FABRICATION OF ALUMINA NANOCOMPOSITES REINFORCED BY A NOVEL TYPE OF ALUMINA NANOFIBER AND GRAPHENE COATED ALUMINA NANOFIBER

Maria Drozdova, Roman Ivanov, Marina Aghayan, Irina Hussainova, Minje Dong, Miguel Angel Rodriguez

Abstract: A novel type of alumina nanofibers (ANF) and alumina nanofibers covered with graphene (ANFC) has been used for fabrication of alumina composites with improved mechanical properties. Al₂O₃–1.5 wt. % ANF and Al₂O₃–1.9 wt. % ANFC composites were consolidated by sinter/HIP technology at 1400 ºC in argon atmosphere under 20 bar pressure. It was demonstrated that the theoretical density of the obtained material strongly depends on the material of reinforcement. The structural homogeneity of the specimens was studied by SEM. The macro-hardness was measured by Vickers method. Key words: Ceramic composite; fibers; graphene; sintering

1. INTRODUCTION

Alumina (Al₂O₃) is one of the most well-known advanced ceramic materials that is widely used for its high strength, corrosion- and wear-resistance as well as good biocompatibility [1]. However, application of this material is somewhat limited by its brittleness. In comparison with traditional alumina ceramics, the reinforced alumina nanocomposites have proved to show better mechanical properties such as fracture toughness, for example [2-7]. Particularly, carbon nanofillers, such as carbon nanotubes (CNTs) and graphene platelets (GPLs), have recently attracted considerable attention as they demonstrate high tensile strength, stiffness, good flexibility and low density combined with a potential to improve electrical and thermal properties of the material. Presence of CNTs or GPLs inhibits the alumina grain growth [4-10] and can improve fracture toughness up to 53 % [9], whereas hardness remains uneffected or insignificantly decreased. Nowadays, the main challenge is producing composites with uniform distribution of reinforcing media throughout the matrix.

The objective of the present study is to produce alumina composites reinforced by Alumina Nano-Fibres (ANF) and Alumina Nano-Fibres covered with graphene (ANFC) which represent a novel type of nanostructured fillers. The effect of the reinforcements on the sintering behaviour, microstructure and mechanical properties of the ceramic composites are studied.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

Commercially available α-alumina nanosized powder TAIMICRON TM-DAR with average particle size of 100 nm (TAIMEI CHEMICALS Co., Ltd., Japan) was used as a matrix material. Bundled ANFs described in detail in [11] with 50 mm in length and average single fibre diameter of 7 nm as well as ANFs covered with 20 wt.% graphene (ANFC) were used as reinforcing materials. The mixtures of Al₂O₃ powder with additions of 1.5 wt.% ANF and with 1.9 wt.% ANFC (which contains 20 wt.% of graphene deposited on the same volume of ANF) were prepared. As reference, a sample of
Al₂O₃ without any additions was sintered. ANFs and ANFCs were ground intensively in a mortar and then mixed with alumina nanopowder. The obtained mixture was subjected to dry ball milling during 24 hours with ZrO₂ balls of 6 mm in diameter. Pure alumina nanopowder was used as a reference to study the effect of ANFs and ANFCs on the mechanical properties of alumina. The resulting mixtures as well as pure Al₂O₃ powder were uniaxially pressed in 12 mm diameter discs at 1000 kg. The pressed samples were compacted by sinter-HIP routine as following: (1) heating up to 700 ºC at heating rate of 3 ºC/min in vacuum; and then continued by (2) heating up to 1400 ºC with heating rate of 7 ºC/min under pressure of 20 bar in argon. A dwell time at the maximum temperature was 1 hour. A cooling rate was 10 ºC/min. The density of the samples before and after sintering was measured by a conventional geometric method. The samples were polished to 3 µm with diamond paste. Structures of the sintered samples were characterised by scanning electron microscopy EVO MA 15. Hardness was measured by Vickers tester (Indentec 5030 SKV) under the load of 500 N. Room-temperature electrical properties were studied by impedance analysis meter HP 4294A.

3. RESULTS AND DISCUSSIONS

SEM micrographs of the surfaces of the sintered composites are shown in Fig.1. The microstructure of the sintered pure alumina with initial size of 100 nm was inhomogeneous with presence of irregular and abnormally grown grains as shown in Fig.1(a, c). There were plenty of large and small pores distributed all over the samples. The relative density of the sintered samples was 94% (Table 1), while the green density was 54%. As the reference sample exhibits quite low bulk density and high pore profusion, it can be concluded that sintering routine was not well adjusted and needs correction for achieving fully dense ceramics (99% or higher). Excessive porosity implies low mechanical reliability of materials and therefore, the sintered material possesses lower hardness (20.9 GPa) than it could be expected for nanostructured alumina. Hardness of about 21 GPa just slightly outperforms the hardness of alumina commonly produced from micro-sized powders (18.0-19.5 GPa) and is noticeably lower than hardness of poreless alumina obtained with SPS technique from the same type of nanopowder (26-27 GPa) [10].

Incorporation of ANFs reinforcements into alumina matrix does not result in significant changes in microstructure of the sintered composite (Fig.1d). Also, no fibres were detected in the composite. It is believed that the ANFs were broken down to the very short whiskers or particulates during milling and heating to 1400 ºC. The parts of the fibres could easily fill a space between the larger particles of commercial alumina and, therefore, lead to the slightly higher density of the pre-sintered sample (55%). This results in higher density of the sintered composite (95%). The presence of ANF also improves composite hardness to the value of 21.6 GPa.

However, for the composite containing graphene coated alumina nanofibers the microstructure differs visibly. The grain sizes are quite uniform throughout the specimen and close to the particle size of the precursor alumina particles. It can be demonstrated that there was no evident particle clustering and/or growing during
sintering process. The grains were much finer than that of the alumina and alumina reinforced with ANF. This should be attributed to the presence of carbon (0.35%), which could be distributed along the grain boundaries and preventing rapid grain growth. Although the green density of the ANFCs containing composite was of the same level as for pure Al₂O₃, the relative density of the sintered sample decreased to 90%. With lower density the hardness of the composite dropped to 19.6 GPa as the result of higher amount of intergranular defects.

The room-temperature electrical conductivity measurements of the Al₂O₃-ANFC sample showed that the composite is dielectric. The impedance is high in all the frequency range and the phase angle is very close to -90 degrees according to dielectrical material (Fig. 2).

4. CONCLUSIONS
Addition of alumina nanofibers to alumina ceramics does not significantly affect the mechanical properties and sinterability of the composites because of severe loss of fibres integrity during milling and following heat treatment. However, fibres covered by graphene significantly influence composites microstructure serving as grain growth inhibitors while decrease sinterability of alumina due to low affinity of carbon and oxides. The presence of graphene as well as a carbon polymorph in the sintered materials should be thoroughly studied in the nearest future.

5. ACKNOWLEDGEMENTS

Estonian Ministry of Education and Research (targeted project IUT 19-29) and Archimedes targeted grant AR12133 (NanoCom) is gratefully acknowledged for supporting this research.

6. REFERENCES


### 6. ADDITIONAL DATA ABOUT AUTHORS

1. Maria Drozdova
Tallinn University of Technology,
Department of Materials Engineering,
Ehitajate tee 5, 19180 Tallinn, Estonia
maria.drozdova@ttu.ee

2. Marina Aghayan
Tallinn University of Technology,
Department of Materials Engineering,
Ehitajate tee 5, 19180 Tallinn, Estonia
marina.aghayan@ttu.ee

4. Roman Ivanov
Tallinn University of Technology,
Department of Materials Engineering,
Ehitajate tee 5, 19180 Tallinn, Estonia
roman.ivanov@ttu.ee

5. Minje Dong
Tallinn University of Technology,
Materials Research Center,
Ehitajate tee 5, 19180 Tallinn, Estonia
minje.dong@ttu.ee

6. Dr. Miguel Angel Rodríguez
Instituto de Cerámica y Vídrio (CSIC),
Campus Cantoblanco, 28049 Madrid,
Spain / mar@icv.csic.es

### 7. CORRESPONDING ADDRESS

Dr. Irina Hussainova
TUT, Department of Materials Engineering
Ehitajate tee 5, 19086 Tallinn, Estonia
Phone: 372+620 3371,
Fax: 372+620 3250,
E-mail: irhus@staff.ttu.ee