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Phase stability and microstructure of $MgAl_2O_4$/SiC composites sintered in argon atmosphere

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Abstract

The phase stability of $MgAl_2O_4$-SiC composites was studied under low oxygen pressures. Mixtures of spinel and silicon caribide were isostatically pressed and then treated at 1550 and 1650°C in argon atmospheres. Sintered samples were analyzed using XRD, pycnometry, EDAX and SEM. A second alumina-rich spinel appeared due to surface reactions of spinel and SiC grains. This was accompanied by a weight loss of samples due to Mg volatilization. Sintered composites did not reach high densities.

Keywords: D. Spinel; D. Silicon carbide; Composite sintering

1. Introduction

Magnesium-alumina spinel is one of the most common compounds in a family of mixed oxide spinels having a cubic structure [1]. This compound offers a good combination of physical and chemical properties such as high melting point, high resistance to chemical attack, high mechanical strength and consequently it can be used in metallurgical industry, cement, glass, etc. [2]. Some of these properties would be enhanced if a second phase, like SiC, is added to spinel as in Al_2O_3/SiC ceramic composites [3,4]. When SiC is incorporated into an alumina matrix as whiskers, the best mechanical properties are achieved. However, it is possible to add, as an alternative SiC in platelet or powder form due to unhealthiness of whiskers [5].

SiC is easily oxydized in air, so low pressure oxygen atmosphere is required for sintering of silicon carbide ceramics. Spinel sintering has been mainly studied in air. It is well known that reducing atmosphere produces the reaction and volatilization of Mg. This fact is easily verified through thermodynamic studies and it is frequently observed in ceramics and refractories based on MgO at high temperature [6]. Weight loss by volatilization is observed as a result of this phenomenon. However, there exist few data and studies of the magnesium spinel behaviour under reducing atmospheres with respect to its stability as well as its microchemistry.

Silicon carbide can act as a reducer of oxide compounds under low oxygen pressures. $MgAl_2O_4$ in contact with carbon at temperatures below 1500°C and oxygen partial pressure higher than $Po_2 > 10^{-10}$ starts to develop some intergranular porosity. This is produced by the faster diffusion of Mg (relative to Al) towards the higher oxygen potential [7,8]. This process of spinel reduction does not lead directly to alumina but it produces an alumina rich spinel [8,9].

In this work, $MgAl_2O_4$/SiC powders are sintered under low oxygen atmosphere (argon). Phase stability and microstructure of the obtained $MgAl_2O_4$/SiC composites are studied.

2. Experimental

Two stoichiometric spinels were used as starting materials. One commercial Baikoski (spinel A) and the other one was obtained by reaction of $Mg(OH)_2$ (purity > 99%) and alumina A 16SG of ALCOA (spinel B).

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Table 1
Chemical analysis of the spinels (wt%)

	A	B
Al_2O_3	71.9	71.9
MgO	26.01	27.3
SiO_2	0.16	0.17
CaO	0.20	0.17
Na_2O	0.005	0.03
K_2O	0.011	0.002
TiO_2	0.004	0.01
Fe_2O_3	0.11	0.06
LOI	0.39	0.60

The chemical analyses of spinels are shown in Table 1.

The SiC used was provided by Fabril Casale (Argentina) and its composition is shown in Table 2. Two grain sizes of SiC were used. One of them of fine grain called (1200) $d_{50} = 5$ μm and the other of coarse grain named (325) $d_{50} = 20$ μm. The argon utilized had impurities lower than 10 ppm (O_2, N_2, H_2O). In some experiments, carbon monoxide (CO) of high purity was used as the reaction atmosphere.

Mixtures with a content of 10 and 50% of SiC with spinel were prepared by weighing the calculated amounts of spinel (A or B) and the SiC (1200, 325). These mixtures were wet mixed using plastic vessels and zirconia balls, then they were dried and passed through a 70 ASTM sieve. The mixtures were isostatically pressed as cylinders of 2 mm in diameter and 5 mm in length at 200 MPa. Sintering was carried out in a sintered alumina tube with gas circulation. The pressure used was 0.05 MPa above the atmospheric pressure. The gas flow was near 0.5 l/min. The heating rate was 10°C/min. The densities were measured with Hg pycnometry. Crystalline phases were characterized by XRD using a XPERT (Philips) equipment. The lattice parameters were determined using the Rietveld method [10]. The weight loss was determined by weighing the samples before and after the occurrence of the reaction. Micrographs were obtained with a SEM Philips 505 and the Mg/Al ratio was analyzed by EPMA.

Table 2
Chemical analysis of SiC

	%
SiC	98.5
SiO_2	< 1
C	< 1
Si	< 0.1
CaO	< 0.1
MgO	< 0.1
Fe_2O_3	< 0.3

3. Results and discussion

The use of graphite crucibles as containers for sintering (and graphite powder) reduced the O_2 content in the argon gas. Under these conditions, a partial oxygen pressure is lower than 10^{-15} atm.

The detailed analysis of the reaction products by XRD does not show the presence of crystalline phases of the Si–Al–O–Mg system such as cristobalite, magnesium silicates, etc. Glassy phases are not clearly detected by this method. However, XRD analyses showed: the appearance of double peaks of spinel, the intensity reduction of SiC peaks in some samples exposed to extreme conditions and the appearance of small amounts of α-Al_2O_3. Figs. 1 and 2 show the double peaks of spinel which appear after sintering.

The detailed analysis of the double peaks of spinel was carried out using the Rietveld method. Thus, the higher peak corresponds to one spinel with lattice parameter (a_0) equal or slightly lower than that of the original (stoichiometric) spinel. Table 3 shows the lattice parameters obtained of both spinels, the double (new) peaks have a lower height corresponding to a spinel with a cell parameter a_0 between 8.017 and 7.980 Å. This second spinel has a structure with parameters slightly deformed ($a = b \neq c$) while the majority of spinels have an only a_0 cubic parameter.

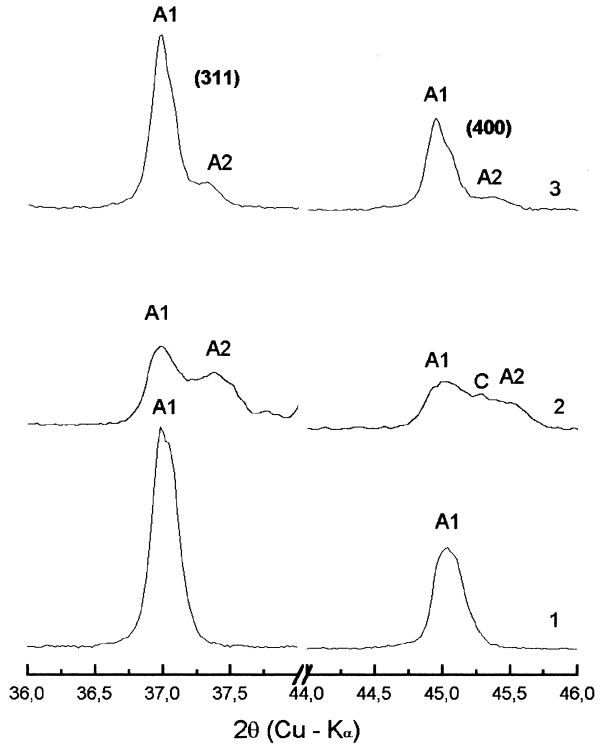

Fig. 1. X-ray diagram of (311) and (400) spinel peaks of: (1) original spinel A (without SiC); (2) spinel A with 50% of SiC treated at 1550°C; (3) spinel A with 10% SiC treated at 1600°C.

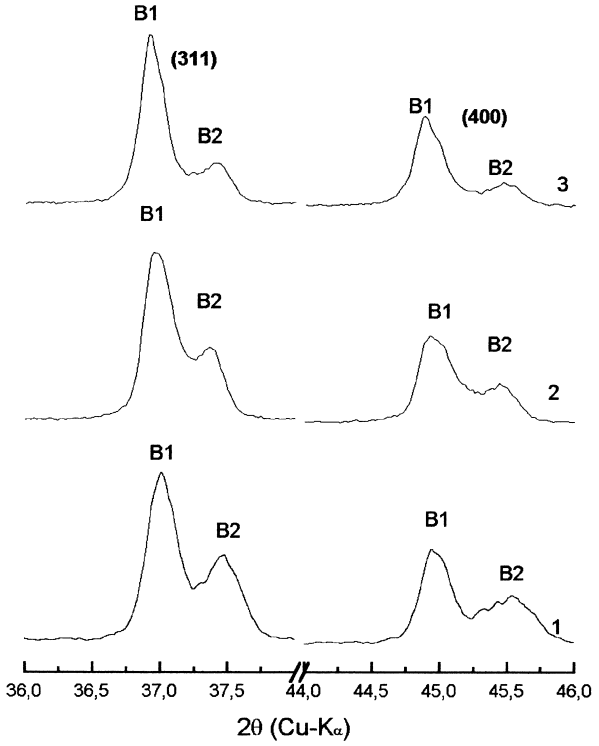

Fig. 2. X-ray diagram of (311) and (400) spinel peaks of: (1) original spinel B with 10% SiC (1200) treated at 1650°C; (2) spinel B with 10% SiC (1200) treated at 1550°C; (3) spinel B with 10% SiC(325) at 1650°C.

Fig. 3 shows the relation between the lattice parameter and the spinel stoichiometry [11]. Alumina magnesium spinel has a cubic structure. This structure is maintained up to 92% of alumina content accompanied with a decreasing lattice parameter a_0. This would be the limit of the solid alumina solution in spinel corresponding to a MgO.5 Al_2O_3 spinel with a cubic structure. γ-Al_2O_3 appears as second phase when the solubility limit is reached. Alumina is transformed into α-Al_2O_3 phase if high temperatures are employed. In our sintering conditions alumina enrichment can be associated with Mg loss through an equation of the type:

$$a\mathrm{SiC} + b[n(\mathrm{Al_2O_3})\mathrm{MgO}] \rightarrow (b-2a)[n'(\mathrm{Al_2O_3})\mathrm{MgO}] + 2a\mathrm{Mg_{(g)}} + a\mathrm{CO_{(g)}} + a\mathrm{SiO_{(g)}} \quad (1)$$

This reaction would be favored by the circulating atmosphere that removes the gaseous products. This reaction is similar to the Mg elimination in the SiC–talc–N_2 system studied by Mazzoni et al. [12]. Reaction (1) is responsible for the weight losses in the samples and for the appearance of the alumina-rich spinel.

The quantitative analysis by using the Rietveld method [10] on some selected samples is shown in Table 4. Some general tendencies may be established: The amount of original (stoichiometric) spinel tends to decrease with increase of temperature and reaction time. At the same time, the alumina-rich spinel increases with these parameters. Comparing with the XRD patterns of both spinels, it is found that the alumina-rich spinels have greater peaks width.

The sintered samples are affected by weight losses in the range between 9 and 23%. This indicates an important degree of the reaction in this system. Spinel B seems to be more reactive than spinel A.

The $SiO_{(g)}$ loss was proved in an indirect way by the amorphous SiO_2 deposition in the graphite crucibles, while the Mg loss was proved by comparative measurements using EDAX.

The experimental results reported by Mazzoni et al. [12] with SiC–talc–N_2 and SiC–clay–N_2 systems showed that, the reaction occurs on the mineral surface due to the low porosity and the covalent structure of SiC grains. So, MgO diffuses towards the SiC and a simplified reaction can occurr:

$$\mathrm{SiC} + 2\mathrm{MgO} \rightarrow \mathrm{SiO_{(g)}} + \mathrm{CO_{(g)}} + 2\mathrm{Mg_{(g)}} \quad (2)$$

The appearance of the alumina-rich spinel is in accordance with the weight loss measured in the

Table 3
Cell parameters of the sintered samples

Sample	Reaction conditions	Spinel 1 normal a_0 (Å)	Spinel 2 Al_2O_3 rich a_0 (Å)
A (0% SiC)	1600°C, 120 min	8.082	—
A325 (10% SiC)	1550°C, 120 min	8.065	8.015
A1200 (10% SiC)	1550°C, 120 min	8.081	8.011
A 325 (50% SiC)	1550°C, 120 min	8.054	7.981
A1200 (50% SiC)	1550°C, 120 min	8.054	8.000
A1200 (10% SiC)	1650°C, 42 min	8.065	$a=b=7.99$; $c=7.97$
A1200 (10% SiC)	1650°C, 120 min	8.077	8.13
B (0% SiC)	1600°C, 120 min	8.076	—
B1200 (10% SiC)	1550°C 120 min	8.069	7.997
B1200 (10% SiC)	1650°C, 42 min	8.081	$a=b=7.981$; $c=8.008$
B325 (10% SiC)	1650°C, 120 min	8.074	7.980

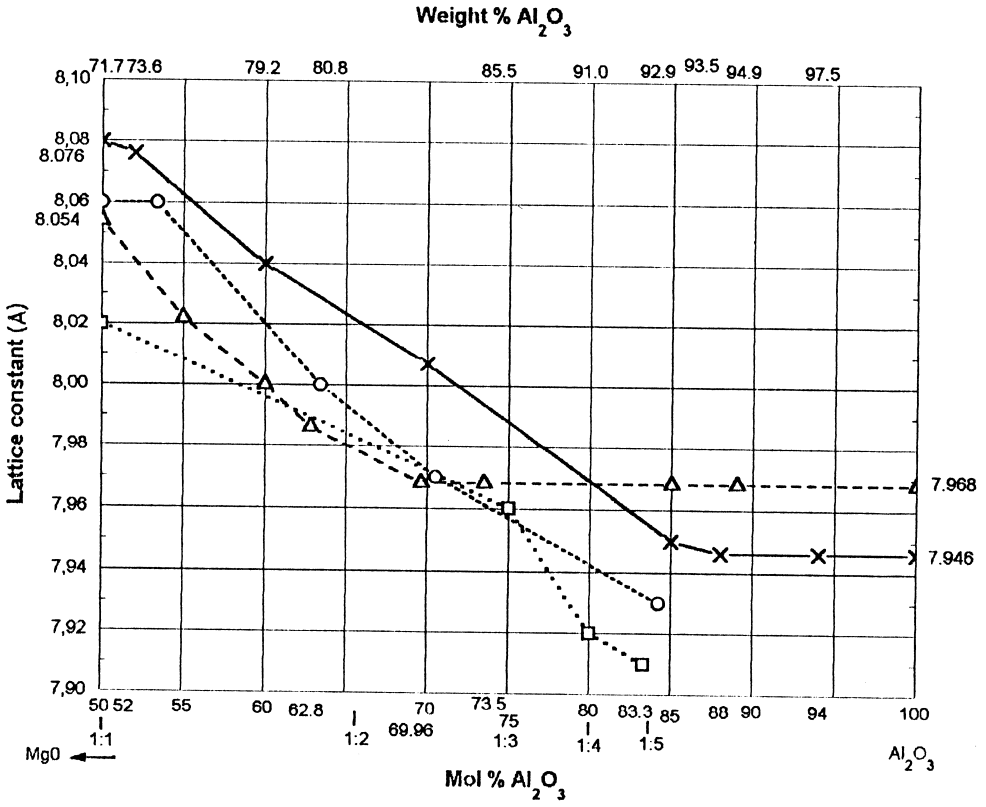

Fig. 3. Relation between lattice parameter (a_0) of ss-$MgAl_2O_3$ and Al_2O_3 content; from Navias [11].

sintered samples. A correlation between the phases formed (amount) (both spinels + alumina) and the weight loss was observed.

The grain size of the SiC used did not have a great influence on the present reaction. The increase of SiC content (50%) in the original mixture generates a greater amount of alumina-rich spinel.

The reaction produces a MgO removal with a subsequent alumina-rich spinel zone around the SiC grain. The presence of two kinds of spinels shows that MgO volatilization on the SiC surface is faster than the diffusion from the spinel towards the SiC. So a zone near SiC with an alumina-rich spinel is obtained and the remainder is one spinel similar to the original one.

The increase of SiC content produced an extent of reaction due to the higher possibility of SiC-spinel to contact surface.

Reaction (1) as well as reaction (2) produced CO gas as a reaction product. Some experiments in CO atmosphere were carried out as additional verification. The sintered products obtained did not show the formation of alumina-rich spinel except traces in some samples with high content of SiC (50%) and temperatures of 1650°C. Weight losses detected were smaller than 5%

Table 4
Quantitative determinations in some selected samples

Sample	Initial SiC content (%)	Reaction conditions (°C-min)	Spinel 1 (normal) *a*	Spinel 2 (Al_2O_3 rich) *b*	α-Al_2O_3 *c*	SiC[a]	Total phases[a] $a+b+c$	Weight loss (%)
A 1200	50	1550–120	25	18	2	55 (51.3)	45 (48.7)	7.1
A 325	50	1550–120	22	22	5	51 (52.3)	49 (47.7)	11.9
A 1200	10	1550–120	80	12	0	8 (8.3)	92 (91.7)	6.9
A 325	10	1550–120	73	14	2	11 (8.7)	89 (91.3)	5.33
B 1200	10	1550–120	62	30	0	8 (5.7)	92 (94.3)	15.7
A 325	10	1650–42	81	10	0	9 (8.8)	91 (91.2)	5.0
B 1200	10	1650–42	74	18	0	8 (7.4)	92 (92.6)	10.2
A 1200	10	1650–120	68	23	0	9 (6.8)	91 (93.2)	12.2
B 325	10	1650–120	55	36	0	9 (5.7)	91 (94.3)	15.6

[a] Theoretical calculation ( ) based on weight losses and Eqs (1) and (2)

and the SiC peaks did not vary their height in XRD patterns. These facts evidence the repressing effect of CO, and that reactions (1) and (2) certainly occur.

Fig. 4 shows the micrographs of the reaction products. The SiC grains are separated by the matrix probably due to the reaction produced. In the photograph, it can be observed that several SiC grains were removed during polishing. The EDAX analysis reveals that the matrix is enriched in alumina near the SiC grains. Alumina concentrations of 84–86% corresponding to MgO. $5Al_2O_3$ (Fig. 3) were measured near the SiC grain. Silica was also detected in the matrix, around the SiC grains.

The density of sintered compacts was measured and some of these data are shown in Table 5. Densities were relatively low by the weight loss and by the removal of the gaseous products. The theoretical density of the spinel-SiC mixture (9:1) is 3.54 g/cm^3. The formation of alumina-rich spinels did not produce increases of density because there were similar densities in all the composition range [7]. The high density of sample (B 325) was reached because a low weight loss was measured in this sample after sintering.

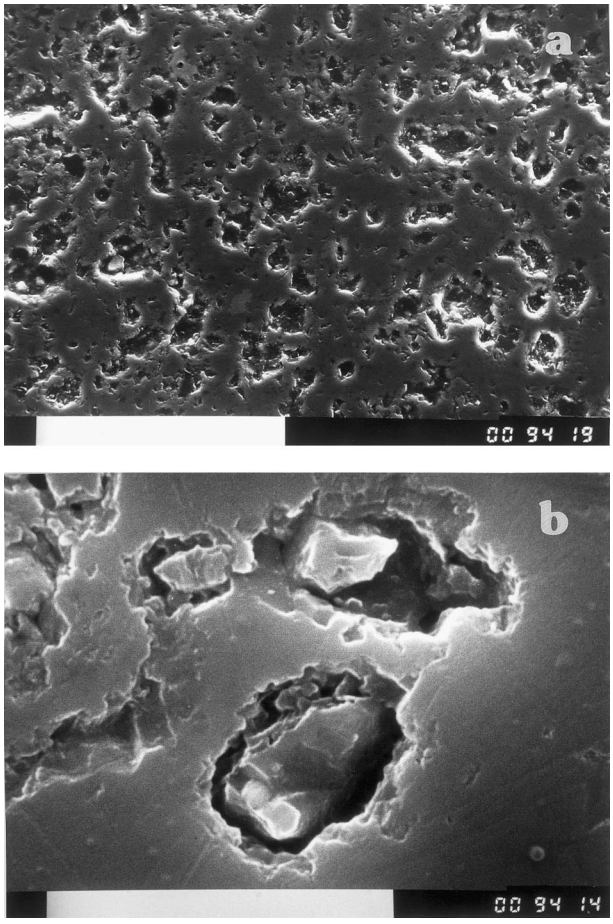

Fig. 4. Micrographs of spinel-SiC composites [spinel A with 10% SiC]. (a) scale bar 100 μm; (b) scale bar 10 μm.

Table 5
Density determined on samples with 10% of SiC (1650°C, 120 min)

Sample	Density	% Theoretical
A 325	3.08	87.0
A 1200	3.10	87.5
B 325	3.11	87.9
B 1200	2.91	82.2

4. Conclusions

$MgAl_2O_4$/SiC powders were sintered under argon atmosphere in the range 1550–1650°C. The composites obtained were studied and analysed using: XRD, EDAX, SEM and pynometry techniques. During sintering the spinel reacts with SiC, and a defined alumina rich spinel (MgO.5 Al_2O_3) is formed in the interface.

A weight loss due to magnesium volatilisation is observed during sintering. Final composites have a density near to 87% of the theoretical one.

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