SYNTHESIS AND PROPERTIES OF ZIRCONIA-GRAPHENE COMPOSITE CERAMICS: A BRIEF REVIEW

A.G. Glukharev^{1,2} and V.G. Konakov^{1,2}

¹Institute for Problems of Mechanical Engineering RAS, Bolshoy 61 VO, St. Petersburg, 199178, Russia

²Saint Petersburg State University, Universitetskaya nab. 7/9, St Petersburg, 199034, Russia

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Abstract. The paper summarizes current data on ceramic zirconia-graphene composites. Basic types of graphene-containing additives and the main approaches for composite synthesis are considered. The effect of the additive type and synthesis procedure on the composite structure, mechanical (microhardness and crack resistivity) and electrical (conductivity at room and at elevated temperature) properties of the material is discussed.

1. INTRODUCTION

Over the past decade, graphene has attracted increasing attention of investigators working in the different field of science and technology; this interest resulted in a growing number of papers and patents dealing with graphene and graphene-based materials. Obviously, the above interest is due to the fact that graphene (Gr) possesses a set of unique properties: high specific surface area (2630 m²/g, [1]), high electron mobility (2 10⁵ cm²V⁻¹S⁻¹, [1-3]), high Young modulus value (≈1 TPa, [4]), and good thermal conductivity (≈ 500 W/mK, [5]). Regarding for these properties, graphene itself and graphene-based materials are widely used for the development of functional materials with a tailored structure and high mechanical properties. Note that the aim of such studies is not limited by theoretical in-

terest only, specific applications in modern technology are also widely discussed.

Analysis of recent literature indicated the significant progress in the development of “coarse-grained metal graphene” and “ultrafine-grained metal graphene” composites [6,7-10], approaches for such materials modeling could be found in, e.g., [11]; “polymer matrix-graphene” [1,12-15]. As for ceramic materials, the effect of Gr addition to a non-oxide ceramic matrix (SiC, Si₃N₄, BN, etc., see, e.g. [16-18]) on the material structure, their electrical conductivity and mechanical properties is studied well enough. At that, the same information for the case of oxide ceramics matrix and, in particular, ZrO₂ is rather limited: the effect of carbon-base additives on physical, chemical, and mechanical properties of the sintered materials is unclear. Zirconia-based composites reinforced by carbon nanotubes (CNT)

Corresponding author: A.G. Glukharev, e-mail: gluharev1@gmail.com

were widely studied over the past decade [19-25], an ambiguous effect of such additive has been shown. From one hand, carbon nanotubes addition increases some mechanical characteristics of the material (e.g., crack resistance); however, the strength of the materials is usually decreased. The onset of electron conductivity was reported for zirconia-CNT composites at the significant amount of nanotubes (1-6 wt. %) [26-28]; the authors of [27] consider this effect as following from the problem of uniform introduction of CNT in the ceramics structure, CNT agglomeration, as well as by partial CNT destruction at thermal treatment.

Since some of the above problems could be successfully solved in the case of 2D materials, the attempts to use graphene as a carbon additive to zirconia matrix were carried out, most of these works focuses on the tetragonal ZrO_2 due to the fact that this material is widely used in dentistry for dental crowns and implants production [29,30]. However, the information reported in the available literature is rather incomplete and contradictory; thus, the effect of graphene addition to zirconia matrix on the composite properties is still unclear. Generally, this is due to the well-known non-stability of the graphene monolayer causing the wide variety of Gr-containing additions which are more stable; in turn, approaches for their introduction into the ceramic matrix, composite compacting and heat treatment differ significantly. As a result, characteristics of the composites with the same composition as well as the conclusions of their nature and properties could be quite inconsistent.

Summarizing the above discussion, one can conclude that the task of the intentional synthesis of ZrO_2 -Gr composites with necessary properties requires the systematic analysis and critical review of the synthesis approaches. The aim of the present work is to summarize the available data on the effect of type and amount of Gr-containing additives along with the techniques of their introduction into zirconia matrix on the structure, electric conductivity and mechanical properties of ZrO_2 -Gr composites.

2. SYNTHESIS APPROACHES FOR ZIRCONIA-GRAPHENE COMPOSITES MANUFACTURING

The development of synthesis procedures providing the production of ZrO_2 -Gr composites with the preset properties requires the analysis of physical and chemical properties of the composite components and their advantages and drawbacks.

2.1. Brief characterization of physical, chemical, and mechanical properties of zirconia and stabilized zirconia

ZrO_2 at 1 atm exists in the following three crystalline modifications [31]: monoclinic ($m\text{-ZrO}_2$, $\rho=5.83 \text{ g/cm}^3$) thermally stable up to 1170°C , monoclinic modification is usually used as a raw material for refractories production [32]. The phase transition into the tetragonal modification ($t\text{-ZrO}_2$, $\rho=6.1 \text{ g/cm}^3$) occurs at temperatures exceeding 1170°C , this modifications at cooling stays in the metastable state. At higher temperatures ($\geq 2370^\circ\text{C}$) tetragonal modification transfers into the cubic one ($c\text{-ZrO}_2$, $\rho=6.09 \text{ g/cm}^3$) that possesses the most symmetric crystalline structure, however, $c\text{-ZrO}_2$ is unstable at low temperatures.

Due to the above mentioned instability of t - and c -zirconia at low temperatures, ZrO_2 -based solid solutions with a number of oxide additives (alkali-earth and rare-earth metal oxides) and are widely produced, these materials are known as "Ceramic steels". This name was used for the first time in [33], the authors manifested the excellent mechanical properties of the ceramics based on stabilized zirconia. So, the name "Ceramic steel" was chosen to highlight the similarity of such ceramics with steel since the thermal expansion coefficient and shear modulus of the materials were shown to be quite close. Obviously, the melting temperature of the ZrO_2 -based ceramics was significantly higher: 2680°C for ceramics against $1420\text{-}1450^\circ\text{C}$ typical for steel. Note that mechanical and electrical properties of the stabilized zirconia depend on the type and amount of doping oxide, the materials are generally subdivided into:

- CSZ (Cubic Stabilized Zirconia): cubic solid solution based on ZrO_2 ; the content of MgO or CaO to synthesize this material should be more than 12-15 mol.%, while the amount of Y_2O_3 is usually ≥ 8 mol.%. CSZ possesses relatively low strength properties: bending strength σ_{bend} is usually below 250 MPa and crack resistivity K_{Ic} is less than $3 \text{ MPa m}^{1/2}$. These materials are usually used as refractories, in addition, they are used in solid electrolytes technologies [34-36];
- ZTC (Zirconia Toughened Ceramic): dispersed $t\text{-ZrO}_2$ particles are distributed in the ceramic matrix, they are stabilized by compressive stresses. Al_2O_3 - ZrO_2 (ZTA: Zirconia Toughened Alumina) composites are most important for technical applications, primarily, they are used as tool materials. Optimal

Fig. 1. The common scheme of graphene additives synthesis, summary of the approaches reported in [45-47].

mechanical characteristics here are usually achieved at ZrO_2 content ~ 15 vol.%, the values of σ_{bend} up to 1000 MPa and K_{Ic} up to 7 MPa $\text{m}^{1/2}$ could be obtained [37].

- **PSZ (Partially Stabilized Zirconia):** these composites are formed as a result of Mg, Ca, and Y oxides addition into zirconia matrix. At that, rather coarse cubic zirconia grains with the average linear dimensions $\sim 60 \mu\text{m}$ are formed at high temperature baking in the region of cubic phase homogeneity, while tetragonal particles coherently linked with the cubic phase appear in the double-phase region. The typical size of $t\text{-ZrO}_2$ particles in $\text{ZrO}_2\text{-MgO(CaO)}$ systems should be less than $0.25 \mu\text{m}$ since the coherence is broken in the case of $t\text{-ZrO}_2$ particles coarsening; as a result, their reinforcing ability is drastically decreased. The content of $t\text{-ZrO}_2$ phase is usually ~ 40 vol.%. PSZ materials are widely used in mechanical engineering due to their high mechanical properties (σ_{bend} up to 1500 MPa and K_{Ic} up to 10 MPa $\text{m}^{1/2}$) [38,39].

- **TZP (Tetragonal Zirconia Polycrystals):** this material can be obtained in $\text{ZrO}_2\text{-Y}_2\text{O}_3$ or $\text{ZrO}_2\text{-CeO}_2$ systems; it contains tetragonal grains only. Material baking here is usually carried out in the region of t -phase homogeneity, it is followed by quenching. The energy dissipation at hardening phase transition into TZP is extremely high resulting (at an optimal structure) in extra high mechanical characteristics (σ_{bend} up to 2400 MPa and K_{Ic} up to 15 MPa $\text{m}^{1/2}$) [40]. In addition, TZP possesses rather high ionic electrical conductivity; however, it is in-

sufficient for the use of the material as solid electrolyte. TZP composites were tested as tool materials, the production of such instruments is reported in EU and in Russia [40-42].

2.2. Graphene additions

Graphene is usually treated as a sheet of interconnected regular hexagons. The characteristics of these hexagons are: sp^2 -hybridized carbon atoms in the hexagon vertices; the hexagon edge length of 0.142 nm, and C-C-C plane angle of 120° . Generally, graphene can be interpreted as a graphite monolayer separated from the bulk.

Graphene in the above discussed form is rarely used for composite synthesis due to the following reasons. The excess free surface energy of the material results in its instability; it also gives rise to agglomeration and folding [43,44]. In additions, the approaches used for pure graphene production involve the necessity of some substrate; graphene is usually closely connected with such a substrate.

As an alternative to pure Gr, graphene derivatives are usually used to produce Gr-containing composites (see Fig. 1): Gr-nanoplatelets and nanoribbons, as well as so-called graphene oxide (GrO) and reduced graphene oxide – (rGO). Let us discuss the in some more detail.

Graphene nanoplatelets – GNPs. GNPs are usually the sheets consisting of Gr monolayers with the typical linear dimensions $\sim 20 \times 20 \mu\text{m}$ and a number of Gr monolayers from 1 to 10. GNPs tend

Fig. 2. The structure of the terminal atoms in the graphene nanoribbons: (a) chair and (b) zig-zag, adapted from [52].

to agglomerate possessing high specific surface area being 400-700 m²/g [48]. Note that the above area is very high, however, it is much less than those calculated theoretically for pure Gr – 2630 m²/g. Since the linear dimensions of GNPs is rather low, relatively high number of unsaturated terminal carbon atoms are present here; they are easily connected with each other, with another atoms or with functional dopant groups, strongly affecting the basic GNPs properties, foremost, electrical conductivity [49-51]. GNPs are usually produced by intercalation approaches or by mechanical delamination in the mills in the liquid ambient, in an inert gas, or in the air.

Graphene nanoribbons – GNRs. GNRs are the graphene sheets with the width less than 50 nm (up to 20 hexagons), usually they are produces by carbon nanotubes unfolding [46], other approaches are quite rarely used. GNRs possess very interesting properties: in contrast to GNPs, their electrical and optical characteristics depend on the type of hexagon package in the Gr sheet, see Fig. 2 [57].

Two GNR modifications are considered depending on hexagons package in the ribbon, “chair” modification is shown in Fig. 2a and “zig-zag” modification in Fig. 2b. Theoretical modeling of GNRs properties showed that metal properties could be expected for “zig-zag” modification, while the “chair” could have either metal or semiconductor properties, [53-56] (Fig. 3). At that, experimental data on GNRs are fairly contradictory.

Graphene oxide – GrO. GrO is a graphene sheet with the oxygen introduced in the form of carboxyl, epoxy, and hydroxyl groups. GrO is usually manufactures by graphite oxidation under the harsh conditions (so-called Hammer’s method [57]). As a result of such oxidation, the interplane distance between the graphite monolayers increases from 3.35 Å up to 7 Å. Further mechanical, thermal or ultra-

sound treatment brakes the bonds between the monolayers providing graphene-like structures. The basic GrO advantages are the production simplicity and the possibility of its water dispersion in contrast to organic solvents used for nanoplatelets and nanoribbons. In turn, the main drawback of the material is its low conductivity not allowing to use it as an electron conductor in the composites.

Reduced graphene oxide – rGrO. Graphene oxide subjected to reduction is called the reduced graphene oxide, usually the reduction is carried out thermally or by some strong reducing agents (hydrazine, sodium borohydride, etc.) [58]. Such a reduction partially increases the electron conductivity of the material. However, till now, no approach providing the complete regeneration of the graphene structure has been suggested.

Summarizing the above consideration, one can conclude that zirconia cubic solid solutions possess high ionic conductivity, but their mechanical characteristics are significantly lower than that typi-

Fig. 3. Zone structure in the graphene nanoribbons for the : (a) chair structure and (b) zig-zag structure with $N=20$, adapted from [52].

Fig. 4. Mechanisms applied for the precursor powder homogenization, based on data reported in [47,59].

cal for tetragonal or partially stabilized zirconia. In turn, high mechanical properties of TZP are usually due to martensitic hardening and monoclinic phase formation resulting in the material instability: indeed, slow TZP destruction is observed in a water-containing ambience. The possible pathway to develop new composites free of the above discussed drawbacks is the introduction of graphene or Gr-containing additives with high mechanical properties into the zirconia matrix. The key point of this approach is the procedure of Gr-containing additions since this procedure determines both the final composite structure and the uniform additive distribution in the oxide matrix. Let us consider these approaches in more detail.

2.3. Approaches to the Gr-containing additions dispersing in the zirconia matrix

Similarly to the approaches used for the ceramic composites sintering, manufacturing of ZrO_2 -Gr composites could be considered as containing the following main steps: (i) manufacturing of the homogeneous precursor powder for the composite; (ii) powder compacting, and (iii) baking. There are a number of possible pathways to obtain the uniform distribution of the Gr-containing additive in the ceramic precursor powder, see Fig. 4.

• **Joint zirconia and Gr-additive milling in ball or planetary mills.** This approach is cheap and

quite available to mix zirconia powders with Gr-additives and to get proper uniform distribution of the additive. Ball and planetary mills as well as mechanical agitators [60] are used here. Rather high process temperatures could be obtained during the milling in the dry state (without wet binders); that high temperature treatment additionally promotes partial GrO reduction.

• **Mechanical mixing in the solvent ambience.** Note that mixing could take place in the dry form as well as in solvent ambience. The dispersion of the Gr-additive and the ceramic precursor powder in the liquid may be performed in one vessel as well as separately. Water (for GrO) [61] or organic liquids (for GNP, GNR, and rGrO) [62] are usually used as solvents here. Authors of [63] investigated the effect of 3 mol.% yttria-stabilized tetragonal zirconia (3YTZP) ceramic matrix with GNP mixing approach on the structure and properties of the composites manufactured by spark plasma sintering (SPS).

Summarizing the results reported in [63], one can conclude that, in spite of the fact that the obtained density for all samples studied was close to theoretical one, the effect of mixing approach was quite evident. GNPs with the significant surface area mainly oriented in the direction perpendicular to the compression axis were observed in the composites synthesized from powders mixed by ultrasound or ball milling in a planetary mill in the isopropyl alcohol presence, i.e. by “wet” mixing. The above GNPs shape and orientation resulted in some significant

anisotropy of the composite properties. On the contrary, composites synthesized from the powders mixed by “dry” approach showed smaller GNPs dimensions and lower monolayers number. As a result, GNPs were able to “adapt” to the structure of the ceramic matrix covering its grains. In this case, uniform GNPs distribution in the composite matrix is observed and the composite properties are isotropic.

- **Homogenization using colloid systems.** This approach is based on the use of stable ZrO_2 suspensions possessing negative surface charge. The addition of the GrO suspension characterized by positive surface charge leads to the stable agglomerates formation due to electrostatic interactions. Well mixed precursor powders could be obtained here after the solvent removal.

- **Sol-gel processes.** Sol-gel processes are widely used to synthesize oxide powders, they are based on the hydrolysis of soluble substances resulting in the formation of non-soluble hydroxides (sols). Sols could be transferred to gels and, after the water removal, to monodispersed powders. In case of zirconia, soluble ZrO_2 -containing compounds are precipitated in the form of $\text{Zr}(\text{OH})_4$ sol; it is transferred into gel and the residual water is removed. The final product here is ZrO_2 powder. The advantage of the process is the possibility to vary the process conditions obtaining the required powder particles size (from 10 nm [60]), in addition, the approach is rather simple. Sol-gel synthesis can be used to manufacture Zr-based graphene-containing precursor powders. The precipitation here is carried out in the suspension of the Gr-containing additive, GrO-water suspension is usually used here. Note that the Gr-containing particles in such an approach could act as crystallization centers, hence, the obtained particles could be larger than in the case of pure sol-gel process.

- **Alkoxides pyrolysis.** Theoretically, alkoxides pyrolysis is an alternative approach to manufacture well-mixed precursor powders. We have not found works describing the application of this method to Zr-based Gr-containing composites production; however, its application to ZrO_2 compounds was reported in [59,64,65]. Authors of [59] showed the possibility to produce well-formed nanostructured yttrium stabilized zirconia (YSZ) with a high conductivity using the pyrolysis of aerosol mixture containing the following acetylacetonates: 0.025M $\text{Zr}(\text{acac})_4$ and 0.01M $\text{Y}(\text{acac})_3(\text{H}_2\text{O})_x$, silicon substrate was used here. It is expected that further modification of this approach could make it more competitive.

Summarizing the above consideration, we can state that all the approaches used for the homogenization of Gr-containing Zr-based precursor powders possess advantages and drawbacks; no one can be assumed as an ideal one. However, one can expect better results using sol-gel approaches or “dry” mixing.

2.4. Zr-based ceramics compacting and baking

As was mentioned above, the next steps of the composite synthesis are compacting and baking. Spark plasma sintering coupling both processes is one of the most perspective approaches here, this method bases on pressing with simultaneous Joule heating under electric current. At that, the press is also the current conductor here [66]. Pressing is usually carried out in the graphite press-forms which also are the current conductors. Sometimes, the refractory metal foil is added as an interlayer simplifying further sample from press-form separation. Obviously, the process should be carried in vacuum or in inert atmosphere to prevent press-forms oxidation at elevated temperatures. Both direct and alternating currents are used in SPS method, some approaches use impulse or another less common regimes.

SPS approach is fairly different for conductive and non-conductive materials due to the difference in heating mechanisms. Conductive samples are heated by electric current passing through the sample bulk, while non-conductive samples are heated via the convective mechanisms, the press-form here acts as a heat source.

Note that Zr-based matrix is a non-conductive material and Gr-containing additive is a conductive one, both heating mechanism could be expected during ZrO_2 -graphene composites production by SPS approach. As a result, non-uniform heating could be expected here.

The basic advantage of SPS method is a high heating rate determining rather short synthesis duration (usually, it is some minutes); this is a real advantage in a work with nanopowders since the short process time provides an opportunity to retain their unique properties. In addition, no processes are taking place in the ceramic matrix, so, the grain growth is prevented. Another advantage of the method is the possibility to get the ceramics density close to the theoretical one. In addition, vacuum or inert gas atmosphere prevents the Gr-containing additive oxidation.

Table 1. Summary on baking/pressing results.

Matrix	Gr-containing additive	Gr-containing additive content	Baking temperature, °C	Obtained composite structure	Density, % of theoretical one	Ref.
Yttria stabilized tetragonal zirconia (3YTZP)	rGrO	0-3 vol.% 4 vol.%	1350	rGrO is uniformly distributed in the matrix with some excess in the intergrain space	> 98 < 98	[78]
Zirconia toughened alumina (ZTA)	GNP	0-8 vol.%	1450-1650	GNPs are uniformly distributed in the matrix, some excess of them is extruded into the intergrain space	94-98	[67]
Yttria stabilized tetragonal polycrystalline zirconia (3YTZP)	GNP	5, 10, 20 vol.%	1250	GNPs are uniformly distributed in the matrix, the excess of them is extruded into the intergrain space causing properties anisotropy	> 99	[68]
Spray-dried granulated 3 mol.% yttria-stabilized zirconia powders	GrOrGrO	0.05, 0.09, 0.2 wt.% 0.05, 0.09, 0.2 wt.%	1350 1350	In-situ GrO and rGrO reduction is reported providing uniform and dense samples	> 99 > 99	[69]
3YTZP	GNP	10 vol.%	1250	Four mixing approaches tested resulting in different structures	>98%	[63]

The drawbacks of the method are non-isostatic pressing leading to the anisotropy of the final material and non-uniform heating resulting in cracking and non-uniform baking.

Some alternative compacting and baking approaches are used sometimes: hot pressing, hot isostatic pressing, baking in vacuum without pressing, convective baking in air ambience, etc. These approaches possess some advantages; however, process duration and energy consumption typical for them make them noncompetitive compared to SPS approach.

Let us discuss the results reported in modern literature in some more detail, see also Table 1. Paper [78] reported SEM results for 3YTZP matrix (with 3 mol.% Y_2O_3) reinforced with 0.6, 1.8, 3.0, and 4.1 vol.% of rGrO; pure 3YTZP was used as a reference sample. It was shown that is possible to obtain sample density being as high as 98% of the theoretical one. The increase in the rGrO additive content gives rise to some small decrease in the sample density. The further increase in graphene additive contents over 4 vol.% resulted in the significant density decrease indicating the fact that large rGrO contents prevents ceramics densification. The reference sample was characterized by monolithic structure, ZrO_2 grains had similar sizes, moreover, linear grain dimensions were similar uniaxially. rGrO additives were distributed in the intergrain space, the effect of additive extrusion into the intergrain space is more evident at high additive contents.

Authors of [68] investigated the same 3YTZP matrix with high amount of GNP additive of 5, 10, and 20 vol.%; samples were sintered at 1250 °C by SPS. Similarly to the previous case, GNPs were not destructed during sintering, they were also extruded into the intergrain space. However, the evident GNPs orientation in the direction perpendicular to the pressing axes was observed, this type of GNPs orientation negatively affect electrical properties of the material. The regions with maximal GNPs concentration were clearly observed at the maximal Gr-containing additive contents of 20 vol.%.

GNPs were also used as Gr-containing additives in [67], they were introduced in zirconia hardened Al_2O_3 matrix. Similarly to the above discussed work, GNPs were uniformly distributed in the ceramic matrix; the extrusion of Gr-additives in the intergrain space was stated; the material had the density close to the theoretical one. The same trend for density decrease at GNPs contents increase was shown. It should be noted that rather high sintering temperature of 1650 °C did not destroy graphene nanoplatelets.

Authors of [69] investigated 3YTZP composites with 0.05, 0.09, and 0.2 wt.% GrO contents. In addition, they performed SPS synthesis using the preliminary reduced ZrO_2 -GrO powders in argon atmosphere at 850 °C; SPS synthesis was performed at 1350 °C. Composite density close to the theoretical one (>99) was obtained for both material type (with GrO and preliminary reduced GrO), graphene nanosheets were detected in the intergrain boundary of the final composite. Similarity of the results obtained for both additives type gives an opportunity to conclude that preliminary GrO reduction (i.e. rGrO formation) does not significantly affect on final composite properties. It should be mentioned that authors of [70] reported similar effect – GrO reduction to rGrO in SPS process.

Summarizing the above discussion, one can state that SPS approach provides manufacturing of dense composites with the density close to the theoretical one (98-99%) and with the uniform distribution of graphene-containing additives in the ceramic matrix. However, information on the effect of the additive type and its contents and the composite properties is still insufficient.

3. ZrO_2 -Gr COMPOSITES CHARACTERIZATION

3.1. Mechanical properties

At the moment, there are a lot of works dealing with mechanical characteristics of ZrO_2 -Gr microstructure with different microstructure: porous, non-porous, lamellar, etc. [69, 71-79].

Authors of [78] studied the properties of 3YSZ-rGrO composite produced by SPS approach. Vickers hardness and crack resistivity data are presented in Fig. 5 as a function of rGrO contents. It was shown that composite hardness slowly decreases with the increase in rGrO concentration; on the contrary, the crack resistivity is increasing. The increase in the composite hardness is usually explained by grain size decrease, see, e.g. [80]. Since the average grain size in the produced composites also decreases with the rGrO contents increase, the observed hardness behavior could not be assumed as being due to the grain size effect, but it can be discussed through decreasing in the bulk density (residual porosity increasing) at rGrO addition [81].

Significant density decrease is also observed for some other ceramics-graphene composites [82]. Crack resistivity of monolithic 3YSZ itself is rather low (4.4 MPa $m^{1/2}$), authors of [78] assumed this effect as being due to low average grain size [85].

Fig. 5. Vickers hardness and crack resistivity of 3YSZ ceramics produced by SPS approach vs rGrO contents, data reported in [78].

The introduction of 4.1 vol.% rGrO leads to the significant crack resistivity increase up to 5.9 $MPa \cdot m^{1/2}$; note that the effect is more evident than in the case of single wall CNT addition. Authors of [78] suggested that the nature of this effect is based on zirconia grains folding by 2D graphene nanosheets [83].

The comparison of the results reported in [78] and [84] is fairly interesting. Similar 3YSZ ceramic matrix was used with the same Gr-containing additive (GNP). The difference was in the synthesis approach only: the authors of [78] were using SPS approach, while plasma assisted sintering (PAS) was used in [84]. The basic difference of PAC procedure is the impulse current regime promoting the evaporation of impurities from the particle surface. The results on the mechanical characteristics of the obtained composites – microhardness and crack resistivity (measured by single-edge notched beam method) along with the data on the composites relative density obtained in [84] are demonstrated in Table 2. As seen from the table, the characteristics

of the composites produced using PAS approach are higher than that presented in [78]; in particular, crack resistivity values were increased up to 8.9–9.5 $MPa \cdot m^{1/2}$ for pure 3YSZ and up to 15.3 $MPa \cdot m^{1/2}$ for graphene-containing composites (Fig. 6), the increase in crack resistivity here can be estimated as $\approx 60\%$. In turn, sample hardness also demonstrates some increase, the authors of [84] explain this fact by crack deflection, crack bridging and microcrack formation.

Results reported in [84] were argued in [86]. The authors of [86] considered that Gr-containing addition does not affect significantly the mechanical properties of the composite, in particular, the above mentioned mechanisms concerning crack and microcrack behavior were criticized. It was assumed that graphene additive acts as some lubricant and all positive effects deal with this effect only.

GrO and carbon nanofibers (CNFs) were used as carbon additions in [86], synthesis procedure was similar to those described in [78]. It was shown that the crack length in case of monolithic ZrO_2 and in case of carbon-containing composites is quite close, while crack resistance changes are within the experimental error limits for all samples studied, see Table 3.

3.2. Electrical characteristics

Introduction of graphene or Gr-containing additives should increase composite conductivity, however, the exact results strongly depend on the synthesis approach. Paper [87] reports 2 vol.% of GrO addition to the mixed ZrO_2 - Al_2O_3 ceramics. As a result, resistivity decrease of $10 \pm 1.0 \Omega \cdot cm$ was achieved, this result is four orders of magnitude lower than that obtained at CNFs addition ($2.5 \cdot 10^4 \Omega \cdot cm$) and 9 orders of magnitude lower than in case of pure zirconia [88].

Table 2. Mechanical properties and the relative densities of zirconia-graphene composites obtained by PAS approach, data from [84].

Graphene (wt. %)	Temperature ($^{\circ}C$)	Relative density (%)	Hardness (GPa)	Fracture toughness ($MPa \cdot m^{1/2}$)
0	1200	97.5	11.36	8.9
0	1300	99.2	12.46	9.5
0	1400	99.1	10.95	9.0
0.01	1200	98.9	13.56	11.2
0.01	1300	99.4	12.33	15.3
0.01	1400	99.3	12.69	9.3
0.03	1300	99.2	12.58	13.5
0.05	1300	98.9	13.02	10.5

Table 3. Mechanical properties and crack characteristics for ZrO₂ ceramics with graphene and carbon additive, data from [86].

Sample	Crack characteristic (the size of the indentation) 2a (μm)	Crack characteristic (twice the length of the crack+ the size of the indentation) 2c (μm)	Hardness (GPa)	Fracture toughness (MPa·m ^{1/2})
ZrO ₂	112±1	264±2	15.7±0.2	4.6±0.1
ZrO ₂ -GO	114±1	260±6	15.0±0.2	5.0±0.3
ZrO ₂ -CNFs	115±1	257±6	14.7±0.2	5.3±0.3

The effect of synthesis approach on the composite conductivity can be illustrated by Fig. 7. As was discussed above, SPS synthesis could significantly decrease ZrO₂-Gr composite resistivity; but, the significant anisotropy can be seen: indeed, at lower GNP contents $\sigma_{||}$ and $\sigma_{\perp}$ values are fairly different. Note that this effect does not manifest itself at the maximal GNP contents of 20 vol.% [68]. As it was mentioned above, this effect is attributed to GNPs orientation that is perpendicular to the compression axis. Anisotropy coefficient could achieve rather high values: basing on results of [68] it can be calculated as $\sigma_{||}/\sigma_{\perp} = 6.84 \pm 0.11$ for the sample with 10 vol.% of GNPs. Note that the same ratio for the sample with 5 vol.% of GNPs is 3.36 ± 0.05 ; hence, one can consider the evident dependence of the resistivity on Gr-containing additive contents. This effect is usually assumed as being due to the bonds formation between GNP nanosheets in the *ab*-plane similar to the case of highly oriented pyrolytic graphite [89,90] and graphite monocrystal [91]. The significant increase of $\sigma_{||}$ input is observed

at 20 vol.% of GNPs, it decreases anisotropy factor down to 1.18 ± 0.05 . In fact, material becomes isotropic here and 3D GNP network is formed.

Similar behavior is typical for other ceramic matrixes [92-95]. However, it should be mentioned that the maximal conductivity value ($\sim 276 \text{ S m}^{-1}$) obtained in [68] for zirconia matrix is much lower than that shown for Al₂O₃-GNP composites ($\sim 1000 \text{ S m}^{-1}$ at 15 vol.% of GNPs) in [96] and Si₃N₄-GNP composites ($\sim 4378 \text{ S m}^{-1}$ at 25 vol.% of GNPs) in [93]. However, this effect is probably not due to the matrix, but to the Gr-containing additive characteristics: number of monolayers, synthesis approach, agglomeration, etc.

Note that most of the papers discussing ZrO₂-Gr composites discuss composites based on tetragonal ZrO₂ matrix. However, other zirconia modifications and, in particular, cubic ZrO₂ could be also treated as being very promising. The possibility to

Fig. 6. Mechanical characteristics (hardness and crack resistivity) of the zirconia-graphene composites (3YSZ-GNP) synthesized by PAS approach [84]. **Fig. 7.** Illustration of the electrical resistivity anisotropy in the 3YSZ-GNP composites with varying Gr-addition contents, measurements at room temperature, image based on results reported in [68].

Fig. 8. Electrochemical impedance spectra of the electrochemical impedance for YSZ-GNP samples: (a) 2.5 wt.% GNP, (b) 3.75 wt.% GNP, and (c) 5.0 wt.% GNP, replotted from [99].

combine high electronic conductivity typical for graphene with ionic conductivity and high thermal stability of the cubic zirconia are very attractive for different applications.

Let us discuss the mechanism of cubic fluorite-like zirconia conductivity in some more detail. Yttrium oxide Y_2O_3 is usually added to stabilize cubic zirconia, the conventional amount of such additive is 8-9 mol.% [97], this composition is known as yttria stabilized zirconia YSZ). YSZ ion conductivity appears due to heterovalent substitution of Zr^{4+} by Y^{3+} ion; the difference in charge is compensated by the formation of oxygen vacancies; the process is described by Kröger–Vink notation (1).

Double charged oxygen vacancies are characterized with high mobility and can migrate into the material bulk exchanging with oxygen ions via co-called “jump” mechanism [98].

At the moment (year 2018) only one work reporting the detailed study of the electrical properties of cubic YSZ-GNP composites as a function of temperature is available [99]. Composites containing 2.5, 3.75, and 5.0 wt.% GNP were synthesized by SPS. Both pure YSZ and the composite with minimal GNP contents (2.5 wt.%) possess dominant ionic conductivity (volume and surface

components) at a temperature range 500-900K (Fig. 8). Some small deviations in the electrochemical impedance spectra can be due to some changes in the intergrain space: graphene nanosheets are appearing there preventing the electrical charge transfer between the grains. The values of the activation energy measures for these samples coincide within the limits of the experimental error and can be estimated as $E_a = 1.1$ eV. Such a value of activation energy is typical for oxygen conductivity realized via “jump” mechanism.

At the increase in the graphene-containing additive contents, the composite conductivity increases by four orders of magnitude, this effect is also observed for the sample with a maximal GNP contents of 5 wt.%. At that, the value of the activation energy decreases down to 0.1 eV. Since the behavior of the electrical conductivity is well-described by the Arrhenius plot, the measured electrical conductivity can be extrapolated from temperature at which measurements were carried out to room temperature where the difference in the conductivities is expected to be increased by 11 orders of magnitude. Note that the produced composites appeared to be stable under the reduction atmosphere ($p_{O_2} < 10^{-5}$ atm.), but they are unstable in air, see Fig. 9. Indeed, the sample conductivity (Fig. 9b) drastically decreased after the exposition at 500 °C for 13 hours.

Fig. 9. The effect of YSZ-GNP (5.0 wt.% GNPs) thermal exposure (500 °C, 13 hours) on (a) electrochemical impedance spectra, (b) electric conductivity, data from [98].

The reason of such decrease can be seen from SEM image of the sample, Fig. 9c, an evident cracking as the result of oxidation can be seen there.

4. CONCLUSION

Summarizing the above consideration, one can state that mechanical characteristics of ZrO_2 -Gr composites are well studied, especially for the case of tetragonal matrix modification. Generally, the limits of their application are clear. However, the perspective possibility to use such composites as functional high-temperature materials (cathodes and anodes in solid-oxide fuel cells (SOFC) or membranes in oxygen pumps) is still questionable, additional studies are necessary here.

The another non-zirconia materials developed nowadays (perovskite-like high temperature mixed conductors) possess significant drawbacks, the basic of them is a low stability in reducing atmosphere [100,101] due to partial oxide reduction with further phase lamination.

As it was shown above, carbon component of the discussed composites oxidizes at temperatures >700 °C being even low than the working temperature of most SOFC elements during the exposure for some hours. So, one of the general tasks of the further investigations should be the increase of the composites oxidation resistance.

Additional investigations are also necessary to clarify the effects of the Gr-containing additive type and synthesis approach on the composites characteristics. The available information here is quite insufficient, in addition, the comparison of the available data is complicated by the fact that different

additives are introduced in the different zirconia matrix; moreover, the amount of introduced graphene varies from parts of percent to 10-20 wt.% and even more.

Systematic study of the effect of composite synthesis on the final state of the graphene-containing additive, flake formation, agglomeration, etc. is also necessary.

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