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ABSTRACT OF THE DISSERTATION

„Influence of graphene oxide functionalization on the properties of ceramic suspensions and obtained ceramic – graphene composites"

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In the technology of ceramic and composite materials an increasing emphasis is put on the use of colloidal processing. These techniques allow for better control over the distribution of the reinforcing phase in the matrix compared to die pressing methods. The application of colloidal processing in the case of ceramic – graphene composites may additionally allow to avoid the drying stage of graphene oxide which is one of the main factors responsible for its agglomeration. Aqueous ceramic – graphene oxide colloidal systems are characterized by high viscosity and a tendency to agglomerate (especially for high graphene oxide content). These problems make it difficult to prepare the suspensions with a high content of well dispersed graphene oxide. The application of aqueous colloidal processing methods in fabrication of ceramic – graphene composites is not well described in the scientific literature. For this reason, it is especially important to elaborate solutions which would allow shaping of ceramic – graphene materials through colloidal methods.

The aim of the research was to develop a chemical functionalization of graphene oxide aimed at the improvement of its dispersion degree in multiphase colloidal systems used in shaping of ceramic – graphene composites as well as determination of interactions between graphene oxide (GO) and functionalized graphene oxide (f-GO) with other components of the suspensions. The additional application goal of the research was to obtain ceramic – graphene samples by slip casting, gelcasting and tape casting methods and pressureless sintering in a nonoxidizing atmosphere.

In the research a suspension of graphene oxide with a concentration of 4.5 g/dm^3 was used as one of the suspensions' components and precursor of graphene in the obtained composites. Graphene oxide was subjected to the chemical functionalization process. The procedure was to add glucosamine to the carboxyl groups present on the surface of the graphene oxide through the nucleophilic substitution reaction. Analysis of FT-IR and Raman spectra and elemental analysis confirmed that the proposed functionalization was effective. Additionally, the results of particle size distribution and rheological properties of non-functionalized (GO) and functionalized (f-GO) graphene oxide proved that suspensions of f-GO are much less agglomerated.

In the research two ceramic powders were used: ZrO_2 (TZ-PX-245) of a mean particle size of 40 nm and Al_2O_3 (TM-DAR) of a mean particle size of 120 nm. Both of them were used as one of the suspensions' components. A number of dispersing agents were used in the research: diammonium hydrocitrate, polyethyleneimine, Duramax D-3005, glucuronic acid and lactobionic acid. The zeta potential in function of pH for ceramic powders and graphene oxides was determined. In the case of ceramic powders, this relationship was determined for samples with the addition of the abovementioned

dispersing agents. Based on the obtained results, it was determined whether heterocoagulation will occur.

In the next stage of the research the rheological properties were examined for suspensions used in slip casting. At this point, it was proven that in the case of ceramic – graphene oxide systems heterocoagulation is an unfavourable effect, especially for suspensions with a high content of graphene oxide, where ceramic particles are immobilized by graphene oxide flakes. It was also proved that suspensions with diammonium hydrocitrate – an anionic electrostatic dispersing agent exhibited the best properties. All of the suspensions exhibited shear thinning or thixotropic properties, the thixotropy was observed mainly for systems for which heterocoagulation occurred.

Then, the influence of the binder (Sinapol SP-650) and the monomer (2-hydroxyethyl acrylate) on the properties of the suspensions used in tape casting and gelcasting was determined. The results showed that partial adsorption of these particles on the surface of graphene oxide and their interactions with other components in the dispersions result in an increase in the viscosity of the suspensions. Additionally, polymerization idle time of the slurries used in gelcasting of ceramic – graphene composites was determined.

The obtained materials in a green state had been characterized in terms of their density and microstructure. In the case of zirconia materials the type of graphene oxide had a large influence on the relative density, while in the case of alumina composites, the same could be said about graphene oxide's content. This may indicate that different mechanisms of structure formation occurred for both powders. Microstructure analysis revealed that graphene oxide existed locally in the samples in the form of few-layer flakes.

Furthermore, thermal analysis of GO and f-GO was performed. On the basis of the obtained results it was determined that thermal reduction of graphene oxide occurs at 220°C and decomposition of r-GO to gaseous products starts in the temperature range of 450-550°C.

The last stage of the research was characterization of the sintered composite bodies in terms of their: density, microstructure, phase composition, hardness, fracture toughness and electric conductivity. The obtained composites exhibited hardness comparable to the reference materials (without graphene reinforcement) and increased fracture toughness (by a maximum of 76%). The composites did not exhibit electric conductivity most probably due to low content of r-GO hindering reaching the percolation threshold. In order to increase r-GO content in the composites it would be necessary to increase graphene oxide content in the suspensions. However, it was impossible at this stage of research, due to two reasons. Firstly, it was necessary to use highly diluted suspensions of GO for the chemical functionalization process. Secondly, it was necessary to maintain ceramic powder content at a minimum of 25 $_{vol.}$%, in order to avoid sample deformation. This opens up a new direction for research – how to fulfil those two mutually exclusive conditions.

To sum up, the performed research resulted in the elaboration of graphene oxide functionalization reaction which allowed to decrease the agglomeration of its platelets in water, while at the same time maintaining beneficial rheological properties of ceramic suspensions with GO. According to Author's best knowledge, the results presented in this dissertation are the first example of the use of this type of functionalized graphene oxide to improve rheological properties of suspensions used in shaping of ceramic – graphene composites. In the future, this approach may enable the improvement in the properties of ceramic – graphene composites and allow them to find broader applications. Furthermore, this work allows for better understanding of the interactions occurring in the suspensions used in colloidal processing of materials.

Keywords: ceramic dispersions, ceramic – graphene composites, graphene oxide, functionalization, rheological properties, colloidal processing

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