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Preparation and characterization of NGO/Al_2O_3 composite ceramic materials

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The present paper reports on the application of a two-stage technology for the preparation of composite ceramic material of the graphene/ceramic matrix type. Firstly, finely porous corundum ceramic material was obtained using the solid-state sintering method at comparatively low temperatures for corundum materials - 1500°C - by adding graphene at a concentration of 2 mass %, as well as 3 mass % TiO_2. In the second stage of the experiment, graphene oxide was obtained in nano colloid form (2 mg/ml, dispersed in H_2O) which was impregnated into the solid porous corundum samples synthesized to obtain a composite ceramic material of the NGO/Al_2O_3 type. In the characterization of the ceramic samples, mainly infrared spectroscopy, X-ray phase analysis, scanning and transmission electron microscopy, and light microscopy were used. Some important physicochemical properties of the synthesized samples were determined: water absorption (WA, %), apparent density (ρ_{app}, g/cm^3), and apparent (open) porosity (P_{app}, %). The samples were found to have homogeneous, fine-grain, and finely porous structure.

Keywords*:* porous ceramics, graphene nanoplates, graphene oxide nano colloid, composite ceramic materials

INTRODUCTION

Worldwide, intense work is done to obtain new ceramic materials which combine the unique functional (e.g. electric, magnetic, conducting or mechanic) properties of the nanocomposite material with the properties of the traditional ceramic materials [1-4].

The development of polymeric and ceramic composites reinforced with carbon nano-fillers like carbon nanotubes (CNT), graphene nanoplates (GNP), etc., became a rapidly developing research field. Due to the improved functionality and physical properties of these materials, the implementation of the composites in various industrial branches can be significantly widened. By varying the length and shape of the carbon nanofillers, and incorporating them in small quantities, the overall performance characteristics of the matrix can be significantly improved [3-5].

It has been found from the literary survey carried out that the combination of the advantages of the nanotechnology and the classic methods of silicate technology is an innovative approach to the preparation of new composite materials which combine the unique functional properties of the nanomaterials with the properties of the ceramic materials [1-11].

The aim of the present work is to obtain composite ceramic material of the type NGO/Al_2O_3 by applying a two-stage technology. The first stage involves preparation of finely porous corundum ceramic samples with added 2 mass % graphene nanostructures and 3 mass % TiO_2 using low-temperature synthesis. On the second stage, graphene oxide - NGO is obtained in nano colloid form and impregnated into the solid porous corundum samples synthesized.

MATERIALS AND METHODS

Materials

Initially, a finely porous corundum ceramic material containing 2 mass % graphene nanostructures and 3 mass % TiO_2 was obtained by the method of solid-state sintering at relatively low temperatures of about 1500°C.

For the synthesis of the porous ceramic samples from blend C0, the initial raw materials used were highly dispersed powder of Al_2O_3 (Sigma Aldrich) and one graphene source - Gn (graphene nanoplatelets (Sigma Aldrich)). In the blending process, an additive of 3 mass% TiO_2 (Sigma Aldrich, purity of ≥ 99%) was introduced in the mixture. This additive significantly decreases the sintering temperature usually used in such process.

The preparation of the corundum ceramics was carried out as follows: 4% polyvinyl alcohol was added to the powders obtained as a plasticizer and the samples were dry-formed using hydraulic press at a pressure of 40 MPa. The regime of drying the samples was: 120°C - 70 min, 180°C - 50 min. The regime of sintering of the samples prepared from blend C0 was: isothermal period of 20 min at 200°C, 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

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1300°C - 30 min, and at the maximal temperature of 1500°C - isothermal period of 60 min. The aim was to achieve the highest possible densification on the basis of solid-state sintering and to obtain finely porous materials with good mechanical characteristics. After the sintering, the samples were allowed to cool freely.

In the second stage of the experiment, graphene oxide was synthesized in the form of a nano colloid. Here, the initial graphite (Graphite, synthetic powder, < 20 mum (Sigma Aldrich)) was oxidized by the method of Hummer with addition of MnO_4 [5, 12]. The graphene oxide - GO was added to deionized water and the pH of the solution was corrected with NaOH to 11.0. The suspension obtained was treated with high power ultrasound at intensity about 200 W for 2 hours. The aim of this treatment was to obtain colloidal dispersed system: water-dispersed solution of GO with well dispersed nanostructures. The concentration of the graphene oxide nano colloid prepared by this method was estimated to be 2 mg/ml, dispersion in H_2O.

One of the advantages of graphene oxide is that it is easily dispersible in water and other organic solvents, as well as in various matrices, due to the presence of oxygen-containing functional groups. This property is certainly important for effectively mixing material with ceramic or polymeric matrices when the aim is to improve their electrical and mechanical properties [5].

Bearing in mind the considerations above, during the next stage of the experiment the colloid particles of graphene oxide - NGO were impregnated into the solid porous corundum samples synthesized aiming to obtain composite ceramic material of the type NGO/Al_2O_3. The resulting composites obtained from blend C1 were dried in a desiccator at 120°C for 60 min.

Methods

Infrared spectroscopy. The FT-IR studies were performed on a Tensor 27 Fourier infrared spectrophotometer FT-IR (Bruker, Germany) in the interval 400 - 4000 cm^{-1} at a resolution of 1 cm^{-1}. The measurements were taken at room temperature. For each analysis, a sample weighing 0.3 mg was pressed with 100 mg of KBr at a pressure of 2 to 4 atm.

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

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

TEM. The corundum ceramic materials synthesized were studied by TEM EDS analysis carried out using a transmission electron microscope JEOL - JEM 2100 with EDS detector Oxford X-max 80T, at accelerating voltage of 200 kV.

Light microscopy. Light microscopy observations were performed with a Celestron 5 MP LCD Deluxe digital microscope.

RESULTS AND DISCUSSION

The following more important properties of the corundum ceramic samples synthesized (C0) were determined: water absorption (WA, %), apparent density (ρ_{app}, g/cm^3) and apparent (open) porosity (P_{app}, %). The results obtained indicated that the introduction of 2 mass% of graphene - Gn in the initial blends followed by high temperature sintering gave ceramic samples with sufficient density - 3.26 g/cm^3, water absorption - 10.43 % and substantial apparent porosity - 33.46 %. Hence, even at small quantities, the introduced graphene nanostructures serve as pore-forming agents.

Basically, the following methods were used to characterize the composite material obtained: infrared spectroscopy, X-ray powder analysis, scanning and transmission electron microscopy, light microscopy.

The initial blends and the sintered ceramic samples were studied by infrared spectroscopy (*FT-IR*). The result for the sintered corundum samples obtained from blend C0 are presented graphically in Fig. 1. The absorption bands and the corresponding functional groups present in the composition of the sintered corundum ceramic samples containing 2 mass % of graphene nanoplates can be interpreted as follows.

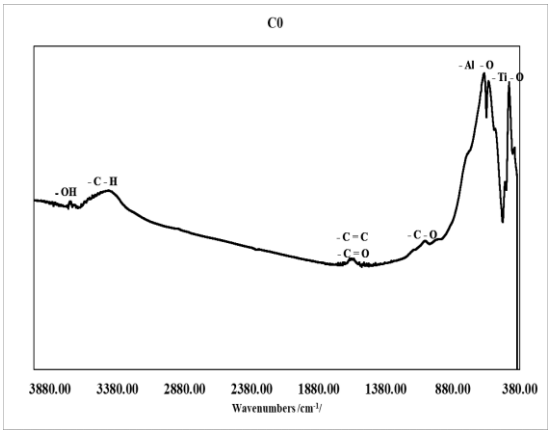


Figure 1. FT-IR spectrum of corundum samples prepared from blend C0 and sintered at 1500ºC

The absorptions at ~3780 cm^{-1} are characteristic for the vibrations of the O-H bond. The vibrations observed at ~1631.49 cm^{-1} can be attributed to the C=C bond [13, 14] which means that part of the carbon structures is preserved after the high temperature sintering and remain within the corundum ceramics while the others are burned. The latter process imparts certain porosity to the ceramic material obtained. The peaks appearing at ~1085.09 cm^{-1} are characteristic for the vibrations of the C-O bond [13, 14]. The FT-IR spectra obtained contain high peaks in the frequency range from ~500 cm^{-1} to ~900 cm^{-1}. They are characteristic for the vibrations of the Al-O bonds in Al_2O_3 [13, 14]. Major part of the absorption bands observed for the sintered ceramic samples were attributed to the vibrations of the Al-O bonds in the high temperature α-modification of Al_2O_3 (corundum). The absorption band at ~460.08 cm^{-1} is characteristic for the vibrations of the Ti-O bond.

XRD analysis. The XRD analysis proved that the main crystalline phases in the ceramic materials synthesized are three: Al_2O_3, Al_2TiO_5 and TiO_2 (Figure 2), with the main phase being corundum. The presence of these phases was proved also by the FT-IR analysis.

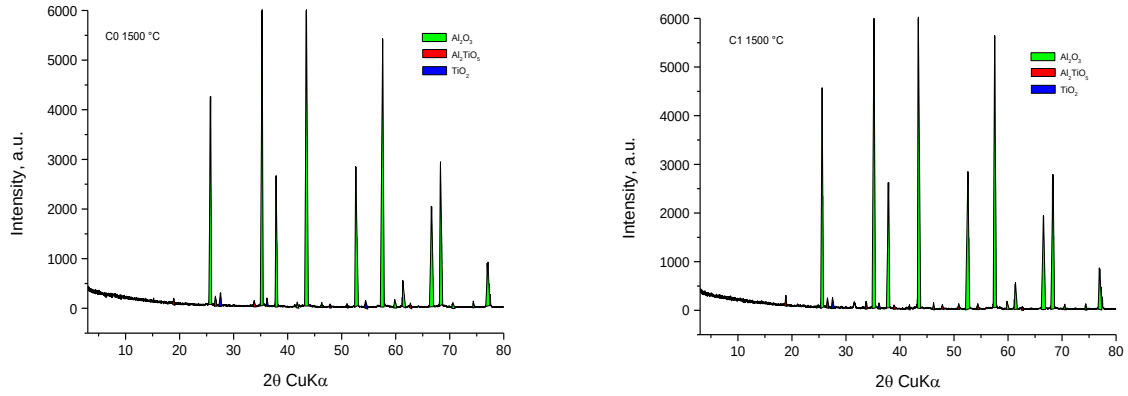
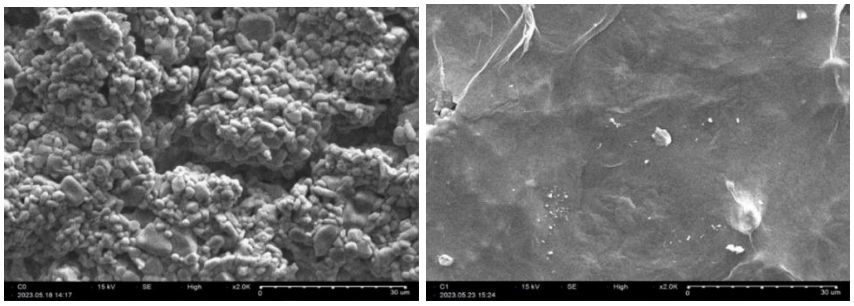
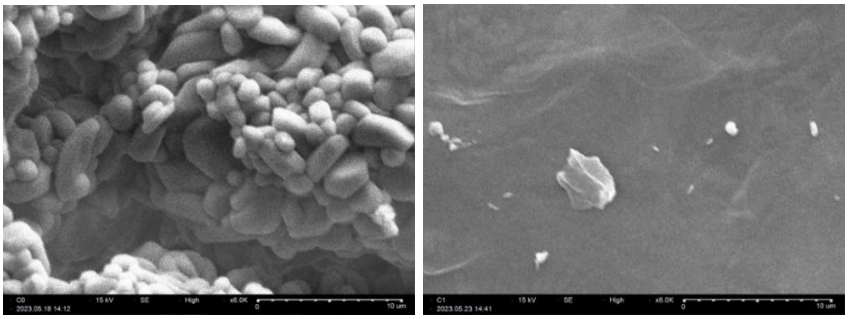


Figure 2. Powder X-ray diffraction patterns of sample with composition C0 and ceramic composite with composition C1



a) SEM of sample with composition C0 - ×2.0K

b) SEM of composite NGO/Al_2O_3 C1 - ×2.0K



c) SEM of sample with composition C0 - ×6.0K

d) SEM of composite NGO/Al_2O_3 C1 - ×6.0K

Figure 3. SEM images of sintered ceramic materials - samples with composition C0 a composite NGO/Al_2O_3 - composition C1

The decreased sintering temperature of the ceramics was due to the addition of TiO_2 (3 mass %) introduced in the initial blend. Part of it forms a solid solution with corundum, thus increasing the defects of the lattice and, respectively, easing the sintering of the ceramics at lower temperature.

The morphology of the objects studied was analyzed by electron microscope observations using SEM, TEM (Figures 3 and 4) and light microscopy (Figure 5).

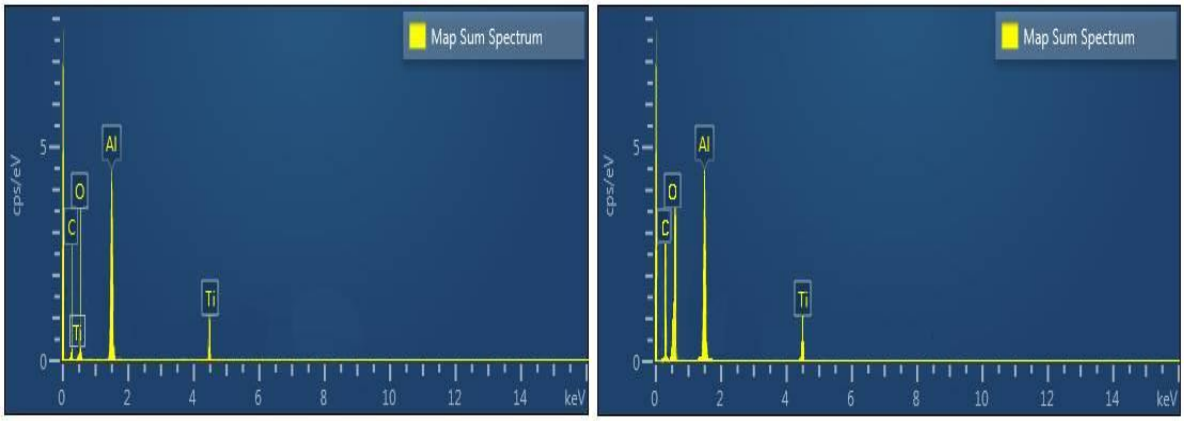
SEM analysis. The microphotographs of the sintered at 1500°C corundum samples without (composition C0) and with impregnated NGO (composition C1) are shown in Figure 3.

The electron microscopy images presented in Figures 3a and 3c show fine-grain fine-pore structure of the ceramic samples with corundum grain sizes from 0.5 to 3 μm. Therefore, they confirm the conclusion stated above that the addition of graphene nanostructures to the initial blends in concentration of 2 mass % followed by high temperature sintering, leads to burning of part of the graphene which results in formation of porosity in the ceramics obtained. The images of the composite material - Figures 3b and 3c indicate that the graphene oxide nano colloid was distributed throughout the sample and, to great extent, occupied the pores of the ceramic matrix.

TEM analysis. STEM images of the sintered sample with composition C0 (2 mass % of Gn) and ceramic composite C1 (NGO/Al_2O_3) are shown in Figures 4a and 4b. The map spectra indicate for the presence of the main elements Al, Ti, O and C.

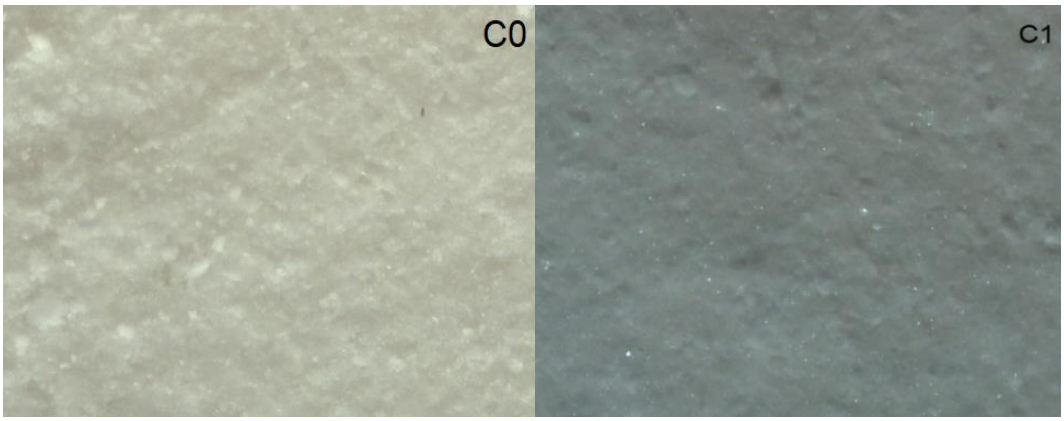
Light microscopy. The surfaces of the corundum ceramic samples containing 2 mass % of graphene Gn (C0) sintered at 1500ºC, as well as these of the ceramic matrices impregnated with nano colloid graphene oxide NGO (C1) were studied by light microscopy (Figures 5a and 5b).

As can be seen from the photographs presented in Figure 5, the surface of the ceramic materials synthesized was homogeneous and finely grained. In the impregnated ceramic matrices (C1), the nano colloid graphene oxide has not only spread across the surface but has also penetrated into material's pores, as verified by the earlier-discussed SEM analysis.



a) b)

Figure 4. (a, b) STEM images of samples with compositions C0 and C1



a) b)

Figure 5. Photographs of the surface of: 5a) corundum ceramic samples with composition C0 and 5b) ceramic composite NGO/Al_2O_3 - composition C1

CONCLUSION

A two-stage technology was applied to prepare a composite ceramic material of the type graphene/ceramic matrix - NGO/Al_2O_3. Finely porous corundum ceramic material was obtained by the method of solid-state sintering at a temperature of 1500°C which is relatively low for corundum materials and this was achieved by adding 2 mass % of graphene and 3 mass % of TiO_2. By introducing of 2 mass % of graphene nanoplates Gn in the initial blends followed by high temperature sintering, part of the graphene added burned out, thus imparting porosity to the ceramics obtained. The ceramic samples synthesized were found to have sufficient density - 3.26 g/cm^3, water absorption - 10.43 % and significant apparent porosity - 33.46 %.

During the next stage of the experiment, graphene oxide was obtained in nano colloid form (2 mg/ml, dispersion in H_2O) which was impregnated into the solid porous corundum samples synthesized aiming to obtain composite ceramic material of the type NGO/Al_2O_3. The SEM analysis confirmed that the graphene added initiated the formation of well-shaped fine corundum grains with sizes in the range 0.5-3 μm. The electron microscopy images of the composite material showed that the impregnated graphene oxide nano colloid was distributed not only on the surface but had also penetrated into the pores of the ceramic matrix. The results obtained from TEM EDS analysis confirmed the existence of carbon originating from the graphene. This carbon content most probably enhances the effect of the TiO_2 addition and accelerates the recrystallization processes. The surface of the corundum based ceramic materials was studied by light microscopy and it was found that the samples are characterized by comparatively homogeneous and fine-grain surface.

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REFERENCES

1. A. Georgieva, F. Yovkova, K. Panayotova, M. Georgieva, M. Minova, 61st Annual Scientific Conference - University of Ruse and Union of Scientists, Razgrad, Bulgaria, *Reports Awarded with BEST References Crystal Prize'22*, 167 (2022).
2. J. Zhu, B. Jia, Y. Di, B. Liu, X. Wan, W. Wang, R. Tang, S. Liao, X. Chen, *Frontiers in Materials*,**1,** 1 (2022).
3. B. Yazdani, Y. Xia, I. Ahmad, Y. Zhu, *Journal of the European Ceramic Society*, **35**, 179 (2015).
4. A. Centeno, V.G. Rocha, B. Alonso, A. Fernandez, C.F. Gutierrez-Gonzalez, R. Torrecillas, A. Zurutuza, *Journal of the European Ceramic Society*, **33**, 3201 (2013).
5. A. Jirickova, O. Jankovsky, Z. Sofer, D. Sedmidubsky, *Materials*, **15**, 920 (2022).
6. X. Wang, J. Zhao, E. Cui, X. Tian, Z. Sun, *Nanomaterials*, 11, 1374 (2021).
7. Z. Sun, J. Zhao, X. Wang, E. Cui, H. Yu, *Nanomaterials*, 10, 1815 (2020).
8. H. Abdel Dayem, B. Salib, F. El-Hosiny, *Fuel*, **227**, 1 (2020).
9. P. Rutkowski, P. Klimczyk, L. Jaworska, L. Stobierski, A. Dubeil, *J. Therm Anal Calorim*, **122**, 105 (2015).
10. K. Broniszewski, J. Wozniak, M. Kostecki, A. Olszyna, *Mater. Today Proc.*, **2**, 370 (2015).
11. S. Wang, S. Kang, T. Fang, Y. Hsiao, *Sci. Adv. Mater.*, **6**, 1951 (2014).
12. D. Markano, D. Kosynkin, J. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, *ACS Nano*, **4**, 4806 (2010).
13. L. Zhang, Y. Li, H. Guo, H. Zhang, N. Zhang, T. Hayat, Y. Sun, *Environmental Pollution*, **248**, 332 (2019).
14. http://www.ioffe.ru/LNEPS/abstracts/rabchinskii.pdf