USING THE ADVANTAGES OF NANOTECHNOLOGY FOR THE PRODUCTION OF COMPOSITE MATERIALS OF THE TYPE NGO/CERAMIC MATRIX

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ABSTRACT

Using the advantages of nanotechnology, composite ceramic materials of the type of graphene oxide nanocolloid/ ceramic matrix were obtained in two stages. First, finely porous corundum (1500ºC) and barium titanate (1300ºC) ceramic samples containing 2 mass % graphene structures nanoplatelets were synthesized. The next stage of the study involved the preparation of graphene oxide in nanocolloid form (2 mg/ml, dispersion in H_2O) which was impregnated in the solid porous ceramic samples to obtain composite materials. For the characterization of the ceramic samples, mainly infrared spectroscopy, X-ray phase analysis, scanning electron microscopy and light microscopy were used. The results obtained from the studies carried out showed that with the introduction of small amount of graphene nanoplatelets in the initial blends followed by solid state sintering, part of the added graphene is burned out which imparts significant porosity to the ceramics obtained. On the other hand, the addition of graphene initiates the formation of well-shaped fine-grain structure of the ceramic samples, and they had sufficient porosity.

Keywords: corundum, barium titanate, porous ceramics, graphene nanoplatelets, graphene oxide nanocolloid, composite ceramic materials.

INTRODUCTION

In the production of ceramic and composite materials with specific properties, nanotechnology plays significant role for the preparation of the initial components in a finely dispersed state. This not only intensifies the synthesis but also leads to improvement and reproducibility of the properties of the products.

Combining the advantages of nanotechnology and the classic methods of silicate technology is an innovative approach to the preparation of new and composite materials which integrates the unique functional properties of the nanomaterials with those of the ceramic materials [1].

In recent years, several research teams worked on the synthesis of ceramic nanocomposites containing nanoadditives (with thickness of several nanometers) of graphene nanostructures or reduced graphene oxide. Due to its excellent mechanical, optical and thermal properties, high electric conductivity and high specific area, graphene is an excellent nanofiller in polymeric, metal and ceramic matrices for composites. The studies of such ceramic composites showed that the introduction of small volume fractions of graphene nanoplatelets (GNP), nanocolloid graphene oxide (NGO) or reduced graphene oxide (RGO) can result in significant increase of the strength at break and the electric conductivity of the ceramic material [2 - 10].

The aim of the present work is to obtain ceramic materials of the type of NGO/ceramic matrix by a two-stage technology. First, obtain finely porous corundum and barium titanate ceramic samples containing about 2 mass % graphene nanoplatelets by low temperature synthesis. Subsequently, obtain graphene oxide in nanocolloid form and impregnate it into the solid porous ceramic samples synthesized.

EXPERIMENTAL

Initial materials and compositions of the blends

The corundum and barium titanate based finely porous ceramics were prepared by the method of solid-state sintering at comparatively low temperatures of synthesis (1500°C for the corundum and 1300°C for the titanate samples) due to the addition of 2 mass % graphene nanostructures.

The initial materials used for the synthesis of the porous ceramics were: finely dispersed Al_2O_3 and $BaTiO_3$ powders (Sigma Aldrich), one graphene source-GNP (graphene nanoplatelets (Sigma Aldrich)). While the mixing the blends, 3 mass % TiO_2 (Sigma Aldrich, purity ≥ 99.9 %) were introduced as an additive strongly decreasing the sintering temperature.

Homogeneous blends were prepared for the experiments and reference and test ceramic samples were synthesized. Part of the working blends are presented in Table 1: C0 for the corundum ceramic samples and D0 for the titanate samples.

Formation and sintering of the porous ceramic samples

The synthesis of the porous ceramic was carried out as follows: 4 % polyvinyl alcohol was added to the prepared blends as plasticizer and then the samples were semi-dry formed on a hydraulic press at pressure of 40 MPa. The regime of drying the samples was: 120°C - 70 min, 180°C - 50 min. The samples obtained from blend C0 were sintered under the following temperature regime: at 200°C - isothermal period of 20 min, at 300°C - 20 min, at 400°C - 20 min, at 500°C - 30 min, at 800°C - 30 min, at 1100°C - 30 min, at 1300°C - 30 min and at the highest temperature of 1500°C - isothermal period of 60 min. For the samples prepared from blend D0 the regime was: at 200°C - isothermal period of 20 min, at 300°C - 20 min, at 400°C - 20 min, at 500°C - 30 min, at 700°C - 30 min, at 900°C - 30 min, at 1100°C - 30 min and at the highest temperature 1300°C - isothermal period of 60 min. The aim was to achieve maximal densification during the solid-state sintering and obtain finely porous ceramics with good mechanical properties.

Preparation of graphene oxide in nano colloid form

In the next stage of the experiment, graphene oxide in nano colloid form was obtained. Here, the initial graphite (Graphite, synthetic powder, < 20 mum (Sigma Aldrich)) was oxidized by the method of Hummer by addition of $KMnO_4$. The graphene oxide (GO) was added to deionized water and the pH of the water was corrected to 11.0 by adding NaOH. The resulting suspension was treated with high power ultrasound (about 200 W) for 2 h. The aim was to obtain colloid dispersed system: water-based solution of GO with well dispersed structures. The concentration of the nanocolloid graphene oxide (NGO) obtained by this technique was estimated to be 2 mg/ml dispersion in H_2O. In the last stage of the experiment, the colloid particles of graphene oxide were impregnated into the solid porous ceramic samples synthesized to obtain composite ceramic material of the type of NGO/ceramic matrix. The composites obtained with compositions C1 and D1 were dried at 120°C for 60 min.

Methods of analysis

The following analysis methods were used to study and characterize the ceramics synthesized:

Infrared spectroscopy

The FT-IR - studies were carried out on an infrared spectrophotometer Tensor 27 Fourier FT-IR (Bruker, Germany) in the wavelength range 400 - 4000 cm^{-1} at resolution 1 cm^{-1}. The measurements were performed at room temperature. The sample (0.3 mg) was pressed into KBr pellet (100 mg) at pressure 2 - 4 atm.

Table 1. Working blends for part of the porous ceramic samples synthesized.

Blend composition, mass %				Sintering temperature, °C
Sample	Al_2O_3	TiO_2	GNP	1500
C0	98	3	2	
Sample	$BaTiO_3$		GNP	1300
D0	98		2	

X-ray powder analysis

The registration of the X-ray diffraction pattern was performed using automated computer controlled XRD system D500 Siemens (Germany) under the following regime: 40 kV, 30 mA, monochromatic copper radiation.

Scanning electron microscopy

The SEM analysis of the ceramic materials obtained was carried out on scanning electron microscope Tabletop SEM HIROX SH-4000M, 30x - 60000x, SE&BSE detector, voltage 5 kV - 30 kV, resolution 15 nm. The samples were preliminarily wired with gold.

Light microscopy

The light microscopy observations were performed on a digital microscope Celestron 5 MP LCD Deluxe.

RESULTS AND DISCUSSION

Some basic physicochemical properties of the ceramic samples synthesized based corundum and barium titanate (blends C0 and D0, respectively) were determined: water absorption (WA, %) apparent density (ρ_{app}, g.cm^{-3}) and apparent (open) porosity (P_{app}, %). The results obtained are presented in Table 2.

The results indicate that with the introduction of small quantity of graphene in the initial blends (2 mass %), followed by solid state sintering, the ceramic samples showed sufficient density. The corundum-based samples - blend C0, were found to have significant apparent porosity - 33.46 % and high-water absorption - 10.43 %. Therefore, the graphene structures introduced at even small quantities play the role of pore forming agent in the ceramics.

The initial blends and the sintered ceramic samples were studied by IR spectroscopy. The IR spectra obtained were thoroughly interpreted and analyzed to establish the main functional groups present in the composition of the samples containing 2 % GNP. The results obtained from the analysis of blends C0 and D0 were summarized, and they are presented in tabular form - Table 3 and graphically - Fig.1.

XRD analysis confirmed the primary crystalline phases in the synthesized ceramics. For blends C0 and C1, the main phases were Al_2O_3, Al_2TiO_5, and TiO_2 (Fig. 2a), with corundum as the predominant phase. In the barium titanate ceramics, the main phase observed was $BaTiO_3$ (Fig. 2b). The presence of these phases was proved also by the FT-IR analysis.

The morphology of the objects studied was determined by scanning electron microscopy observations (Fig. 3) and light microscopy (Fig. 4).

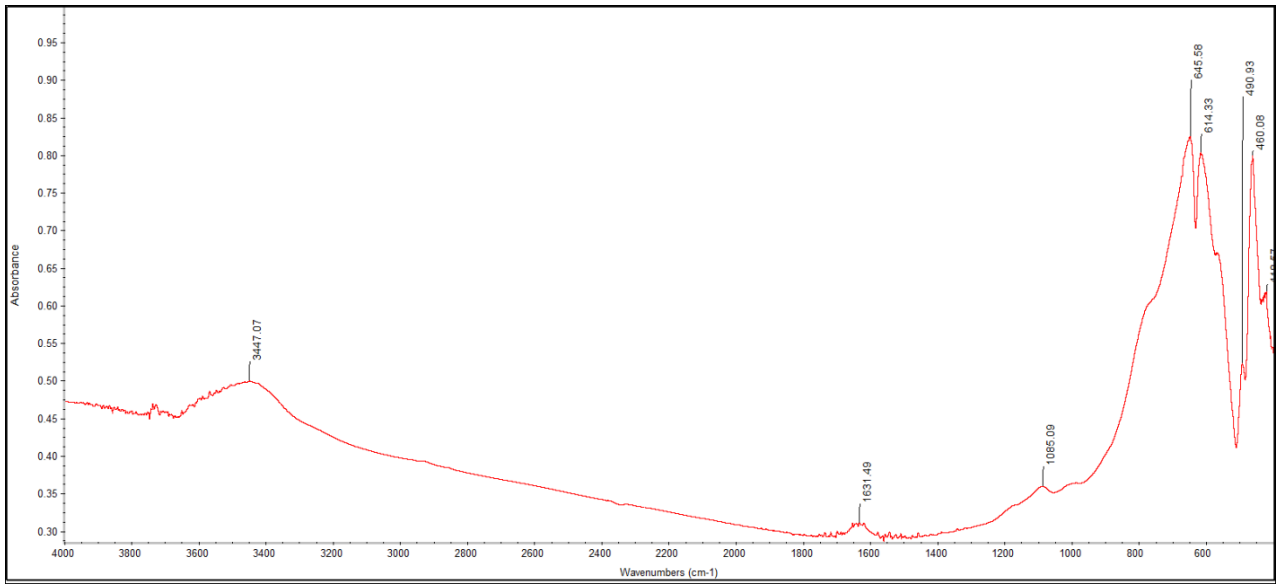
The SEM images of corundum sample without (composition C0) and with impregnated NGO (composition C1) sintered at 1500°C are shown in Fig.3. They exhibit fine-grain fine-pore structure with corundum grain sizes ranging from 0.5 to 3 μm. The results confirm that the introduction of about 2 mass% graphene nanostructures in the initial blends, followed by high temperature sintering, part of the added graphene burns out which results in formation of pores in the ceramics obtained. Following the impregnation of nanocolloid graphene oxide, the latter was distributed throughout the sample and to great extent filled the ceramics matrix pores. This was confirmed by the microphotographs of the composite material - Fig. 3b and d.

Table 2. Basic physicochemical properties of the synthesized ceramic samples with incorporated graphene structures GNP - 2 mass %.

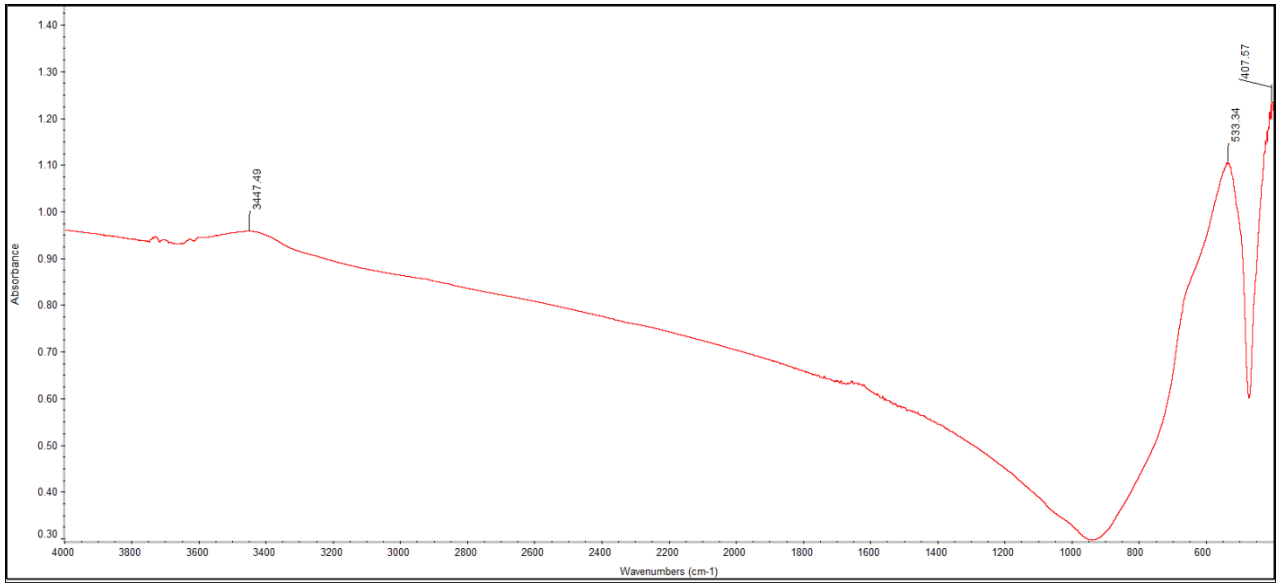
Sample/ composition	WA, %	ρ_{app}, g cm^{-3}	P_{app}, %
C0	10.43	3.26	33.46
D0	0.37	5.51	2.04

Table 3. Absorption bands and functional groups revealed in the composition of sintered ceramic samples containing 2 mass % graphene structures.

Wavenumbers, cm^{-1}		
Samples C0, sintered at 1500°C	Samples D0, sintered at 1300°C	Bond
3447.07	3447.49	C-H
1631.49	-	C=C
1085.09	-	C-O
645.58	-	Al-O
614.33	-	Al-O
-	533.34	Ba-Ti-O
490.93	-	Al-O
460.08	-	Ti-O
-	407.57	Ti-O



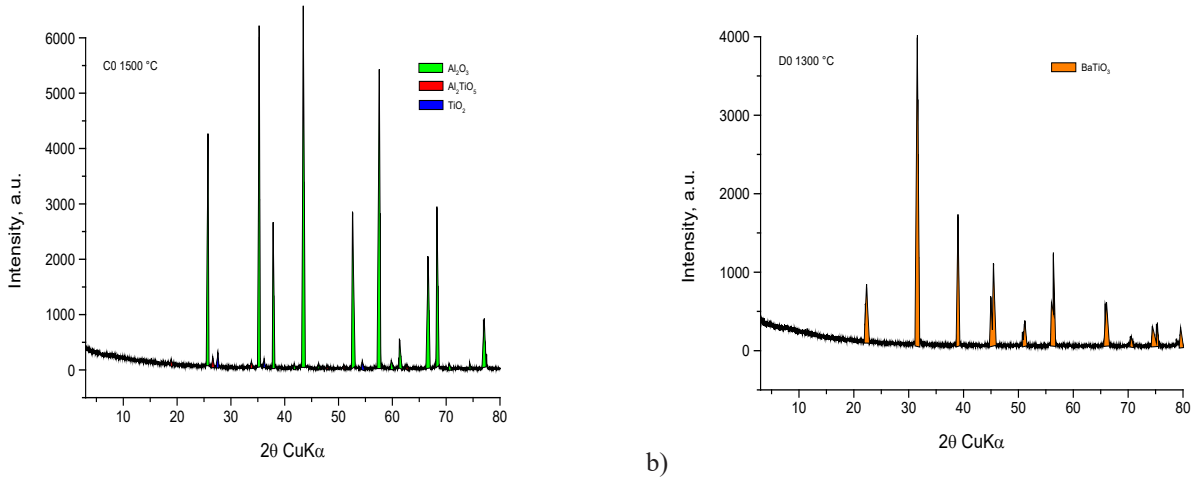
a)



b)

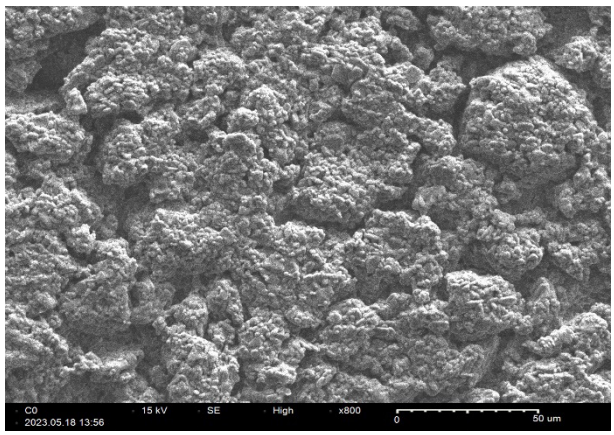
Fig. 1. FT-IR spectra of sintered ceramic samples with compositions C0 and D0: (a) FT-IR spectrum of corundum sample C0 sintered at 1500ºC; (b) FT-IR spectrum of barium titanate sample D0 sintered at 1300ºC.

The surfaces of the ceramic samples synthesized based on corundum (1500°C) and barium titanate (1300°C) with added 2 mass % graphene GNP (C0 and D0), as well as these of the ceramic matrices impregnated with nanocolloid graphene oxide NGO (C1 and D1) were studied by light microscopy. The photographs in Fig. 4 show comparatively homogeneous and fine-grain surfaces of the ceramic materials synthesized. For the impregnated ceramic matrices (C1), the nanocolloidal graphene oxide has been distributed not only on the surface but it has also penetrated in the pores of the material as confirmed by the SEM analysis carried out.

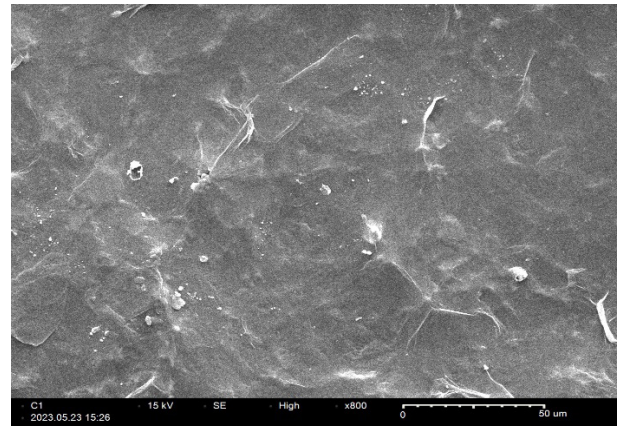


a) b)

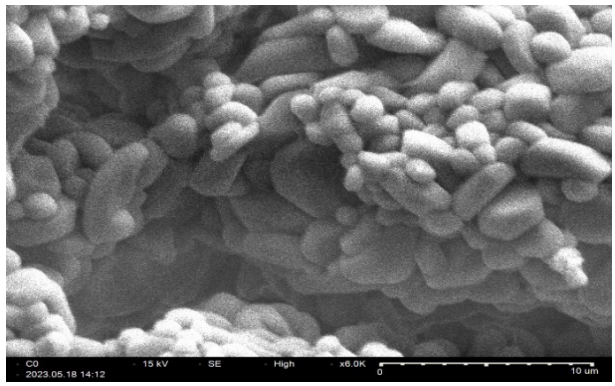
Fig. 2. Powder X-ray diffraction patterns of sample with composition C0 - (a) and D0 - (b).



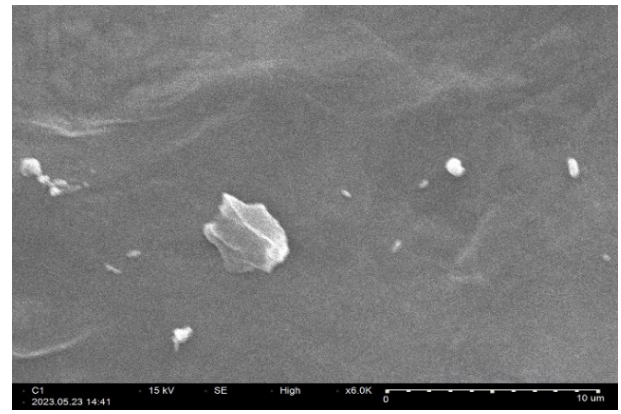
a) SEM of sample with composition C0 - x800



b) SEM of composite NGO/Al_2O_3 C1 - x800.



c) SEM of sample with composition C0 - x6.0K



d) SEM of composite NGO/Al_2O_3 C1 - x6.0K

Fig. 3. SEM images corundum based ceramic samples synthesized from blend with composition C0 and composite NGO/Al_2O_3 - blend C1.

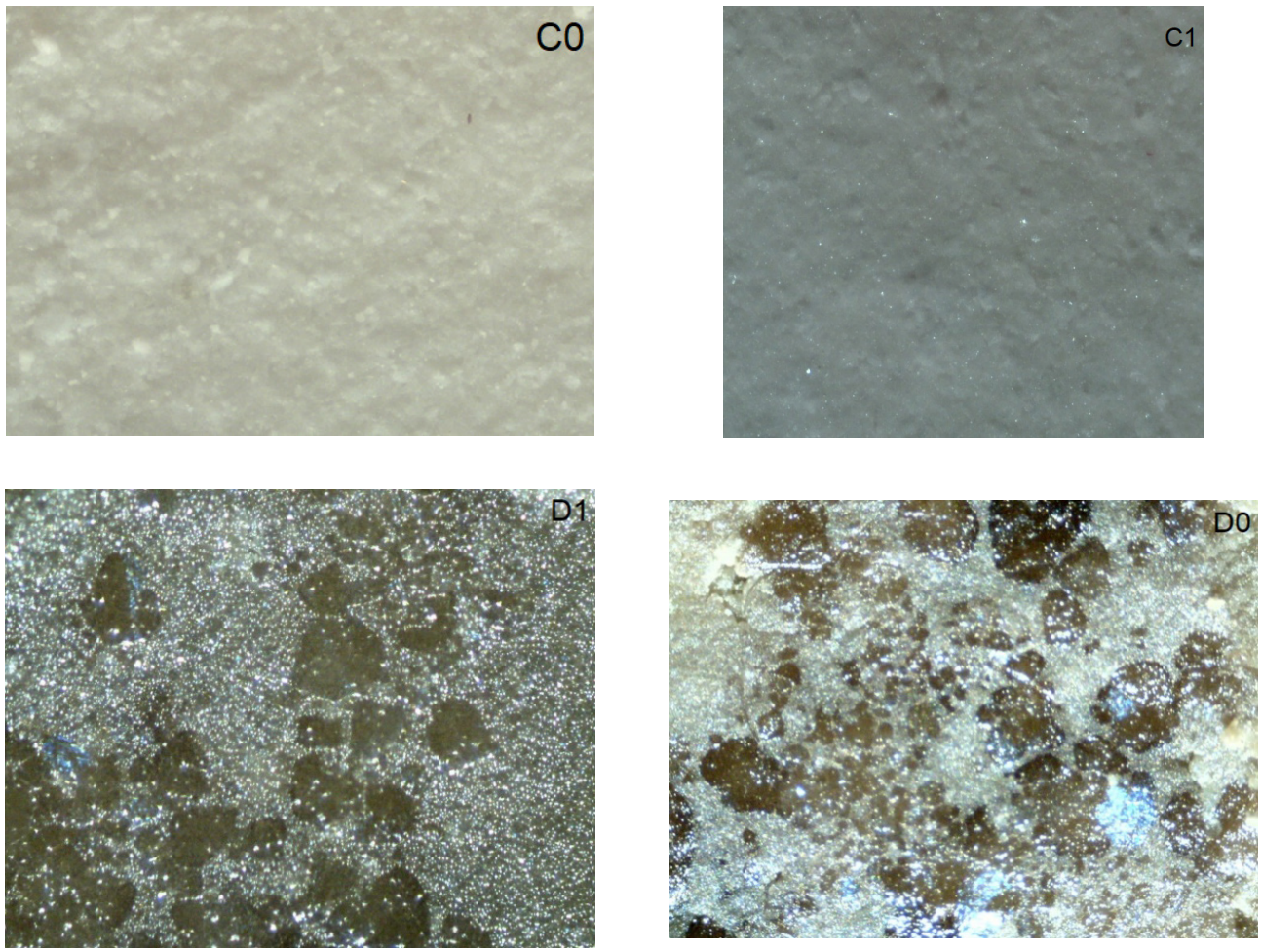


Fig. 4. Photographs of the surfaces of the ceramic materials synthesized.

CONCLUSIONS

Using the advantages of nano technology, composite ceramic materials of the type of graphene/ceramic matrix were obtained in two stages. First, finely porous corundum (at 1500ºC) and barium titanate (at 1300ºC) ceramic samples containing 2 mass % graphene nanostructures were synthesized. The results obtained showed that the introduction of small quantity graphene nano platelets GNP in the initial blends (2 mass %) followed by solid state sintering, gave ceramic samples with sufficient density. Additionally, part of the added graphene burns out which results in formation of significant porosity within the ceramics obtained. The porous ceramic materials are of substantial importance in various fields of application, including heat insulation materials, in processes of filtration, for preparation of biomedical and catalytic substrates, and as dielectric materials in electric capacitors.

In the next stage of the experiment, graphene oxide was prepared in nanocolloidal form (2 mg ml^{-1}, dispersion in H_2O) which was impregnated in the solid porous ceramic samples synthesized to obtain composite materials of the type of NGO/ceramic matrix. The SEM analysis showed that the added graphene initiated to formation of well-shaped fine corundum grains with sizes ranging from 0.5 to 3 μm. Probably, graphene enhances the effect of the TiO_2 additive and accelerates the processes of recrystallization. The SEM images of the composite material revealed that the impregnated graphene oxide was distributed not only on the surface, but it also penetrated the pores of the ceramic matrix.

The surfaces of the ceramic samples synthesized on the basis of corundum and barium titanate with added 2 mass % graphene (C0 and D0), as well as these of the ceramic samples impregnated with nanocolloidal graphene oxide NGO (C1 and D1) were studied by light microscopy. It was found that the samples had comparatively homogeneous and fine-grain structure.

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