

Influence of Graphene Sheet Content on Thermal Expansion of ZrO₂ Nanopowders



Asya AFZAL*, Elena TRUSOVA

Baikov Institute of Metallurgy and Materials Science Russian Academy of Sciences (IMET RAS),
119334, Moscow, Russia

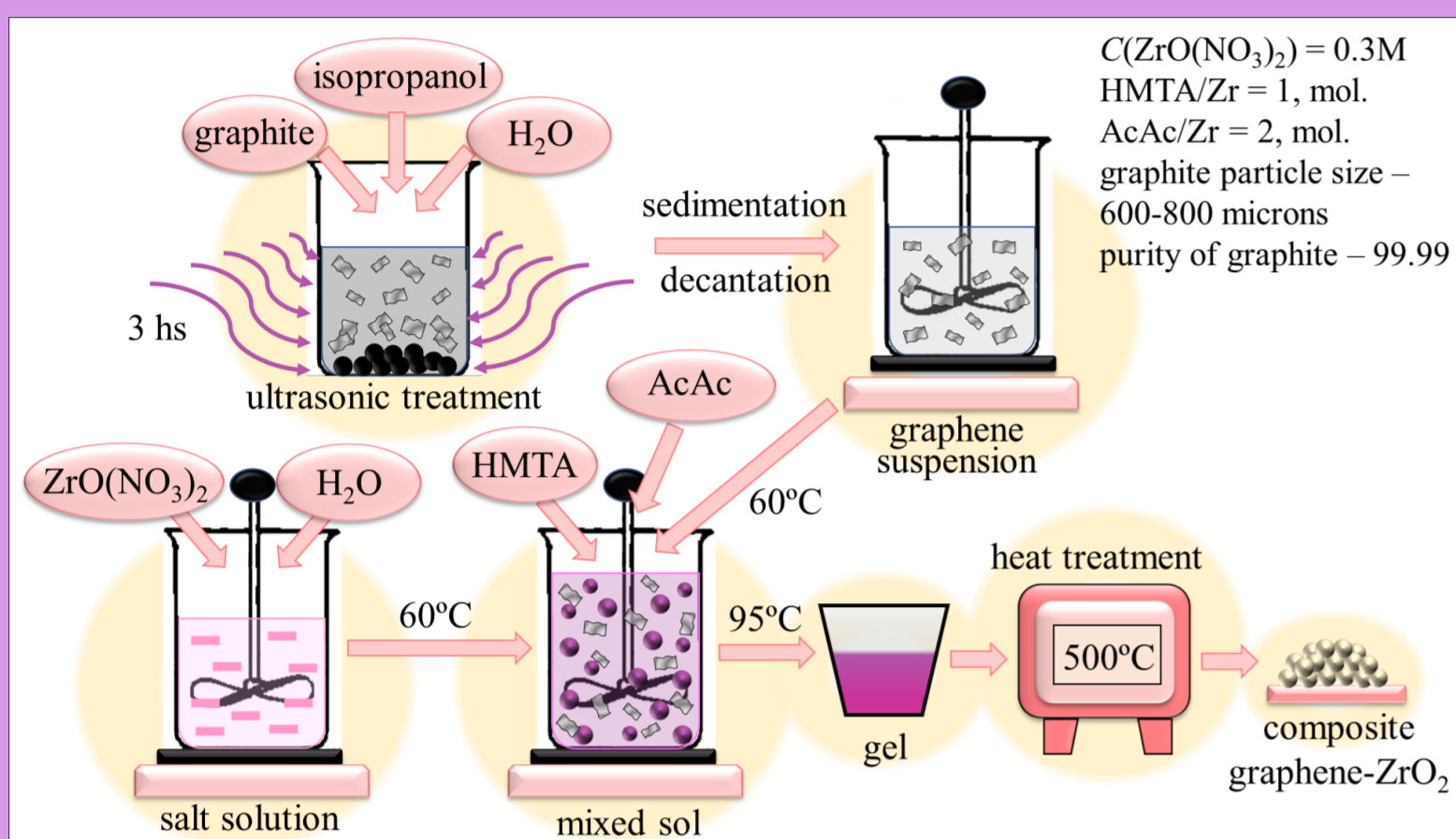
*e-mail: asya.afzal@mail.ru



Introduction: Nanocomposites based on graphene and zirconia attract attention of the developers and researchers of new materials because they have unique physicochemical properties: high specific surface area, improved electrical and thermal conductivity, high (photo/electro)catalytic activity. Composites based on graphene and zirconia are intended for the development fuel cells (catalyst support), solar cells, supercapacitors, electronic devices, catalyst systems, Fischer-Tropsch synthesis, hydroprocesses, synthesis/decomposition of ammonia, photocatalysts for environmental protection (decomposition of organic dyes and solvents), thermal barrier coatings, transistors (advanced gate dielectrics). However, the synthesis of such hybrids is difficult to carry out in practice due to the difficulties of obtaining and preserving graphene without destroying the π -electron system of graphene, the presence of a 3D carbon phase in the composite, uneven distribution of components and low dispersion of metal oxide.

The choice of optimal technological modes is especially important for the production of nanostructured powders and fine-grained ceramics. The study of sintering conditions of graphene-ceramic nanostructured powders is relevant and in demand by developers of new functional materials. In this study, a method for synthesis of composite nanostructures based on oxygen-free graphene and ZrO₂, including sol-gel and sonochemical techniques, is proposed. The influence of graphene content on the sintering dynamics of synthesized composite powders was studied using the dilatometry method.

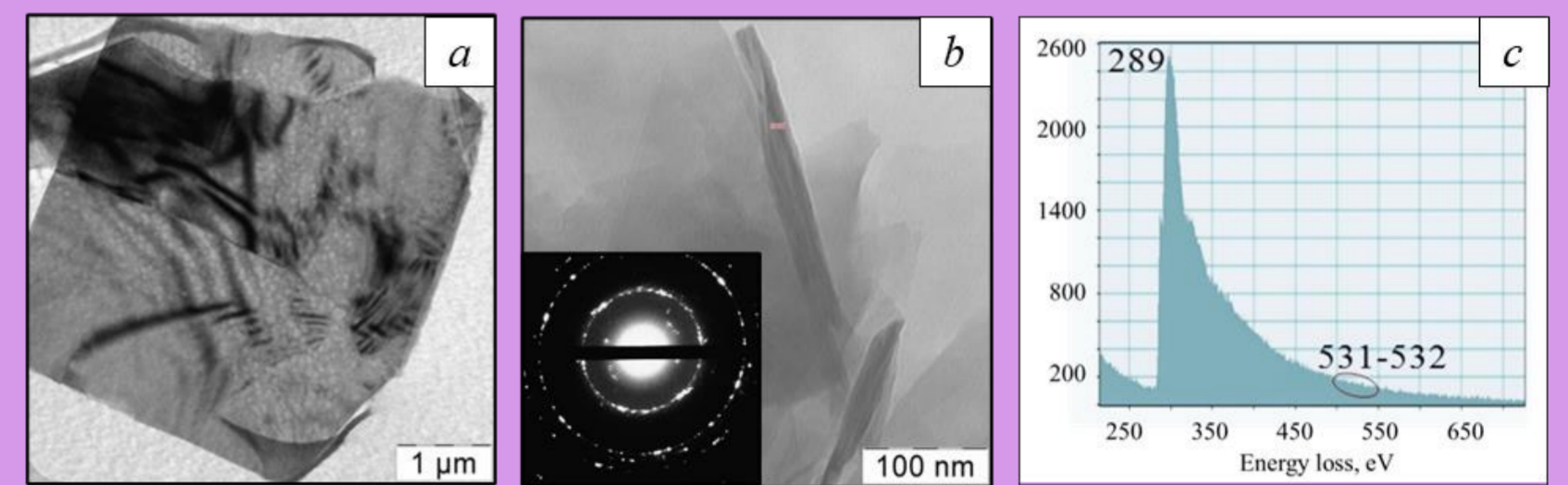
Scheme of graphene-metaloxide nanocomposite preparation from Zr-containing sol and graphene suspension



The feature of this method is combination of sol-gel and sonochemical techniques for the synthesis of nanocomposites based on oxygen-free graphene and nanocrystalline zirconia, the crystalline size of which does not exceed 10 nm. It involves ultrasonic peeling of the graphene sheets from the surface of synthetic graphite in an isopropanol-water mixture (1:1, vol.). Available zirconyl nitrate was used as the source of metal. Hexamethylenetetramine (HMTA) was used as a sol stabilizer, acetylacetone (AcAc) as a complexing agent.

1. RU 2706652 C1 (2018) Trusova E.A., Kirichenko A.N., Kotsareva K.V.
2. RU 2788977 C1 (2023). Trusova E.A., Afzal A.M.
3. Application for the invention of the RF, register № 2023107319 dated 28.03.2023, Afzal A.M., Trusova E.A.

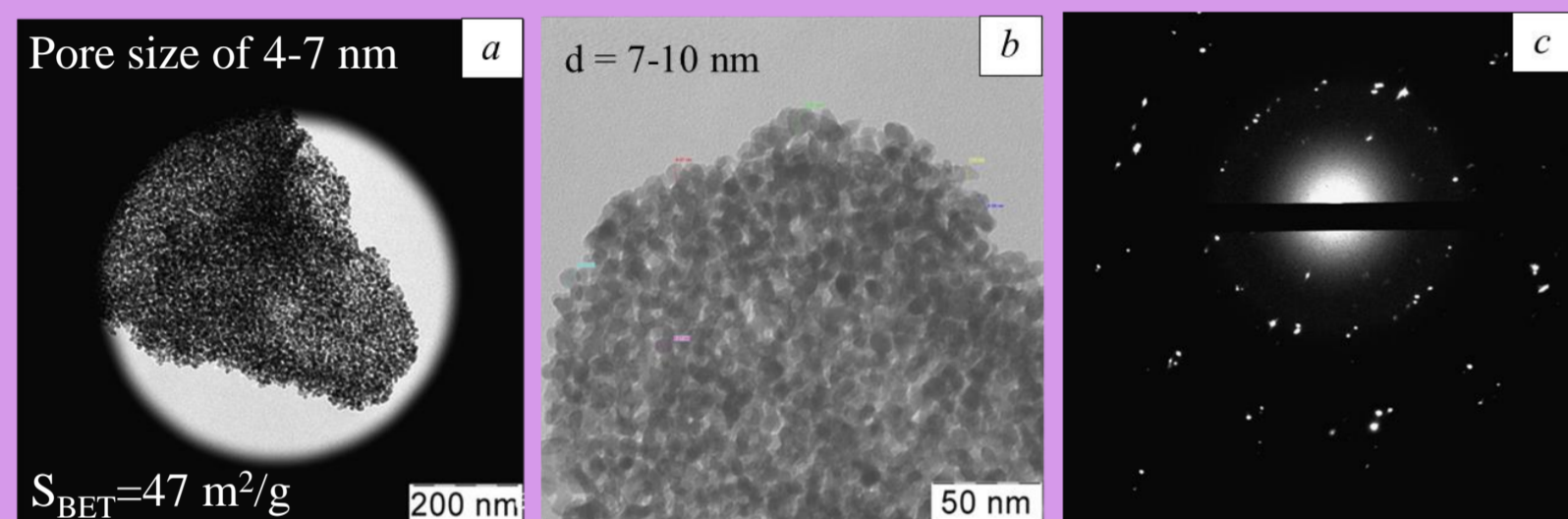
TEM data of graphene sheets



Graphene obtained in the isopropanol-water mixture is represented by relatively large multilayer particles (packets) with sizes up to several microns (a, b). The moiré, clearly visible (a) confirms that the packages consist of 1-2-layer sheets of graphene. Electron diffraction (b, inset) indicates that the particles consist of many differently oriented sheets, the thickness of which does not exceed several nanometers.

According to EELS analysis, graphene oxide was absent in the obtained graphene: 532 eV peak corresponding to oxygen does not appear in the spectrum. At the same time, peak at 284 eV corresponds to $1s \rightarrow \pi^*$ transition, denoting the presence of C_{sp²}.

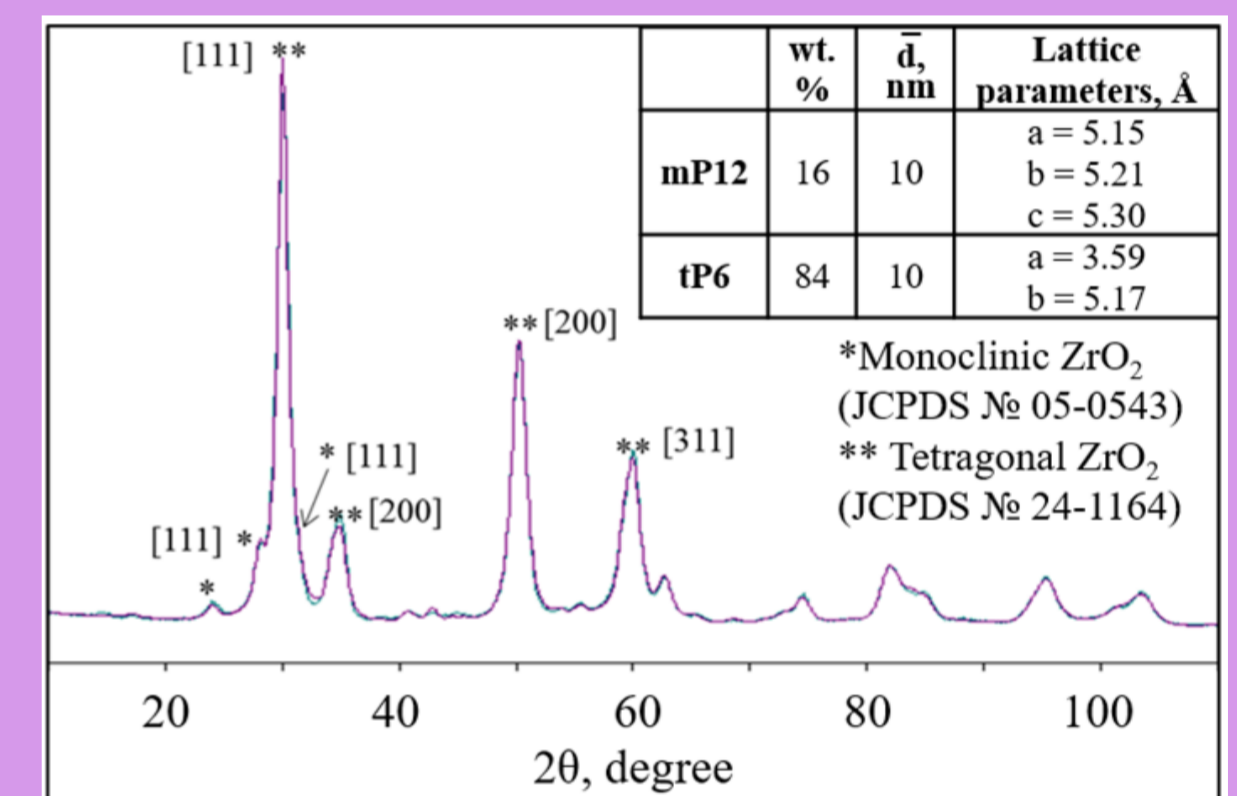
TEM and BET data of the graphene-ZrO₂ composite



According to elemental analysis, the carbon content in the graphene-ZrO₂ composite is 0.706 ± 0.002 wt.%. Figs a and b show that the powder particles are formed by the graphene sheets with linear dimensions of several hundred nm, into which crystallites with sizes of 7-10 nm are discretely incorporated (b). The electron diffraction (c) indicates that the graphene sheets are formed by the chaotically oriented layers.

XRD pattern: phase composition and crystallographic data for the graphene-ZrO₂ composite powder (inset)

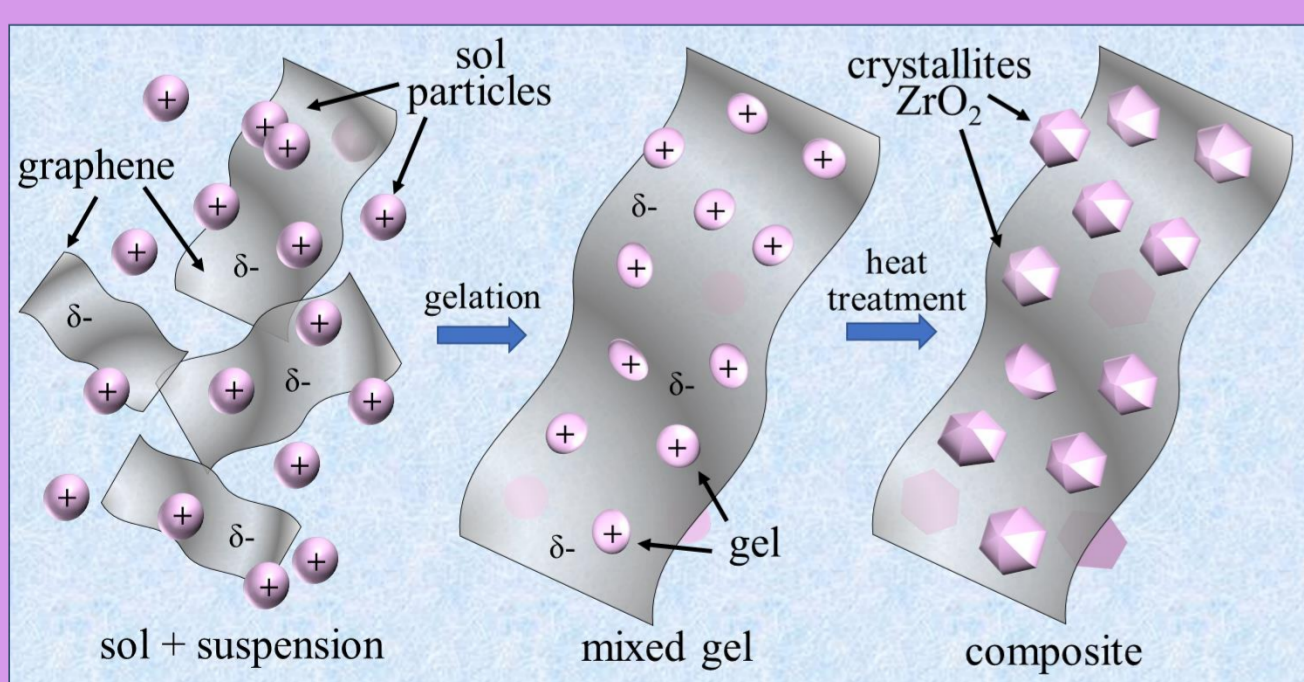
Neither the carbon phase nor the zirconium carbide was detected, which indicates the absence of 3D carbon in the composite. Analysis of XRD data shows that composite consists of two modifications of ZrO₂: tetragonal (tP6) and monoclinic (mP12), with an average crystallite size of 10 nm for both modifications. The elemental composition corresponds to the gross formula ZrO₂, which indicates the absence of partially reduced zirconium and a nonstoichiometric phase.



The turquoise spectrum was obtained used a copper source, the lilac spectrum was obtained used a cobalt source and recalculated by an angle of 2θ to CuK_α.

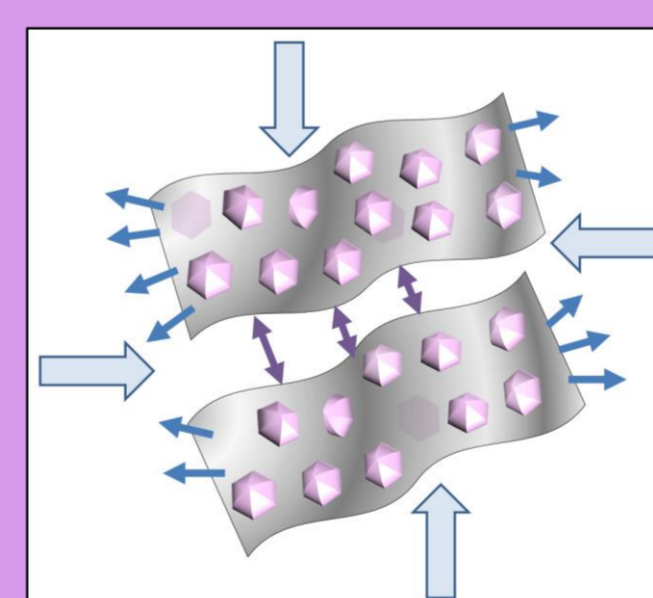
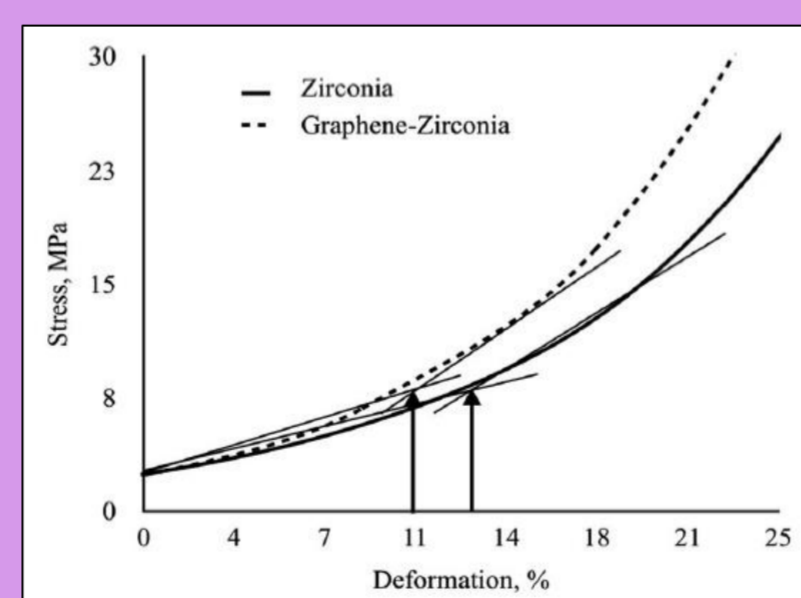
The mechanism of composite formation

When Zr-containing sol and graphene suspension were mixed, sol particles are distributed in isolation between graphene sheets, which create a system of peculiar nanoreactors where sol → gel transition occurs when heated. The formed gel also turns out to be bound to the graphene surface. During subsequent heat treatment, the surface organo-inorganic complex is destroyed, and the crystallization process takes place directly on the graphene sheets.



There are no chemical bonds between graphene and metal oxide, which indicates the van der Waals interaction of the components in the hybrid structure. As a result, graphene retains its electronic properties, being fixed in the composite structure without deformation of the sp²-electron system.

Rheology study

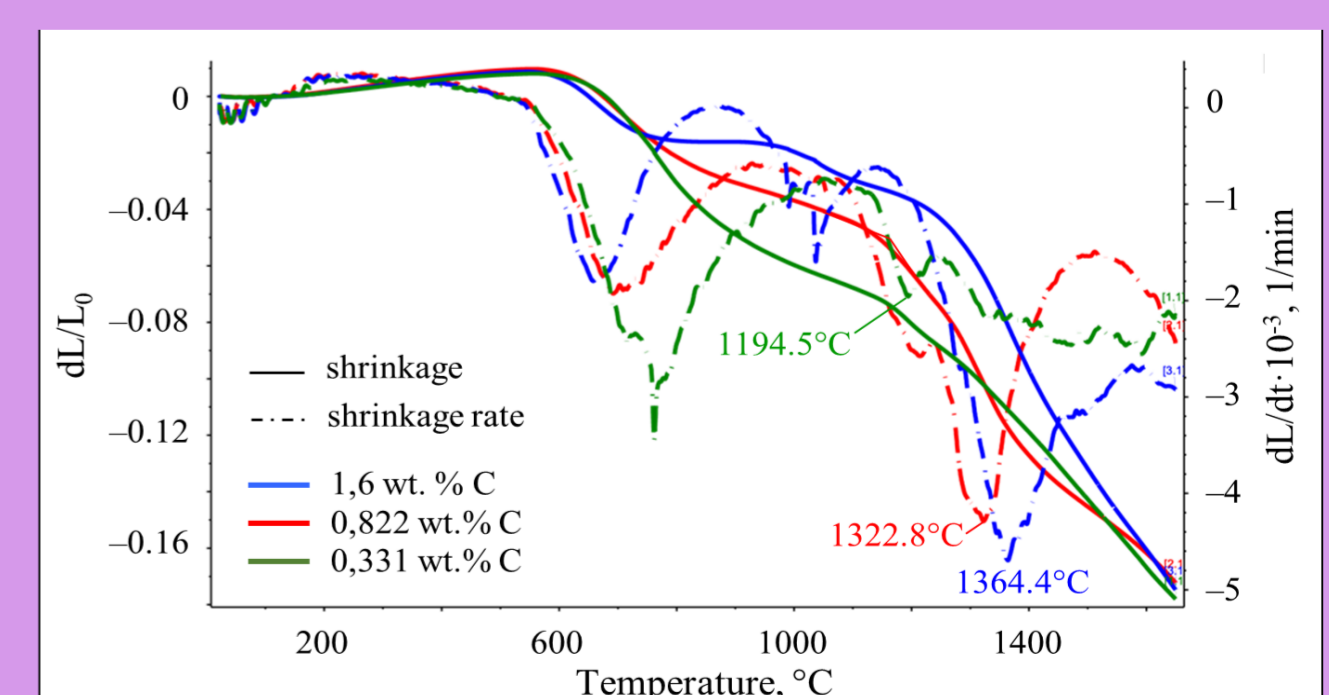


Analysis of rheological data shows that the compressibility of the composite is difficult compared to the compressibility of pure ZrO₂ powder, apparently due to the low elasticity of graphene sheets. It appears in the area of elastic-plastic deformation, when the particle distribution in the sample volume is optimized and compaction occurs due to accommodation and deformation of particles.

Dilatometry study

Analysis of the curves shows noticeable differences in the behavior of composites at temperatures above 600°C: if the graphene content in the composite increases, its ability to shrink decreases. The differences are especially pronounced in the range of 600-800°C: with an increase in the graphene content, the shrinkage rate decreases by more than 2 times and the extrema on the shrinkage rate curves shift to the region of lower temperatures.

With a further increase of temperature (1000-1700°C), differences are also observed, that affect the change in shrinkage rate, and in this case, the sample with the highest graphene content shrinks at the highest rate, and the extremum falls at a temperature higher than for samples with a lower graphene content. The shrinkage curves also differ for analogs with different graphene content, and this difference begins at temperatures above 600°C. In the range of 700-1600°C, the curves diverge, and the one for the sample with a lowest graphene content looks steeper; in this area, its shape is similar to linear. An increase in carbon content leads to difficulty in shrinkage.



Conclusion: Thus it was shown that the addition of 0.3-1.6 wt.% sheets of oxygen-free graphene into the ZrO₂ nanopowder leads to a change in its rheological properties. In the range from room temperature to 1700°C, the shrinkage and shrinkage rate curves have different shapes at temperatures above 600°C: the higher graphene content – the slower the shrinkage. Apparently, the graphene sheets prevent material compaction due to their rigidity. The results of the work will be able to influence the development of methods for the synthesis of nanocomposites and the production of functional graphene-ceramic hybrid materials for a wide range of purposes. The study of the consolidation process of synthesized nanostructured powders based on ZrO₂ using the dilatometric method will make it possible to develop optimal conditions for sintering fine-grained ceramics.