LOW-TEMPERATURE SYNTHESIS OF FINE-POROUS CORUNDUM BASED ON INCORPORATED GRAPHENE NANOSTRUCTURES

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ABSTRACT

In the present paper, the effect of the addition of graphene nanostructures and 3 mass % TiO_2 on the microstructure and properties of sintered corundum ceramics were studied. Fine-porous corundum ceramics were obtained by the method of solid-phase sintering at relatively low temperatures of 1450°C, by adding graphene nanostructures in an amount of 2 % or 20 %. To lower the synthesis temperature, 3 mass % TiO_2 was added to the initial ceramic blends. As a result of the solid solution formed between Al_2O_3 and TiO_2, a well-sintered corundum ceramic is obtained at synthesis temperature lower than that of pure corundum - 1450°C. For the characterization of the initial blends and the ceramic samples, the methods of X-ray phase analysis, infrared spectroscopy, SEM, TEM EDS and visual microscopy were used. Besides, the basic physicochemical properties of the samples synthesized based on corundum were determined, e.g. water absorption (WA, %), apparent density (AD, %) and apparent (open) porosity (P_a, %).

Keywords: *fine-porous corundum, graphene structures, low-temperature synthesis.*

INTRODUCTION

In recent years, the efforts of several researchers have been devoted to the development and synthesis of new ceramic articles with porous structure and developed surface because they are certainly important for various fields of application, e.g. filters for purification of waste waters, adsorbents, heat insulation materials and other components of high thermal resistance, for biomedical and catalytic substrates [1 - 3]. Ceramics where Al_2O_3 is the main component are generally referred to as corundum ceramics since they contain mainly α-Al_2O_3 called corundum [4]. The Al_2O_3 based ceramic filters show high efficiency by filtration of liquids, they have good chemical resistance and can be regenerated [5].

The aim of the present paper is to synthesize finely porous corundum ceramics and study the effect of the addition of various amounts of graphene nanostructures and 3 mass % TiO_2 on the microstructure and he properties of the samples synthesized.

EXPERIMENTAL

The initial materials used for the synthesis of corundum ceramic samples were highly dispersed Al_2O_3 powder (Sigma Aldrich) and two graphene sources - G3 (graphene obtained by the research team using a method combining chemical and physical (ultrasonic) treatment of the original precursor graphite (purity > 99 %) [6] and Gn (commercial graphene - graphene nanoplatelets (Sigma Aldrich). The corundum ceramic samples were synthesized by solid state sintering at relatively low temperatures of 1450°C and 1500°C, with addition of graphene nanostructures in amounts of 2 mass % or 20 mass %, as well as second additive - 3 mass % TiO_2. The compositions of the initial blends A0, A1, A2 and C1 are shown in Table 1.

The preparation of the ceramics was carried out as follows: to the powdery compositions prepared, 4 % polyvinyl alcohol was added as plasticizer and the samples were semi-dry formed on a hydraulic press at

Table 1. Working compositions of part of the corundum samples synthesized.

Sample	Blend composition, mass %				Sintering temperature, °C
	Al_2O_3	G3	Gn	TiO_2	
A0	97	-	-	3	1450
A1	77	20	-	3	
A2	77	-	20	3	
C1	95	-	2	3	1500

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 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 800°C - 30 min, at 1100°C - 30 min, at 1300°C - 30 min and at the maximal temperature of 1450°C or, respectively 1500°C - period of 60 min. The aim was to achieve as high as possible densification during the solid-state sintering and obtainment of finely porous materials with good mechanical properties.

RESULTS AND DISCUSSION

For the characterization of the initial powders and the ceramic samples obtained from them, basically the methods of XRD, SEM, TEM EDS, IR spectroscopy and light microscopy were used.

XRD analysis

The measurement of an X-ray powder diffraction pattern was carried out using automated X-ray diffractometric computer-controlled system D 500 Siemens (Germany) under the following experimental regime: 40 kV, 30 mA, copper monochromatic radiation.

The XRD tests proved that the main crystalline phases in the ceramics synthesized from compositions A1, A2 and C1 were three: Al_2O_3, Al_2TiO_5 and TiO_2 (Fig. 1 and 2) with the main phase being corundum. The decreased sintering temperature of the ceramics was due to the TiO_2 additive introduced in the initial blend (3 mass %). Part of it forms solid solution with corundum, thus facilitating the formation of defects in its crystalline structure and, respectively, easier sintering of the ceramics at lower temperature.

The morphology of the objects studied was determined by scanning and transmission electron microscopy (Fig. 3 and 4), as well as light microscopy (Fig. 5).

SEM analysis

The SEM images were taken by scanning electron microscope JEOL - JSM 6390 with EDS analyser INCA, product of Oxford instruments, at accelerating voltage of 20 kV. The samples were preliminarily coated with gold on an apparatus JEOL - JSF 1200 for 40 s. The microphotographs of the corundum samples with compositions A0, A1 and A2 sintered at 1450°C taken at magnifications of x 15 00 and x 20 000 are presented in Fig. 3. In Fig. 3a where samples of pure ceramics are shown, finely grained and finely porous structures with corundum grain sizes from 0.2 to 1 μm can be observed. The photographs presented in Fig. 3b and 3c show increased size of the corundum grains to about 3 - 5 μm which is due to the recrystallization processes which had taken place most probably caused by the presence of the additive TiO_2 and initiated by the graphene added to the composition.

TEM analysis

The corundum ceramics synthesized were studied by TEM EDS analysis carried out with a transmission electron microscope JEOL - JEM 2100 with EDS detector Oxford X-max 80 T, at accelerating voltage of 200 kV. EDS/EDX spectrum of samples with compositions C1 (2 mass % Gn) and A1 (20 mass % G3) are shown in Fig. 4. The map spectrum in Fig. 4 indicates for the presence of the main elements Al, Ti, O and residue of C resulting from graphene which most probably accelerates the ceramics recrystallization.

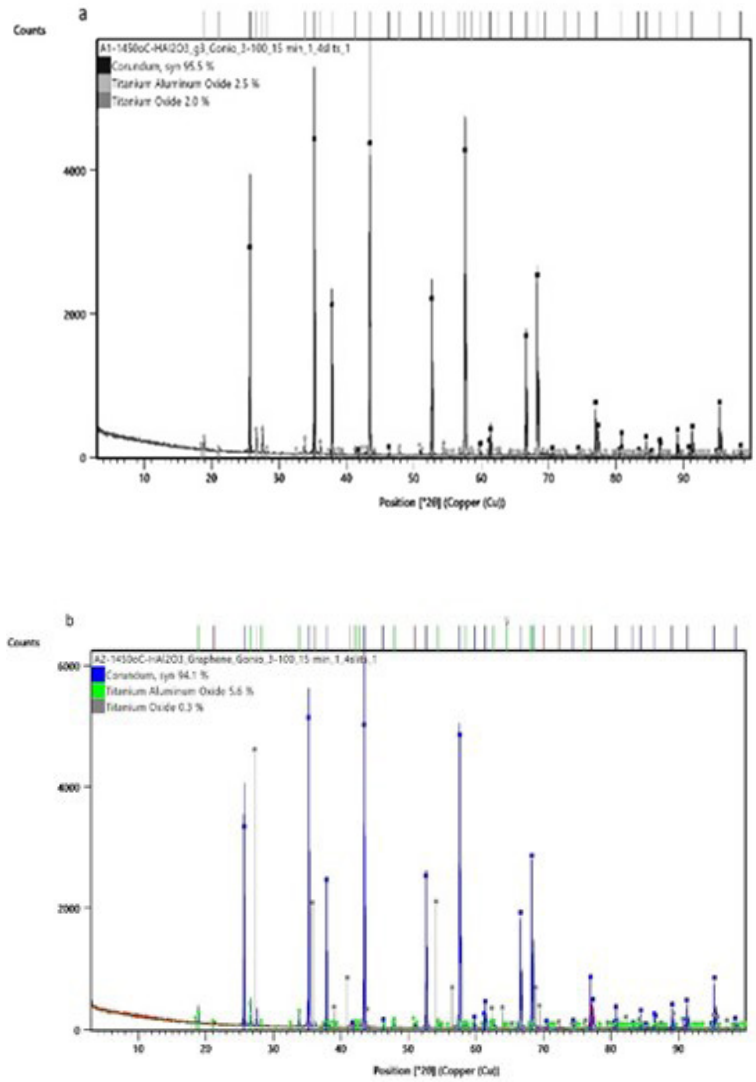


Fig. 1. XRD of ceramic samples synthesized with compositions A1(a) and A2 (b) at 1450°C.

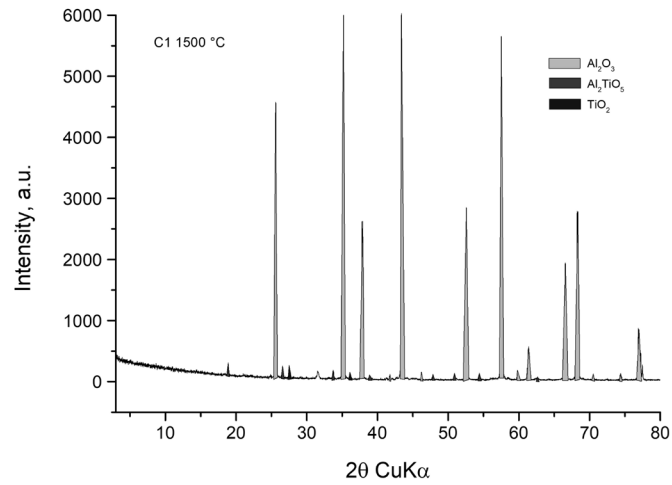


Fig. 2. XRD of sample with composition C1 synthesized at 1500°C.

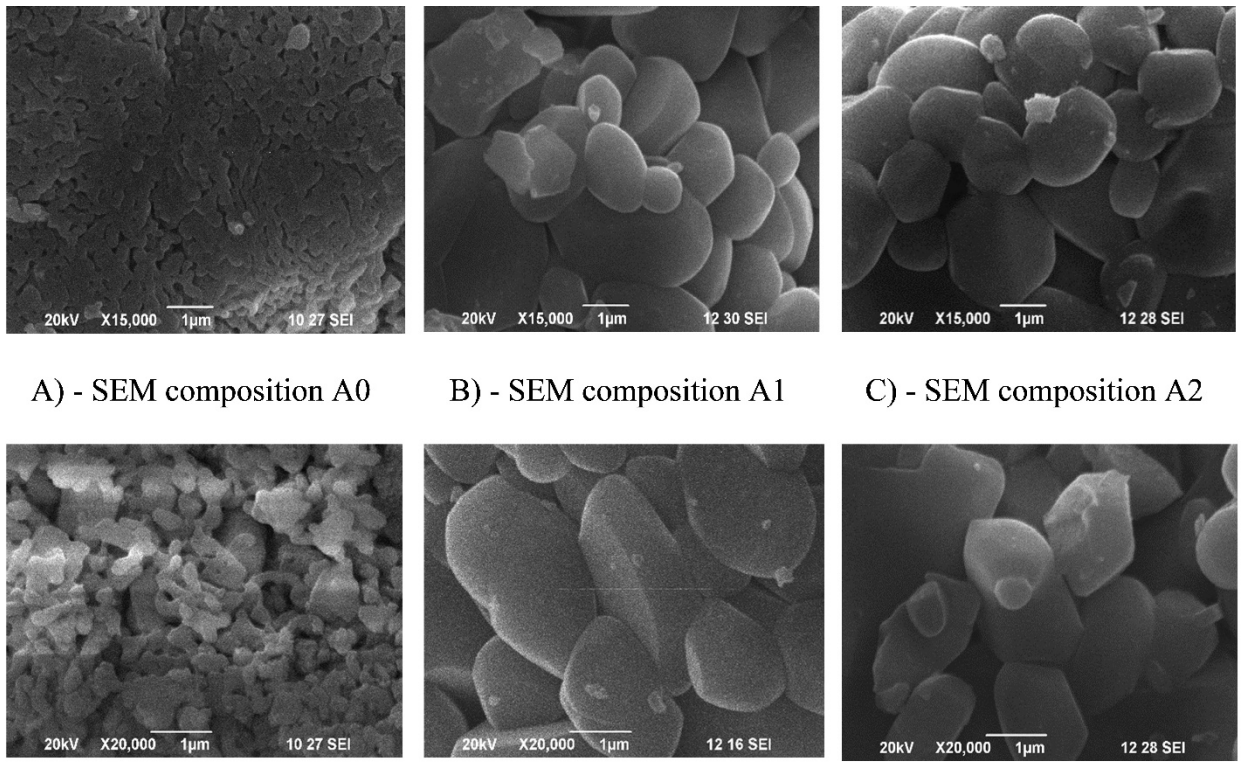


Fig. 3. SEM images of samples with compositions A0, A1 and A2 taken at magnification x 15 000 and x 20 000.

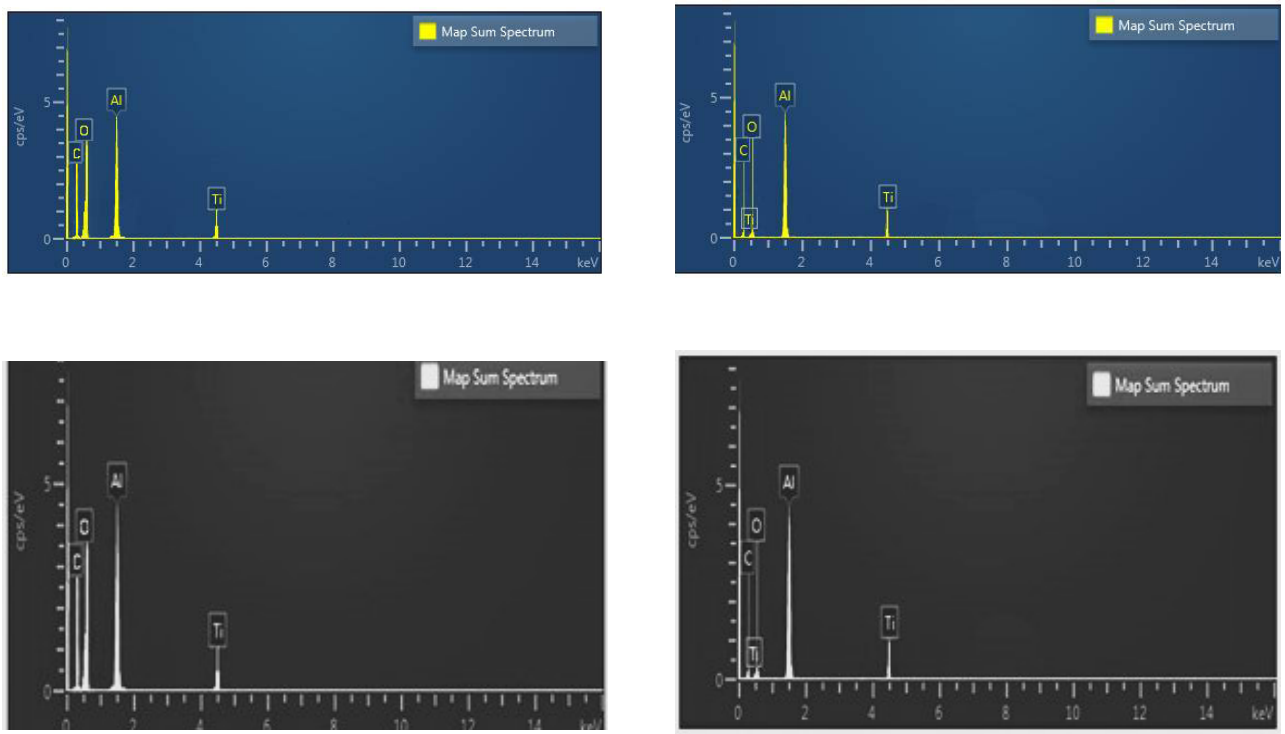
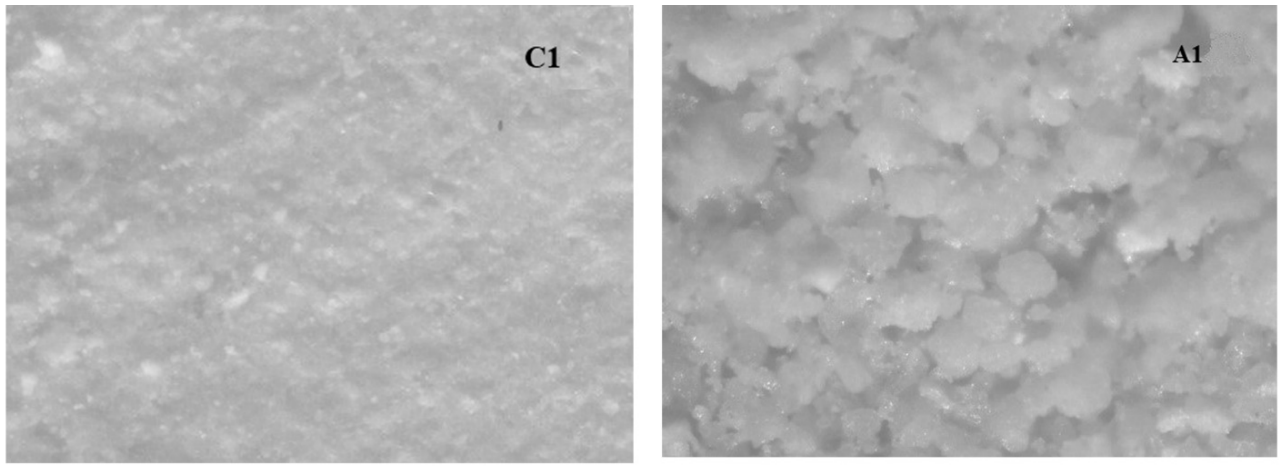


Fig. 4. EDS/EDX spectrum of samples with compositions C1 and A1.



a) sample with composition C1 sintered at 1500°C. b) sample with composition A1 sintered at 1450°C.

Fig. 5. Photographs of the surface of corundum ceramic samples.

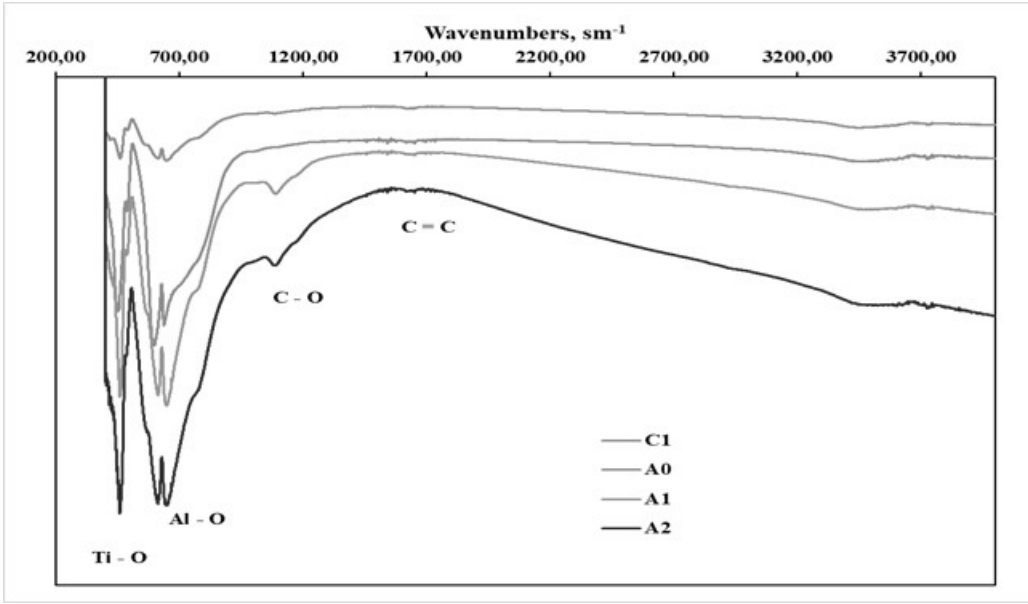


Fig. 6. FT-IR spectra of corundum samples sintered at 1450ºC (blends A0, A1, A2) and at 1500ºC (blend C1).

Light microscopy

The light microscopy studies were carried out with light microscope Celestron 5.

Fig. 5 shows microphotographs of the surfaces of the corundum ceramic samples with compositions C1 and A1 in which 2 mass % and 20 mass % graphene had been added to the initial blends, respectively. Comparing the surfaces of the ceramic samples containing 20 mass % graphene nanostructures G3 (blend A1) with these of the ceramics containing 2 mass % nanoplates Gn (blend C1), it can be seen that the surfaces of the latter is more homogeneous and with finer grains. Their structure is more uniform compared to the blends containing 20 mass % graphene. Therefore, their porosity id finer and more uniformly distributed in the bulk of the samples.

FT-IR spectroscopy

The initial blends and the sintered samples were studied by infrared spectroscopy. The FT-IR spectra were taken with Tensor 27 Fourier infrared spectrophotometer FT-IR (Bruker, Germany) in the interval 400 - 4 000 cm^{-1}. The spectra were recorded at room temperature with

a sample (0.3 mg) tableted in KBr pellet (100 mg) at pressure of 0.2 - 0.4 MPa. The results obtained from the analysis of the sintered corundum samples are presented graphically in Fig. 6.

The vibrations at ~1637.12 cm^{-1} and ~1632.33 cm^{-1} can be attributed to the C=C bond [2] which means that, after the high temperature sintering, part of the carbon structures is preserved and remains in the corundum ceramics while the rest of them are burned thus creating certain porosity of the ceramics obtained. The bands observed at ~1070.71 cm^{-1}, ~1069.50 cm^{-1}, ~1089.22 cm^{-1}, ~1088.43 cm^{-1} [2] are characteristic for the vibrations of the C-O bond. The spectra obtained from the IR analyses contained large absorption bands in the range from ~500 cm^{-1} to ~900 cm^{-1}. They are characteristic for the vibrations of the Al-O bonds in Al_2O_3 [2]. Most of the bands registered from the sintered samples were attributed to vibrations of Al-O bonds within the high temperature α-modification of Al_2O_3 (corundum). The absorptions at ~432.23 cm^{-1}, ~452.17 cm^{-1}, ~459.98 cm^{-1} characterizes the Ti-O bond. The presence of these phases was proved also by the XRD analysis.

CONCLUSIONS

Finely porous corundum ceramics containing 2 mass % graphene nanostructures or 20 mass % TiO_2 were obtained by the method of solid-state sintering at relatively low temperatures for corundum ceramics - 1450°C and 1500°C. Using SEM, it was proved that the graphene added initiated the formation of well-shaped corundum grains with sizes in the range 3 - 5 μm. The results obtained from the TEM EDS analysis confirmed the presence of residual C from graphene which most probably enhances the effect of the TiO_2 additive and accelerates the recrystallization. The surfaces of the corundum-based ceramics obtained by sintering at 1450°C and 1500°C were studied by light microscopy to find that the samples with composition C1 (2 mass % Gn) had the smoothest surface which can be attributed to the better sintering of the ceramics.

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REFERENCES

1. E. Lukin, N. Makarov, A. Kozlov, N. Popova, E. Anufrieva, M. Vartanyan, I. Kozlov, M. Safina, D. Lemeshev, E. Gorelik, V. Bakunov, Nanopowders for preparing a new generation of oxide ceramics, Refractories and Industrial Ceramics, 50, 6, 2009, 425-430.
2. L. Zhang, L. Ying, H. Guo, H. Zhang, N. Zhang, T. Hayat, Y. Sun, Decontamination of U(VI) on graphene oxide/Al_2O_3 composites investigated by XRD, FT-IR and XPS techniques, Environmental Pollution, 248, 2019, 332-338.
3. T. Petrova, Analytical modelling of stresses and strains in layered nanocomposite structures - opportunities and challenges, Bulgarian Chemical Communication, 50, 3, 2023, 349-366.
4. E. Gerasimov, A. Gerasimov, A. Atanasov, Technology of ceramic wares and materials, Sofia, Sarasvati Publishing House, 2003, (in Bulgarian).
5. E. Lukin, A. Kuteinikova and N. Popova, Porous permeable aluminium oxide ceramic, Glass and Ceramic, 3, 2003, 17-18, (in Russian).
6. I. Markovska, F. Yovkova, D. Georgiev, M. Mitkova, Eco-friendly production of low-cost graphene and investigation of its properties as material for supercapacitor electrodes, Journal of Chemical, Biological and Physical Sciences: Section A, 9. 4, 2019, 274-285.