CERAMICI COMPOZITE PE BAZĂ DE CARBURĂ DE SILICIU ŞI OXID DE SILICIU VITROS OBȚINUTE ÎN CONDIȚII DE SINTERIZARE NECONVENȚIONALE
CERAMIC COMPOSITE BASED ON SILICON CARBIDE AND VITREOUS SILICON DIOXIDE OBTAINED UNDER UNCONVENTIONAL SINTERING TREATMENT

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The aim of present work was to obtain ceramic composites based on silicon carbide and vitreous silicon dioxide, under unconventional thermal treatment and sintering conditions.

Due to the low densification ability of silicon carbide, sintering additives were used to enhance the process. Thus, to the studied ceramic composites it was added in fixed proportion (10% wt.) a third component as sintering aid, namely: alumina, mullite and cubic zirconia.

The samples, obtained by uniaxial pressing, were sintered by unconventional methods. A first thermal treatment was performed in oxidizing atmosphere and pressure controlled Tammann kiln with graphite elements and controlled atmosphere at temperatures of 1250°C, 1350°C and 1400°C, and a pressure of 30 MPa, with a soaking time at maximum temperature of 30 min. A second unconventional sintering treatment was performed in microwave field in a multimode microwave oven with a 1600W power at a temperature of ~1320°±30°C.

The obtained ceramic bodies were characterized by phase composition (X-ray diffraction) and structural-textural (scanning electron microscopy) view point. The ceramic properties (density, absorption, open porosity) and compressive strength were determined, as well.

S-a urmărit realizarea unor ceramici compozite pe bază de carbură de siliciu şi oxid de siliciu vitros în condiții de tratament termic neconvențional.

Datorită aptitudinii de densificare scăzute a carburii de siliciu s-a apelat la adaosuri de sinterizare. Astfel, acestor ceramici compozite s-a adăugat în proporție fixă (10%) un al treilea component drept adaos de sinterizare - alumină, mulit şi zirconă stabilizată în forma sa polimorfă cubică.

Probele obținute prin presare uniaxială, au fost sinterizate prin procedee neconvenționale. Un prim tratament termic s-a efectuat în atmosferă oxidantă şi sub presiune, într-un cuptor tip Tammann cu elemente de grafit şi atmosferă controlată, la temperaturi de 1250°C, 1350° şi 1400°C şi presiune de 30MPa, cu un timp de menținere la temperatura maximă de tratament de 30 min. Un al doilea tratament termic neconvențional de sinterizare în câmp de microunde, într-un cuptor cu microunde multimod cu o putere de 1600W, la o temperatură de ~1320°C±30°.

Pe corpurile ceramice obținute s-au făcut determinări de compoziție mineralogică (difracție de raze X) şi structurale (microscopie electronică de baleiaj), determinări ceramice (densitate, absorbție, porozitate deschisă) precum şi determinări de rezistență mecanică la compresiune.

Keywords: *silicon carbide, unconventional sintering, composite, sintering aids*

1. Introduction

In order to obtain dense ceramics, a number of parameters related to powder properties must be taken into account, such as large specific surface area, processing technique used in consolidating of powders and sintering conditions – e.g. temperature and sintering time [1-2]. Controlling the sintering condition is of fundamental importance [3-7].

Related sintering additives could be a solution to promote the sintering of SiC in presence of liquid phase [6-8]. These additives have led to very good results in advanced densification of silicon nitride-based ceramics.

Sintering SiC without applying pressure becomes thus effective by using these additives, possibly by using a similar mechanism described in the case of silicon nitride sintering mechanisms. SiC grain morphology can be controlled by various processing conditions during sintering (such as sintering time, controlled atmosphere, application of strong magnetic field) [3, 6, 9, 10].

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2. Experimental

2.1. Raw materials and sintering conditions

The chemical bonds between silicon and carbon atoms in SiC have a covalent character in proportion of 88%, reducing atomic diffusivity and making it difficult to ensure an advanced densification. Therefore, there were used sintering additives that help densification, and sintering process occurs through solid-phase mechanisms. Thus, to these ceramic composites was added in fixed proportion (10%) a third component as sintering additive - alumina, mullite and zirconia stabilized in its cubic polymorphic form.

The used raw materials were: black silicon carbide from CASIROM – Turda, with a coarse fraction (0.5 mm), belonging to the specific class of G 125; vitreous SiO_2 corresponding to the fraction below 0.2 mm; calcined alumina, Al_2O_3 of grade 99.5%, advanced grinded to an average particle diameter under 4 μm; silica, grade 99.5%, advanced grinded (this additive was used with calcined alumina to form "*in situ*" mullite); zirconia, purity 99.5%, advanced grinded to an average particle diameter under 4 μm. For zirconia stabilizing in its cubic polymorphic form it was used cerium dioxide, of grade 99.9%, (10% CeO_2 related to the amount of ZrO_2 used).

The ceramic composites considered in the present study are presented in Table 1.

The raw materials were weighted and mixed dry for 1 hour. After the homogenization process, the samples were shaped into cylinders with 13 mm diameter and 13 mm height, by uniaxial pressing at 150 MPa.

The obtained green samples were thermally treated by unconventional methods, as follows:

- Thermal treatment in low oxidizing atmosphere and under pressure, in a Tammann-type furnace with graphite elements and controlled atmosphere, at temperatures of 1250°C, 1350°C and 1400°C and pressure of 30 MPa, maintaining for 30 min the maximum temperature.

- Thermal treatment in a microwave field, in a multimode microwave oven (with multiple configurations of electric field), with an output of 1600W. The temperature inside the oven was measured with a thermocouple Pt - PtRh10 in time, when the microwave field was interrupted. For treatment at ~ 1320°C±30°C (for 30 minutes at maximum temperature), the samples were placed on a ceramic substrate susceptible to microwaves. The whole assembly was wrapped in mineral wool, resistant to 1400°C. The advantage of microwave heating is the direct absorption of energy in the entire volume, at heating rates of 100-150°C/min., without cracking the ceramic body [11].

2.2. Methods of characterization

The XRD characterization was made by means of a XRD 6000 Shimadzu difractometer, using a CuKα radiation operated at 40 kV and 30.0 mA. All the diffraction profiles were obtained with a step of 0.02° and a scan speed of 2 °/min.

The morphology of the samples have been revealed by SEM images recorded by means of a Hitachi S-2600N electronic microscope equipped with energy dispersive X-ray spectrometer, with a resolution of 5 nm.

The open porosity, absorption and relative density data were obtained according to the Archimede's method.

The determination of compression mechanical strength was realized using a mechanical testing machine LFM 50kN, no. 596.

3. Results and discussions

3.1. Phase composition determined by X-ray diffraction

The obtained X-ray diffraction patterns for the reference samples, without sintering additives (noted A and B), thermally treated in oxidizing atmosphere, at different temperatures, are shown in Figure 1.

Table 1

Compositions of the considered ceramic composites / *Compozitiile compozitelor ceramice considerate*

Sample code *Cod probă*	SiC	Vitreous SiO_2 *SiO_2 vitros*	Additive / *Aditiv*		
			Al_2O_3	Mullite Mulit	ZrO_2 (with 10% CeO_2)
A	60	40	-	-	-
B	40	60	-	-	-
I_a	25	65	10	-	-
I_b			-	10	-
I_c			-	-	10
II_a	50	40	10	-	-
II_b			-	10	-
II_c			-	-	10
III_a	75	15	10	-	-
III_b			-	10	-
III_c			-	-	10

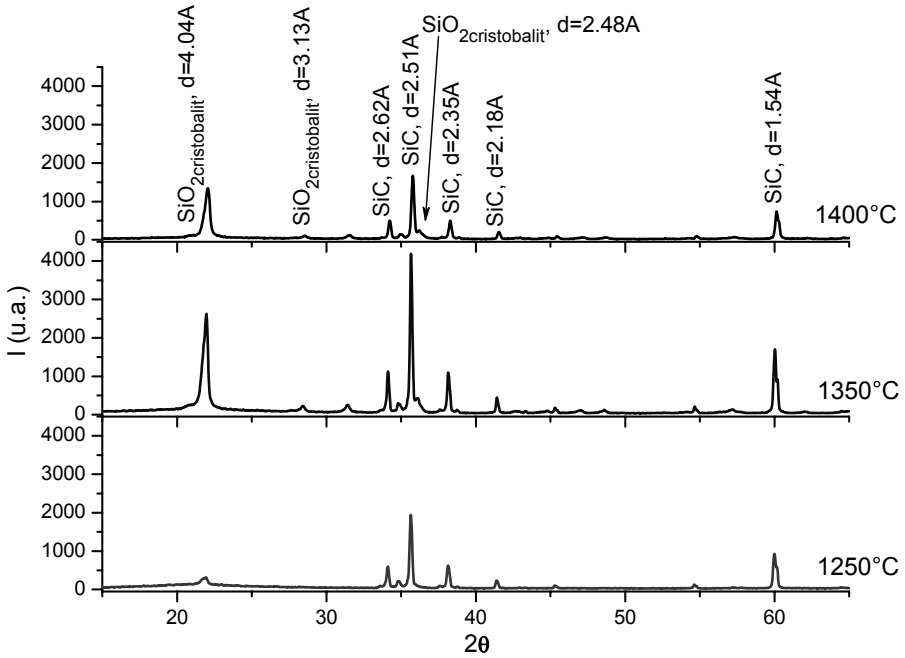


Fig. 1 - X-ray diffraction spectra of the reference samples A (a) and B (b), thermally treated in low oxidizing conditions
Spectrele de difracție a razelor X pentru probele etalon A (a) şi B (b), tratate termic în atmosfera slab oxidantă.

It can be noticed an increase of composites crystallinity, due to crystallization of vitreous SiO_2 used, up to a sintering temperature of 1350°C. Above this temperature, the characteristic peaks of SiO_2 cristobalite decreases, maybe because of a possible melting as a result of the following reaction:

$$SiC_{(solid)} + O_{2(gas)} \rightarrow SiO_{2(solid,liquid)} + C_{(solid)}$$

$$2/3\ SiC_{(solid)} + O_{2(gas)} \rightarrow 2/3\ SiO_{2(solid,liquid)} + 2/3\ CO_{(gas)}$$

$$1/2\ SiC_{(solid)} + O_{2(gas)} \rightarrow 1/2\ SiO_{2(solid,liquid)} + 1/2\ CO_{2(gas)}$$

The intensities of the characteristic diffraction peaks of silicon carbide decrease with increasing of temperature, due to oxidation process of SiC. It appears that, for composite B, with less silicon carbide proportion, its oxidation is slower, because the vitreous silicon dioxide from mixture is covering the SiC grains, preventing their oxidation.

If the conditions of thermal treatment are changed, the samples being sintered in the presence of a microwave field, X-ray diffraction spectra show that vitreous silica on composites does not crystallize, being found only specific diffraction peaks of silicon carbide - Figure 2.

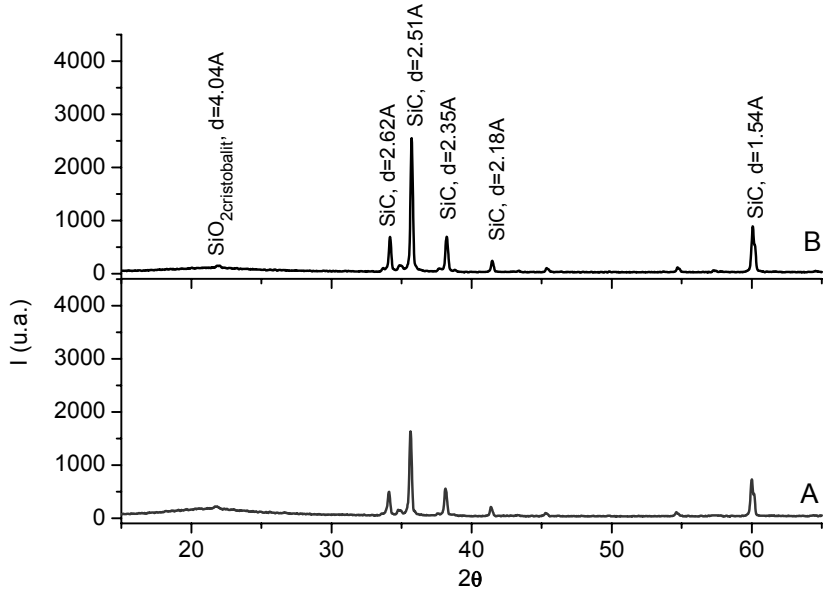


Fig. 2 - X-ray diffraction spectra of the reference samples A and B, thermally treated in microwave field / *Spectrele de difracție a razelor X pentru probele etalon A şi B, tratate termic în câmp de microunde.*

XRD spectra of the composite mixtures with sintering additives, thermally treated in oxidizing atmosphere are shown in Figures 3-5.

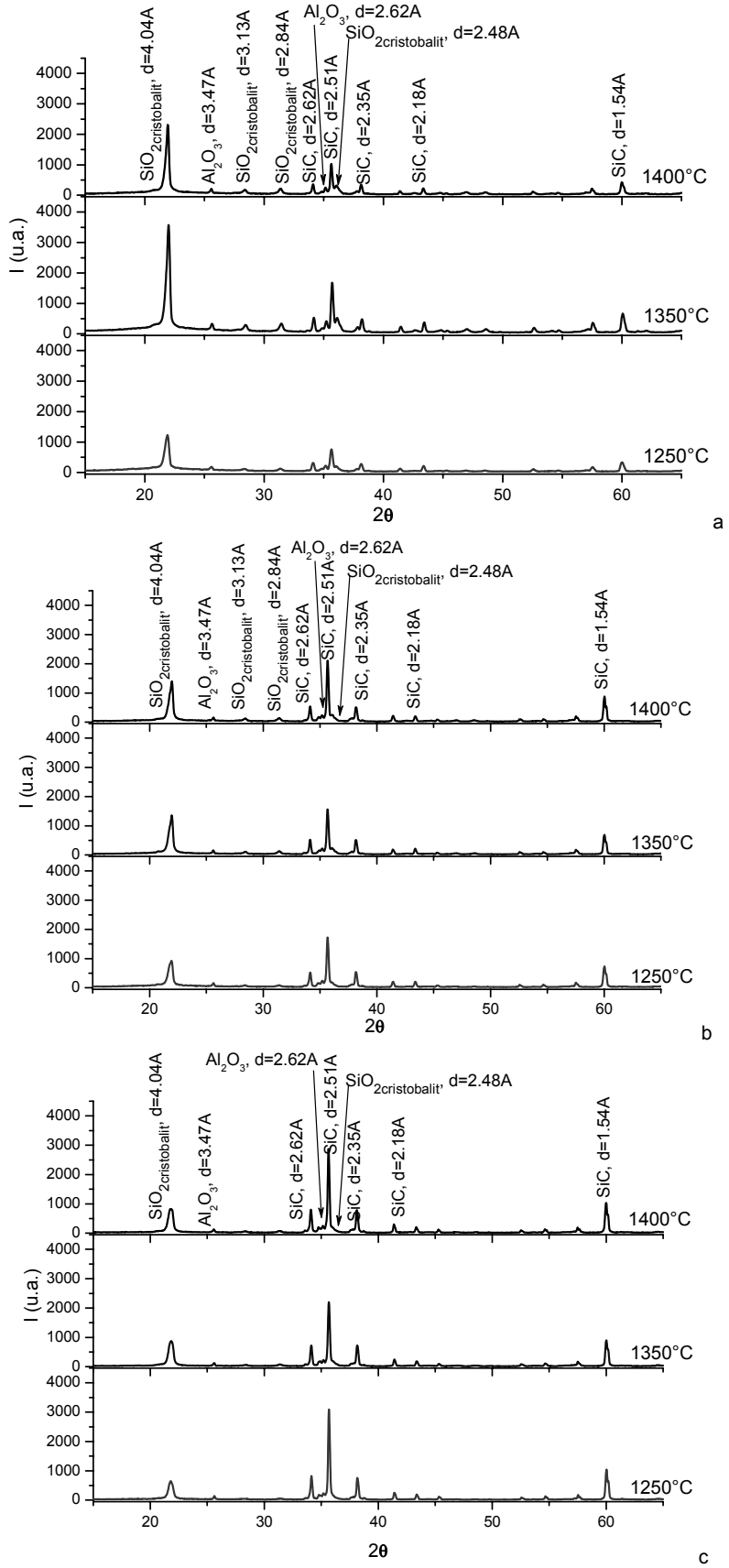


Fig. 3 - X-ray diffraction spectra of the ceramic composites thermally treated under oxidizing conditions, noted I_a (a), II_a (b) and III_a (c)
Spectrele de difracție a razelor X pentru compozitele ceramice tratate termic în atmosfera slab oxidantă: probele I_a (a), II_a (b) şi III_a (c).

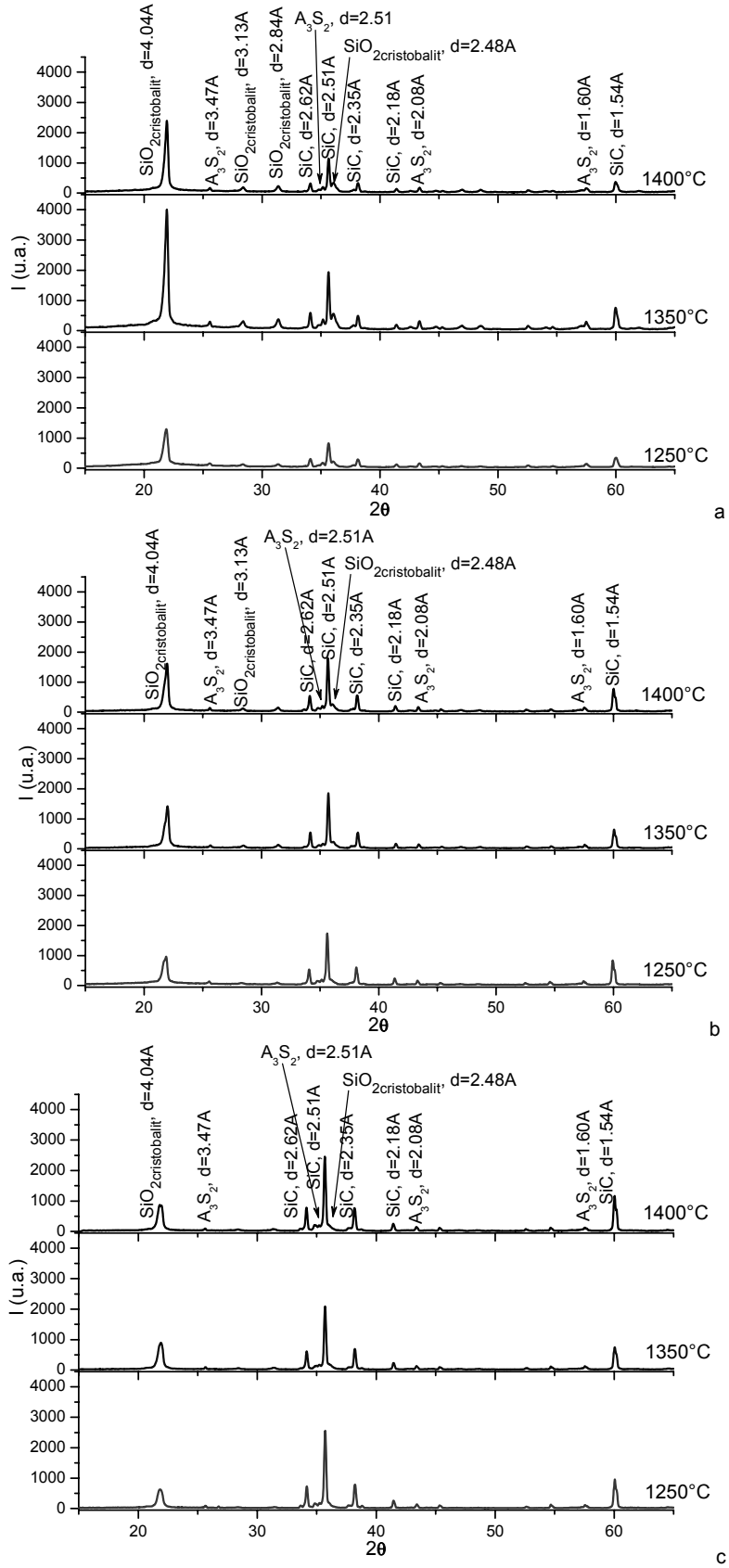


Fig. 4 - X-ray diffraction spectra of the ceramic composites thermally treated under oxidizing conditions, noted I_b (a), II_b (b) and III_b (c) . *Spectrele de difracție a razelor X pentru compozitele ceramice tratate termic în atmosfera slab oxidantă: probele I_b (a), II_b (b) şi III_b (c).*

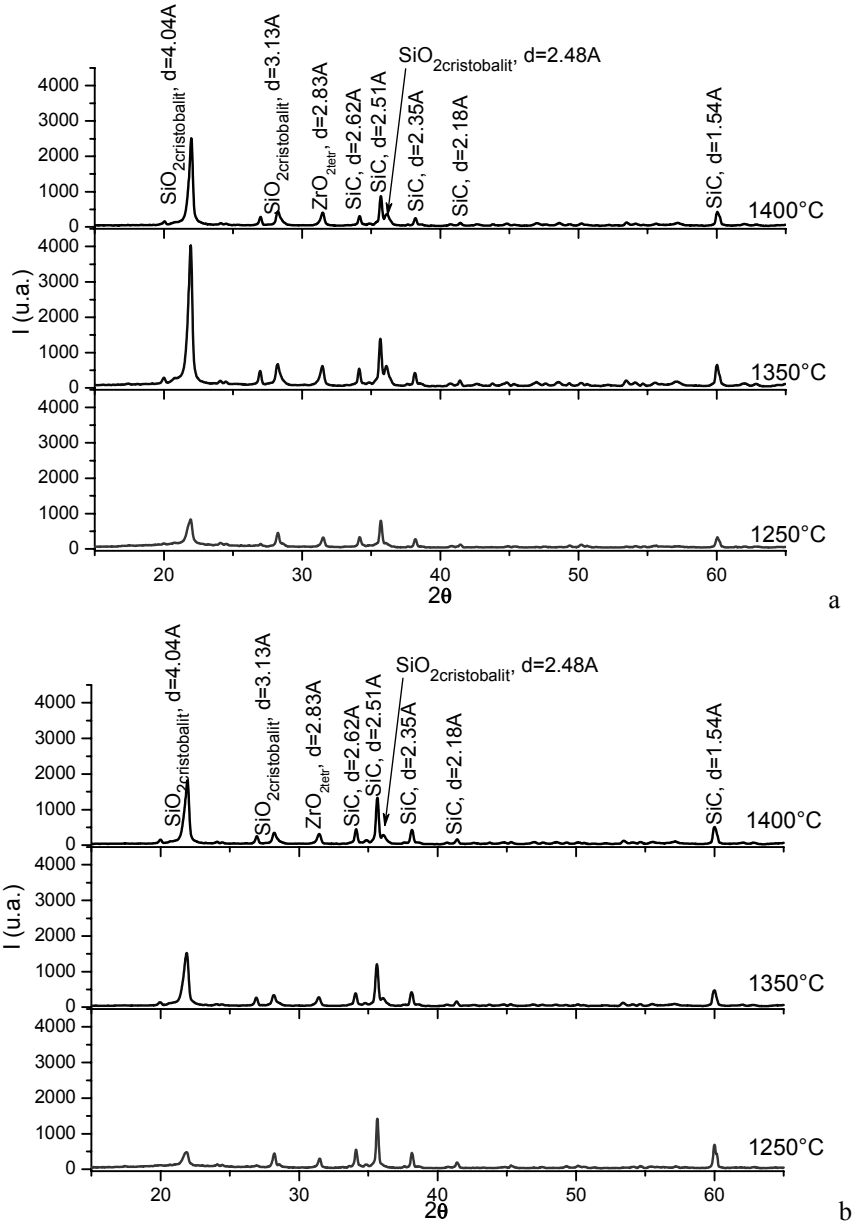


Fig 5 - X-ray diffraction spectra of the ceramic composites thermally treated under oxidizing conditions, noted I_c (a) and II_c (b) / *Spectrele de difracție a razelor X pentru compozitele ceramice tratate termic în atmosfera slab oxidantă: probele I_c (a) şi II_c (b).*

From spectra presented above it can be observed the existence of the same trend in the proportion of crystalline phases, as for the reference mixtures. Also, the characteristic peaks of sintering additives used are observed. It should be noticed that in composites I_b, II_b and III_b the desired formation of the mullite phase is observed. In the case of I_c and II_c samples, the used zirconia did not turned into desired polymorphic form (cubic).

The above figures reveal the following:

- the tendency of oxidation of silicon carbide decreases in the presence of all investigated additives and their influence could be expressed on a scale as follows:

addition of aluminium oxide> addition of mullite> addition of zirconium oxide

- the less positive effect of zirconium oxide of preventing the tendency of oxidation may be due to differences in crystallization systems of silicon carbide (orthorhombic) and zirconia (tetragonal).
- in the case of the addition of aluminium oxide, silicon carbide oxidation is the slowest in any temperature range. The use of an aluminium oxide derivative (mullite) is leading to similar behaviours of inhibitory effect of aluminium oxide, due to similar crystallographic structure of aluminium oxide and mullite.

If thermal treatment conditions are changed by sintering in a microwave field, XRD spectra show, as in the case of reference composite mixtures, that vitreous silica introduced in composites do not crystallize, being found on spectra only the specific lines of silicon carbide - figures 6 - 8, more intense or less intense

depending on its amount in the studied composite. Also, characteristic diffraction peaks of sintering additives used are observed (alumina, mullite or zirconia). However, a weak tendency of SiO_2 crystallization is observed in the composites with zirconia admixture, especially in composites with lower amounts of SiC (25% and 50%).

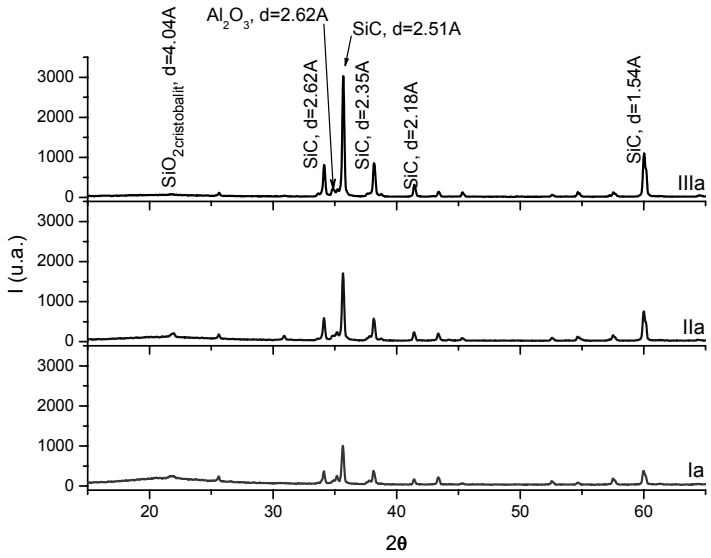


Fig. 6 - X-ray diffraction spectra of the samples with Al_2O_3 additive, thermally treated in a microwave field (for Al_2O_3 was identified only the 100% intensity diffraction peak)/ *Spectrele de difracție a razelor X pentru compozitele ceramice cu adaos de Al_2O_3 tratate termic în câmp de microunde (pentru Al_2O_3 s-a identificat doar maximul de intensitate 100%).*

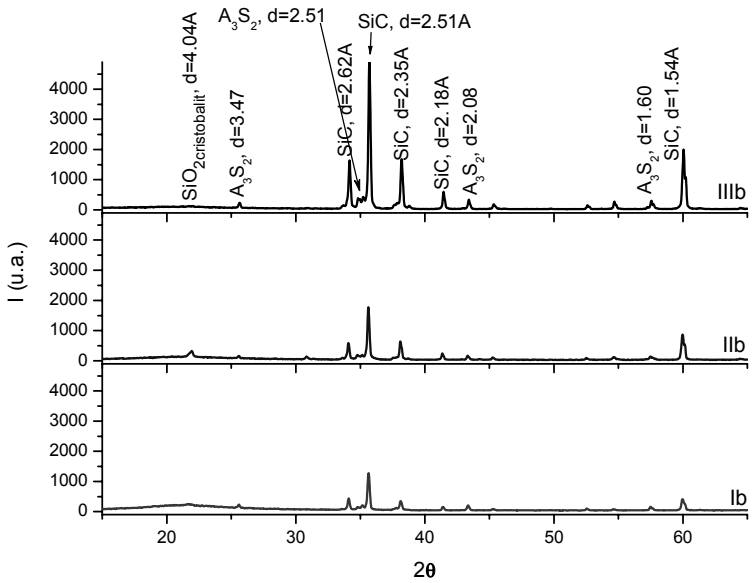


Fig. 7 - X-ray diffraction spectra of the samples with mullite thermally treated in a microwave field / *Spectrele de difracție a razelor X pentru compozitele ceramice cu adaos de mulit, tratate termic în câmp de microunde.*

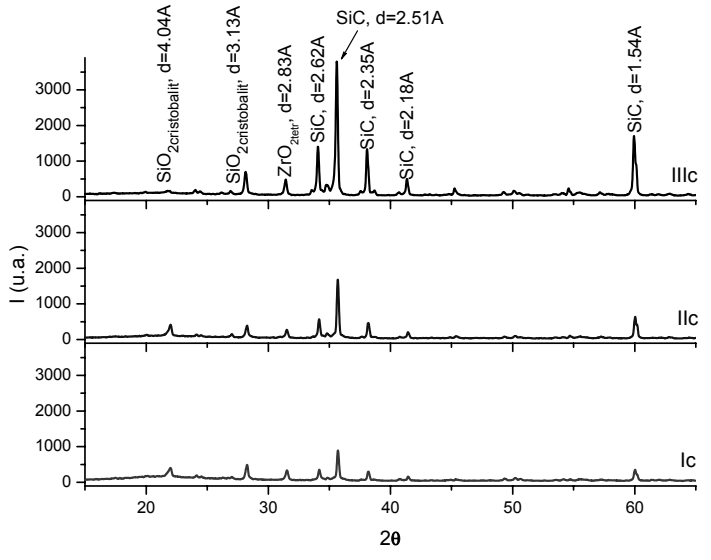
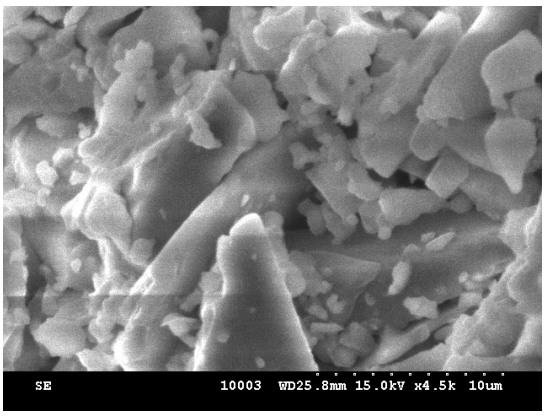


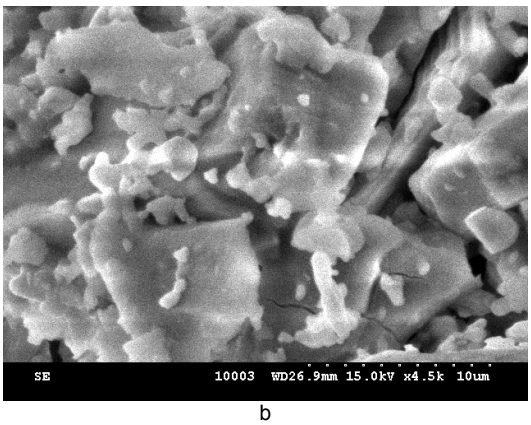
Fig. 8 - X-ray diffraction spectra of the samples with ZrO_2 thermally treated in a microwave field / *Spectrele de difracție a razelor X pentru compozitele ceramice cu adaos de ZrO_2 tratate termic în câmp de microunde.*

3.2. Microstructural analysis

Selectively relevant samples were analyzed by scanning electron microscopy, on resulting fracture surfaces after mechanical testing. The images are shown in Figures 9 - 11.



a



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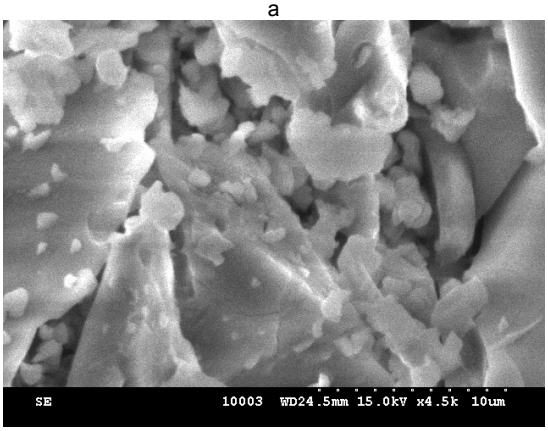
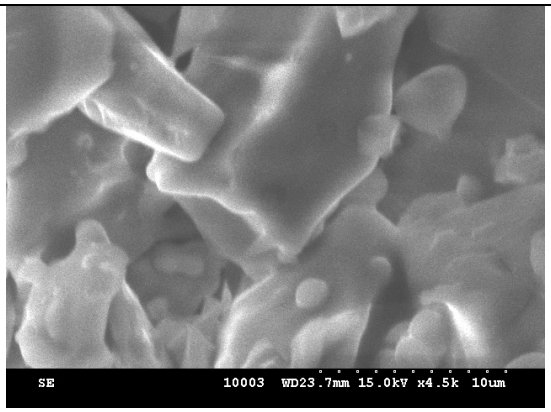


c

Fig. 9 - SEM images of the samples I_b thermally treated in low oxidizing atmosphere at various temperatures: 1250°C (a); 1350°C (b) and 1400°C (c) / *Imagini SEM ale probei I_b tratată termic în atmosfera slab oxidantă, la temperatura de: 1250°C (a); 1350°C (b) şi 1400°C (c).*



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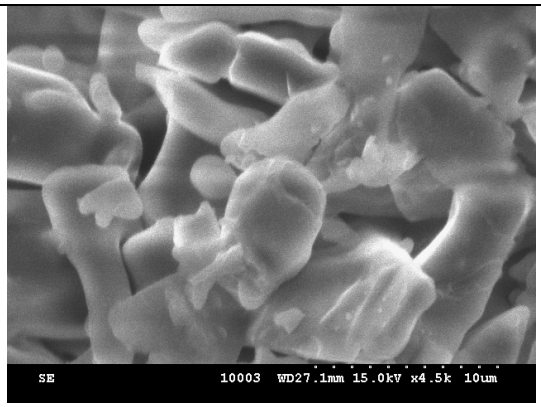

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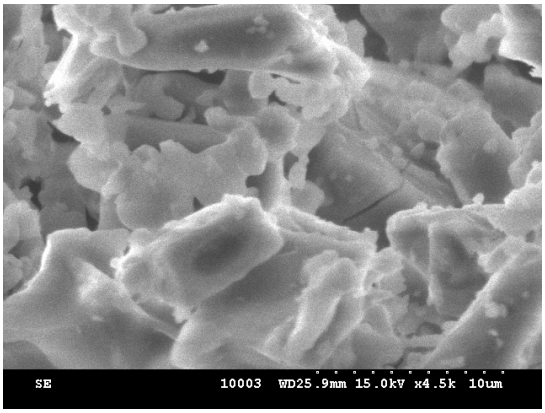

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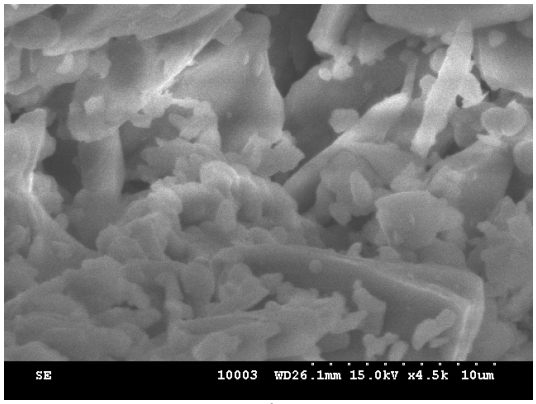
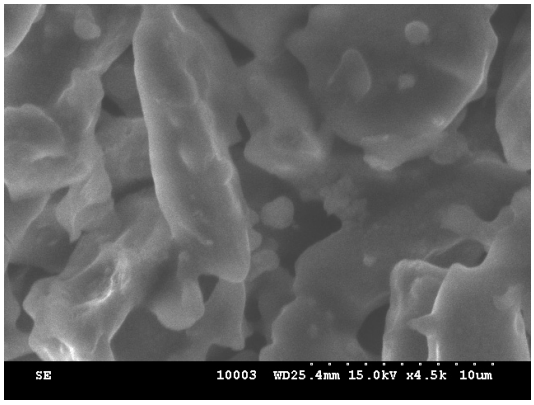


d

Fig. 10



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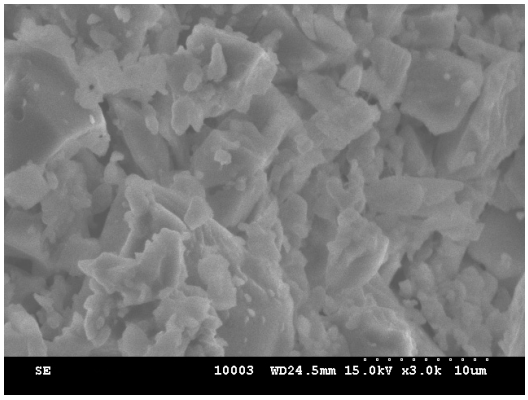

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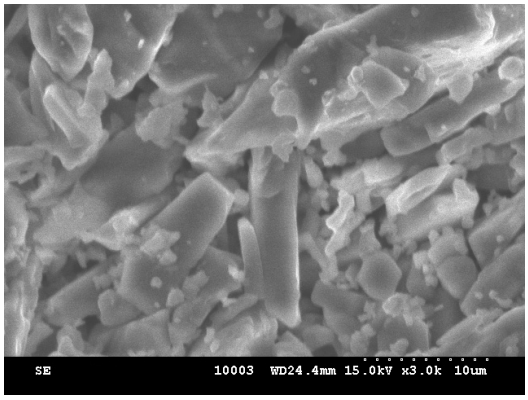
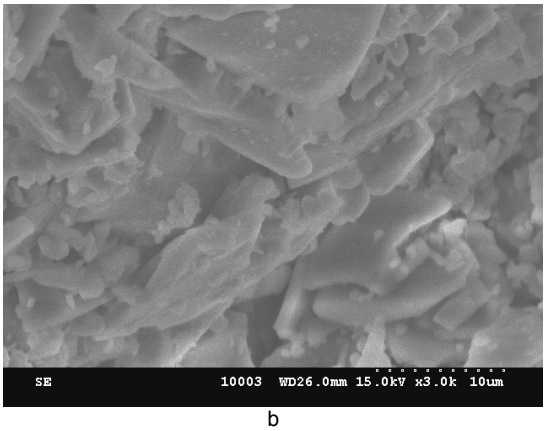


c

Fig. 10 - SEM images of the samples thermally treated in oxidizing atmosphere at 1400°C: sample A (a); sample B (b); sample II_a (c); sample II_b (d); sample II_c (e) / *Imagini SEM ale probelor tratate termic în atmosfera slab oxidantă, la temperatura de 1400°C: proba A (a); proba B (b); proba II_a (c); proba II_b (d) şi proba II_c (e).*



b

Fig. 11 - SEM images of the samples with mullite, thermally treated in oxidizing atmosphere at 1400°C: sample I_b (a); sample II_b (b) and III_b (c) / *Imagini SEM ale probelor tratate termic în atmosfera slab oxidantă, la temperatura de 1400°C: proba I_b (a); proba II_b (b) şi proba III_b (c).*

All micrographs show the presence of grains of different size, functionally different due to samples phase composition. Silicon carbide grains are ragged, with a more or less vitreous appearance (depending on the amount of vitreous silica, but also on the more or less pronounced oxidation of silicon carbide), as well as a reduced porosity with irregular pores especially due to silicon carbide irregular grains.

Figure 9 emphasizes the influence of temperature of the thermal treatment on microstructure. It could be observed that increasing thermal treatment temperature leads to an increase of composite crystallinity, having a more even contour, the amount of vitreous phase decreasing along with temperature.

Figures 10 and 11 reveal the influence of the presence and nature of the additive. Therefore it is confirmed that a greater amount of vitreous silica prevents oxidation of silicon carbide for reference samples A and B, their appearance being different. Using an additive with a minimal positive effect on the oxidation process does not change the morphology of the samples.

3.3. Ceramic characterization of the sintered samples

For all studied compositions sintered in both thermal treatment conditions, there were determined the ceramic properties. The results are presented in Tables 4 and 5.

Therefore, it can be stated that:

- increasing of thermal treatment temperature causes a more pronounced densification of the samples (specific gravity increases and porosity and absorption values decrease).

Table 4

Ceramic characteristics of the samples sintered in low oxidizing atmosphere*
Proprietățile ceramice ale probelor sinterizate în atmosferă slab oxidantă

Sample code *Cod probă*	Relative density / *Densitatea relativă*, %			Absorption / *Absorbție*, %			Open porosity, % *Porozitate deschisă*, %		
	1250°C	1350°C	1400°C	1250°C	1350°C	1400°C	1250°C	1350°C	1400°C
A	75.72	75.47	76.27	17.19	17.03	15.98	38.80	38.86	35.70
B	70.68	71.38	71.60	19.09	18.28	17.42	45.15	44.11	42.29
I_a	76.82	76.61	77.88	17.30	16.38	15.94	40.27	38.45	36.62
I_b	77.63	78.19	79.70	18.85	16.89	15.75	43.73	39.52	35.52
I_c	72.82	72.88	74.08	15.85	15.08	14.85	37.45	35.33	35.40
II_a	72.35	72.27	73.47	17.09	16.37	15.40	41.39	40.02	36.51
II_b	72.24	73.46	74.31	16.49	16.31	15.67	38.50	38.22	37.24
II_c	67.99	69.18	69.62	16.52	16.26	15.13	40.14	40.21	37.21
III_a	64.66	67.81	69.03	16.77	16.92	17.02	43.09	37.28	35.79
III_b	68.79	68.92	70.06	17.73	16.13	15.82	43.77	39.84	38.10

* Values of the properties represent the arithmetic mean of three determinations ($\sigma = \pm 1\%$) /
* *Valorile proprietăților reprezintă media aritmetică a trei determinări ($\sigma = \pm 1\%$)*

Table 5

Ceramic characteristics of the samples sintered in microwave field*
Proprietățile ceramice ale probelor sinterizate în câmp de microunde

Sample code *Cod probă*	Relative density, % *Densitatea relativă*, %	Absorption, % *Absorbție*, %	Open porosity, % *Porozitate deschisă*, %
A	74.93	18.13	41.04
B	71.61	18.91	44.80
I_a	78.15	15.12	35.13
I_b	79.43	14.79	33.60
I_c	72.37	18.10	43.61
II_a	75.57	15.13	37.71
II_b	76.41	15.09	36.82
II_c	71.78	13.41	33.52
III_a	66.08	20.62	51.78
III_b	70.49	19.33	50.00
III_c	62.52	19.00	47.29

* Values of the properties represent the arithmetic mean of three determinations ($\sigma = \pm 1\%$) /
* *Valorile proprietăților reprezintă media aritmetică a trei determinări ($\sigma = \pm 1\%$)*

Table 6

Mechanical properties of sintered samples / *Proprietățile mecanice ale probelor sinterizate*

Sample code *Cod probă*	Compressive strength (MPa) of the samples thermally treated in oxidizing atmosphere *Rezistența mecanică la compresiune (MPa) ale probelor tratate termic în atmosferă slab oxidantă*			Compressive strength (MPa) of the samples thermally treated in a microwave field / *Rezistența mecanică la compresiune (MPa) ale probelor tratate termic în câmp de microunde*
	1250°C	1350°C	1400°C	
A	92.81	92.50	93.48	20.15
B	86.63	87.49	87.76	18.24
I_a	91.54	93.90	95.46	25.30
I_b	95.15	95.84	97.69	27.82
I_c	87.26	89.33	90.80	21.48
II_a	84.25	88.58	90.05	24.14
II_b	88.55	90.04	91.08	25.34
II_c	83.34	84.79	85.33	19.87
III_a	75.24	83.12	84.61	20.65
III_b	82.32	84.48	85.87	20.98
III_c	-	-	-	18.10

* Values of the properties represent the arithmetic mean of three determinations ($\sigma = \pm 1\%$) /
* *Valorile proprietăților reprezintă media aritmetică a trei determinări ($\sigma = \pm 1\%$)*

- thermal treatment in a microwave field does not prove to be very effective, considering the ceramic characteristics obtained.
- the highest values of relative density, whatever the thermal treatment conditions (in low oxidizing atmosphere or in a microwave field), were recorded in the case of the samples with mullite.
- larger amounts of SiC in composite materials cause the decrease of relative density values, and increased absorption and open porosity, because of silicon carbide lower ability of sintering.

3.4. Mechanical characterization

In order to determine the compressive strength, a mechanical testing machine was used, whose software allows the calculation of several mechanical properties. Samples subjected to this analysis were cylinders whose diameter was equal to their height.

Table 6 shows the values obtained from compressive strength determination of the ceramic composite sintered samples.

It can be observed an increase of strength with the temperature, but increasing the silicon carbide proportion causes compression strength to decrease.

It is worth noting the very low values of compressive strength of the samples treated in a microwave field. The reason of this behaviour might be due to the short sintering time in MW field.

Once more, the superiority of the samples with sintering additive of mullite and alumina stands out.

4. Conclusions

The present research aimed the development of ceramic composites based on silicon carbide and vitreous silica through the use of unconventional thermal treatment (oxidizing atmosphere and pressure and microwave field).

In order to increase silicon carbide sintering ability within composites there were used three types of sintering additives, namely: alumina, mullite, and zirconia.

As a result of experimental investigations, the followings were found:

- increasing sintering temperature causes improvement of composite properties
- presence of mullite as admixture proves to be the most beneficial to the studied properties
- increasing amounts of silicon carbide in composites causes loss of performance due to inadequate sintering
- thermal treatment in field of microwave proves to be insufficient in order to obtain adequate mechanical and ceramic properties.

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