obtained by SEM from SiC infiltrated with NY to 1956 °C, for 25 min.

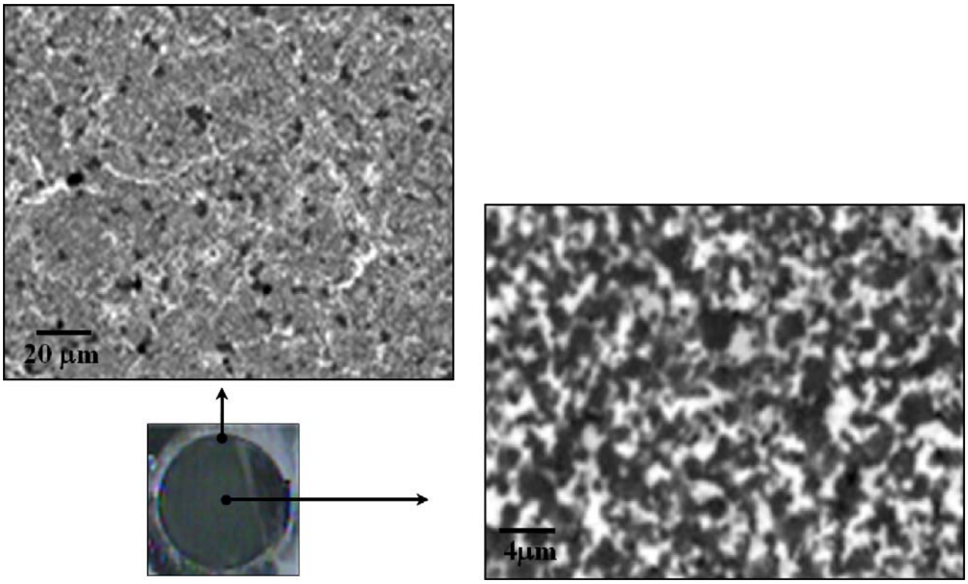

Fig. 6. Micrograph of transversal section of the core and edge from the discarding region of an AY sample.

Although the infiltration height varies according to the temperature, time and systems compositions, all samples containing Al_2O_3 presented similar microstructures to the ones presented in Fig. 4, except ARE sample infiltrated at 1924 °C, which presents an initiation of solution-precipitation, because the infiltration was at 100 °C above the melting point of this system.

Fig. 5 shows the microstructure of SiC infiltrated with NY system at 1956 °C, for 2.5 min, where the solubilization and precipitation processes occurred due to the hexagonal morphology of the SiC grains well dispersed in the additive, different from the one presented in Fig. 4(d).

Even though the SiC substrate has homogeneous microstructure, the formation of preferential channel to the liquid mobility occurs during the infiltration. Fig. 6 shows the microstructure of the central region and superficial of the AY transversal section of discard after infiltration. On the left side, it can be observed that white regions are infiltrated by additives in the micrography of the region next to the edge. The central region presents a complete infiltration and a homogeneous distribution of additive in SiC; justifying the choice of infiltration through the indirect method.

Samples of NY and NS infiltrated for 30 or 60 min, degraded after some days. This degradation occurs because in the following example, Y_2O_3 reacts with carbon (from SiC or furnace atmosphere) and forms yttrium carbide Y_xC_y, that is extremely reactive to environment water external to furnace. The product of this reaction is yttrium hydroxide and acetylene, making the infiltrated part turning into powder, and also degrading the substrate of this region [14,15]. AlN also can react with SiC; however, the carbide of aluminum formed is gaseous and does not contribute to the degradation of yttrium carbide. To avoid degradation of the infiltrated region, it is important that the infiltration must be done in a short time.

Results of X-ray diffraction of samples containing Y_2O_3 present α-SiC, β-SiC, Y_2O_3 and $Al_2Y_4O_3$ phases. The system RE_2O_3 also presented the phases RE_2O_3 and $Al_2RE_4O_3$, as similarities of rare-earth oxides. During infiltration the transformation of phase β-SiC for α-SiC occurred, which is also verified in the liquid-phase sintering of SiC, but there was not a complete transformation due to the short time of the infiltration.

The phase diagram of system AlN/Y_2O_3 does not foresee any transformation on the stable phase between them, only a eutectic formation during all its extension, but the diffraction results of X-rays presented phases Y_2O_3 and $Al_2Y_4O_9$. This happens because AlN and Y_2O_3 decompose and the products of these reactions can react with Y_2O_3 forming $Al_2Y_4O_9$. There is the possibility that the decomposition products of AlN and Y_2O_3 form Al_2O_3, when reacting with Y_2O_3 in the 1:2 proportions, forming a phase $Al_2Y_4O_9$. Phase $Al_2Y_4O_9$ is foreseen in the diagram of the Al_2O_3/Y_2O_3 system, with congruent formation.

Infiltrated substrates with Sm_2O_3 present lower results of the infiltration advance with Al_2O_3 as well as in AlN. The interface between the infiltrated and non-infiltrated part cracked. This indicates a possible difference of the coefficient of thermal expansion. The small advance of infiltration of these systems was studied, and results of X-ray diffraction confirms the formation of $SmAlO_3$ phase, increasing the viscosity of liquid and changing the interfacial energies of the system inhibiting the infiltration on the liquid-phase.

The infiltration degree of SiC compacts was estimated using Eq. (B), only for the system that presented a larger advance of infiltration. The compact density measured by geometry method was 1.71 $g\,cm^{-3}$ and for SiC ceramic it was 3.20 $g\,cm^{-3}$. Relative densities of infiltrated samples were estimated from densities of the respective infiltrated samples and their real density obtained by helium picnometry. Systems containing Al_2O_3 as well as AlN, showed better results of infiltration advance with Y_2O_3. The infiltration degree for system AY and NY was approximately 15% and 97%, respectively; therefore, only system NY presented a significant infiltration degree.

It is very important that the additive wets and infiltrates completely and fast to all SiC particles during the liquid-phase sintering. Considering that all contact angles of all additives were near zero [24–26] and that their densities and radii of pores of SiC substrates are very similar, we conclude that the superficial energy in liquid/vapor of the additives should be different. The fact that the infiltration rate of NY system is superior to other systems indicates that the formed liquid is probably less viscous.

4. Conclusions

In the additive systems of AY, ARE, AS and NS the infiltration is insignificant when compared with the additive systems of NY and NRE. NY system produces a liquid with more capillary rise, being a promising additive for the production of SiC ceramics via infiltration. The system containing AlN, besides infiltrating a lot and very fast the SiC substrate, promotes the solubilization and precipitation process through the all infiltrated region. The solution-precipitation process is responsible for the most expected microstructural modifications to obtain good mechanical properties. However, the use of NY system should critically be to avoid formation of carbides that may deteriorate the ceramics, compromising their mechanical properties. The quantity of NY in the composition of SiC and the time are primarily for the success of the sintering process. High quantities and long time of sintering can damage the SiC/NY ceramics.

The infiltrated ceramics have microstructural characteristics similar to SiC ceramics sinterized by liquid-phase, suggesting a new process to obtain those ceramics in lower temperatures and shorter time. Besides that, the infiltration process permits the production of samples with different shapes, which need a very exact dimensional control that will be very difficult to obtain by liquid-phase sintering.

Acknowledgments

We sincerely thank to CNPq (grants 302612/2004-1 and 142090/2001-8), to FAPESP (grants 01/11339-1 and 01/10664-6), and to Instituto Nacional de Pesquisas Espaciais–INPE, for the density analysis.

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