FLAG-ERA Multifunctional Ceramic/Graphene Thick Coatings for New Emerging Applications

Final Report

In the first year the research team accomplished the WPs scopes of the project, as well as graphene (MLG-multilayered graphene) synthesis by mechanochemical methods was performed by intensive high efficient milling and ceramic-graphene powder mixture preparation by powder technological steps e.g. attriton milling, sieving, drying. Both the starting powders, the synthesised graphene powders and ceramic powder mixtures as well as ceramic/graphene composite modells from partial studies and the composites under development in different stages of their production were considered for overall structural characterisation. The preparation of tailored carbon nano-materials (graphene, grapene oxide-Gos, multilayer graphene- MLG, carbon nanotubes-CNTs) has been widely investigated, revealing the mechanical milling in an attrition milling device as the most common method. The attrition milling method is a type of mechanical exfoliation because the shear component of the applied stress is dominant. Usually low-energy planetary and vibratory mills are used as ball milling equipments, however there are examples for high-energy nanoporous carbon production too.

In the first year of the project we used high efficient attritor mill because it promotes the intercalation or expansion of graphite. Hereby, we combined two method micromechanical and intercalation based exfoliation of graphite to realize a simple and efficient process, which lead us to the mass production of graphene-based materials. Ceramic-graphene or CNTs powder mixtures have been realized by high intensive milling processes. Optimization of mixing process, wet or dry intensive steps and a careful handling of powder mixtures assured to eliminate the agglomeration of nanophases in this first powder technological steps. The ceramic/graphene thick coatings, the design of multifunctional layered structures were realized by dry pressing and hot isostatic pressing (HIP) in the case of Si_3N_4/h-BN (1, 3 and 5wt% BN) composites and by spark plasma sintering (SPS) in the case of ZrO_2/CNTs (1, 5 and 10 wt% CNTs).

Si_3N_4/h-BN composites have been prepared by three different milling procedures. Thorough morphological characterizations have been carried out to reveal the influence of the milling parameters on the size of the h-BN additives. The results confirmed significant decrease in the h-BN particle size by increasing milling time.

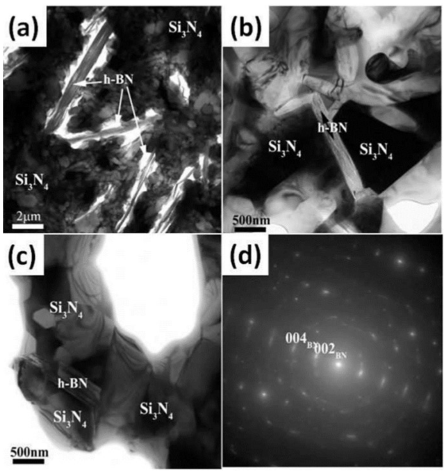

Fig. 1. BF-TEM images and electrondiffraction of the Si_3N_4/h-BN composites showing the h-BN platelets in Si_3N_4.

The BF-TEM images proved that the h-BN platelets were present in the matrix as thin and almost parallel aggregated plate-like particles. The h-BN particles could be clearly distinguished from the main matrix owing to their different form (Fig. 1). According to the XRD measurements, the main phases in all samples are β-Si_3N_4. In addition, BN and $ZrO_{1.87}$ phases were detected. The mechanical measurements showed that the increase of the h-BN content decreased both the hardness and Young's modulus of all the samples.

In addition, the increase in the size of h-BN particles caused also increase in the hardness and Young's modulus (*PROCESSING AND APPLICATION OF CERAMICS 12 : 4 pp. 357-365. , 9 p. 2018*).

For all tested specimens, the rise in thermal shock resistance of Si_3N_4/h-BN composites with the increase of the amount of h-BN particles was observed compared to the monolithic silicon nitride. Also the incorporation of micro BN particles to Si_3N_4 matrix has a positive influence on thermal shock resistance comparing to the nano h-BN addition. The highest thermal shock resistance (over 1000°C) was achieved at Si_3N_4 composites with 3 wt. % and 5 wt. % micro BN particles, with higher fracture toughness 7.0 - 7.5 MPa. $m^{0.5}$ (*KEY ENGINEERING MATERIALS 784 pp. 73-78. , 6 p. 2018*).

The influence of MWCNT addition and milling process on structure and design of composites were also studied (*BOLETIN DE LA SOCIEDAD ESPANOLA DE CERAMICA Y VIDRIO 58 pp. 126-133. , 8 p. 2019*). ZrO_2 – 8mol.% Y_2O_3 (8YSZ) powders were mixed with 1, 5 and 10wt.% MWCNTs and milled by high attrition milling at 4000 rpm in ethanol for 5h. The structural and morphological investigations of as received zirconia powder consisted of the particles with sharp and irregular shape. In fact, the effect of milling on the as received zirconia resulted in a considerable decrease for particle size without phase transformation of 8YSZ particles. The phase analysis proved the existence of two phases; cubic zirconia as a main phase and a small fraction of monoclinic zirconia as a minor phase. The particle size showed a refinement from an average of 50 m to 400 nm. However, no significant damage or structural changes affected MWCNTs after milling were observed. The MWCNTs were observed as a fine fibres forming several agglomerations, networks with approximate length 2.5micrometer, each fibre consisted of an average diameter 3.8nm, an average outer diameter 9.13nm. The number of carbon layers varied from 7 to 9. Raman spectroscopy results showed the presence of the G and D bands for all powder mixtures at peak positions of∼1590 and∼1355cm^{-1} respectively. These bands confirmed the structural integrity of MWCNTs after the milling process. The novel results are follows:

- milling process did not result in phase transformation of 8YSZ only grain decrease;
- the addition of MWCNTs to zirconia matrix introduced a significant change in the surface topology and the distribution of the zirconia grains;
- from the point of MWCNTs structure, non-destructive milling process was confirmed by HRTEM study;
- the structural integrity of MWCNTs after the milling process was confirmed by Raman measurements too.

The investigation was continued on YSZ/MWCNTs composites prepared by attrition milling and SPS at 1400°C conducted mainly to the following conclusions as in *CERAMICS INTERNATIONAL 45 : 4 pp. 5058-5065. , 8 p. (2019):*

- The structural investigation of 8YSZ and 8YSZ/1 wt.% MWCNTs revealed smooth and homogeneous surfaces. Inversely, when MWCNTs content increased the surface unveiled a reduced interfacial bonding between 8YSZ and MWCNTs, and deep open porosity on surface. This in turn led to low mechanical properties.
- Increase of MWCNTs content influenced phase transition from cubic to tetragonal and the increase in the monoclinic phase after sintering.
- The Raman investigations proved the stability and integrity of MWCNTs in composites
- The variation of Vickers hardness with surface displacement was practically homogenous and reached high values 13.49 GPa for 8YSZ and 12.44 GPa for 8YSZ/1 wt.% MWCNTs. The indentation fracture toughness of 8YSZ/1 wt.% composite was mostly equal or higher than that of 8YSZ (÷ 3.2 MPa.$m^{0.5}$).

In the second year the research team performed exhaustive experiments for optimizing the properties of the synthesized ceramic composites that could be established based on the systematic studies on synthesis parameters, microstructure and functional properties. The in-situ characterization on the microstructure and properties essentially contribute to the understanding of the relationship among synthesis parameters, microstructure and properties of carbon nanotube (MWCNT) or graphene/ceramic composites. In our work Si_3N_4/MWCNTs composites with 3wt.% of multiwalled carbon nanotubes were prepared from oxidized α-Si_3N_4 powders and sintering additives by hot isostatic pressing. The influence of the oxidation of silicon nitride powders on the microstructure development, mechanical and tribological properties was studied (*Processing and Application of Ceramics 14 [1] (2020) 25–31*). The main results are the following:

- Composites with un-damaged carbon nanotubes were prepared with increased density
- from 3.16 to 3.24g/cm^3 with the increased time of oxidation;
- The microstructure of the composites consists of β-Si_3N_4 grains, porosity and MWCNTs often in the form of CNTs bundles. The fracture character of the systems is mixed inter and intra-granular often with pulled-out CNTs bundles;
- The mechanical and tribological properties increased with the increasing oxidation time of the composites. Significant improvement can be obtained after optimization of the processing route- homogenization of CNTs and densification of the powder mixture.

The sintering of ceramic matrix composites is usually carried out by raising the sintering temperature below the melting point of components. Spark plasma sintering (SPS) has the capability to densify ceramics at a relatively low temperature in a very short time. Two different additions, multilayered graphene (MLG) and graphene oxide (GrO), were added to Si_3N_4 ceramic matrix in various amounts, 5 wt% and 30 wt%. The influence of reinforcing phase on final properties of spark plasma sintered Si_3N_4 composite was studied. The MLG addition resulted in higher hardness, modulus and bending strength compared to similar GrO additions. The Si_3N_4/graphene composites exhibited lower friction coefficient than for reference. The four-time decrease was observed for 30wt% graphene content, independent of graphene type (MLG, GrO). The 5 wt% amount of graphene was sufficient for the electrical percolation effect to take place. In this way, an increase in electrical conductivity could be achieved. In conclusion, uniaxial-pressure-assisted sintering such as SPS applied on MLG and GrO added Si_3N_4 resulted in lower mechanical behavior but better tribological and electrical properties (*Ceramics 2020, 3, 40–50*).

A set of 8YSZ composites with (0wt%, 1wt%, 5wt% and 10wt%) of MWCNTs contents were synthesized by attrition milling and SPS at 1400°C. The tribological properties of the composites have been investigated using Si_3N_4 balls, low (V1=0.036m/s), high (V2=0.11m/s) sliding speed and dry sliding conditions.

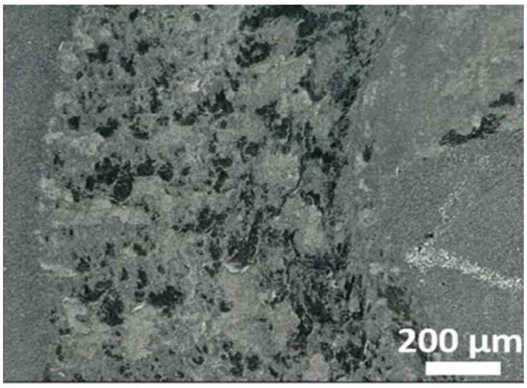

Fig. 2. Keyence Digital microscope micrographs illustrating the wear tracks after Tribo-test at V2 = 0.11 m/s sliding speed in 8YSZ– 10wt% MWCNTs composites.

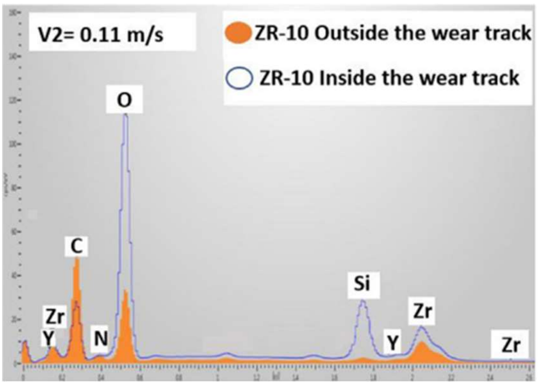

Fig. 3. Energy dispersive X-ray spectroscopy (EDS) inside and outside the wear track profile of 8YSZ–10wt% MWCNTs composites tested via V1 via V2 = 0.11 m/s.

At the speed of V1=0.036m/s, 8YSZ–1wt% MWCNTs exhibited 99.9% improvement in the wear rate followed by 95% in 8YSZ–5wt% MWCNTs and 64% in 8YSZ–10wt% MWCNTs composite compared to pure 8YSZ. Furthermore, the observation of grain pull-outs, micro cracks and high amount wear debris in pure 8YSZ give the evidence of abrasives wear behavior as main wear mechanism. This is shown to be linked with its coarse microstructure and the dry sliding condition. The outstanding wear improvement marked in 8YSZ–1wt% MWCNTs is in good agreement with the formation of continuous and uniform tribofilm on the worn surface. However, at 10wt% of MWCNTs content the tribofilm is discontinuous and does not protect from the brittle fracture due to the structural defects such as agglomeration and porosity. At the speed of V2=0.11m/s, minimal wear rate values have been recorded in all the composites regardless MWCNTs content. Further, the steady state friction coefficient decreased in the case of 8YSZ–5wt% MWCNTs and 8YSZ– 10wt% MWCNTs composites, reflecting easier sliding between the rubbing surfaces and friction improvement (Fig. 2 and Fig. 3). In fact, this friction improvement is shown to be linked with the apparition of intrinsic solid lubricant effect due to MWCNTs exfoliation (carbon peak decrease) and Si incorporation as confirmed by EDS spectrum (*Wear 430–431 (2019) 280–289).*

In the third year of the project the research team investigated the influence of the various content of the multilayered graphene (MLG) on the structural and mechanical properties of the final bulk porous silicon nitride-zirconia (Si_3N_4-ZrO_2) based ceramic composites. The results have been published in two leading journals (Q1/D1) in the field: *JOURNAL OF THE EUROPEAN CERAMIC SOCIETY 40: (14) pp. 4792-4798., 2020 and JOURNAL OF ALLOYS AND COMPOUNDS 832: 154984, 2020.* Furthemore, the scientific results have been disseminated as invited presentations in several prestigeous international conferences with high impact in respective fields, just name two: *44th International Conference and Expo on Advanced Ceramics and Composites (ICACC 2020), USA, 2020 and 8th International Congress on Ceramics (ICC8), South Korea, 2021 - online events.*

The performed experiments were in-line with planned workplan, the scientific achievements may be summarized as follows:

1. The ceramic composites were prepared in the form of the laminated structure with different 5-30-5 wt% and 30-5-30 wt% MLG content by hot isostatic pressing. Homogeneous distribution of the MLGs, a completed phase transition from alpha to beta-Si_3N_4 in case of 5 wt% MLG have been observed. The porosity of sintered composites increased by almost two times (from 38% to 66%) when the MLG content increased from 5% to 30%. The density values were lower for samples with higher MLG content owing to the porous microstructure of the samples induced by increased amount of MLG particles e.g. 2.71 g/cc and 1.84 g/cc for 5 and 30% MLG.

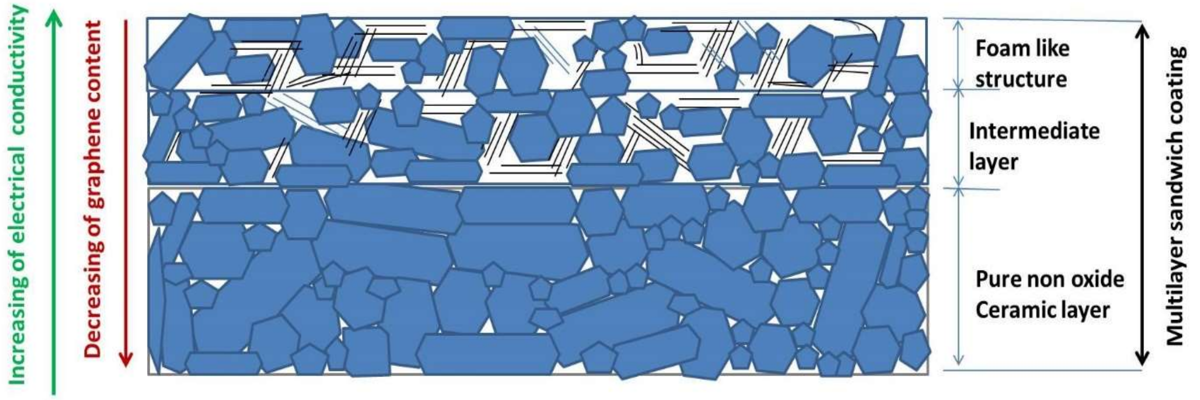

Fig. 4. The schematic view of the proposed MLG/Si_3N_4 layered structure

2. The structural examinations revealed that the multilayered graphene and zirconia particles owing to their different sizes and shapes influenced the porous microstructure evolution and the related mechanical properties of the composites. Novel laminated sandwich structure containing 5-30-5 wt% MLG in Si_3N_4-ZrO_2 matrix and 30-5-30 wt% MLG have been realized as well. The thickness of each ceramic layer in sandwich structure was changed between 1.0 and 1.6 mm.

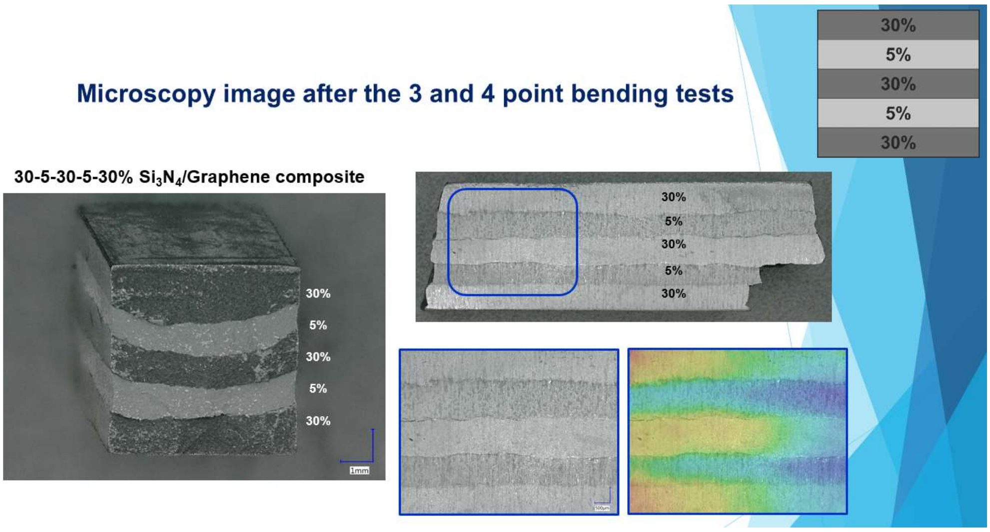

Fig. 5. The fracture surface of the 5 layered MLG/Si_3N_4 composite.

3. Morphological investigations and elemental analysis of reference composites have been performed by scanning electron microscopy (SEM). In both cases, the spherioid ZrO2 particles and thin plate-like multilayer graphene platelets were found to be incorporated into the mainly polygonal and rod-like Si_3N_4. The size of Si_3N_4 particles varies between 200 nm and 600 nm, while the average size of ZrO_2 particles were 1-2 micrometer. The 30 wt% MLG causes the higher porosity in structures. This structural observation is in agreement with the numerical calculations from density measurements of sintered composites. The elemental maps demonstrate that the MLG addition and other elements as Zr, O were homogeneously distributed during preparation process. Detailed study of microstructure by transmission electron microscopy (TEM) showed the optimal distribution of MLG in the ceramic composite matrix. The MLG addition distributed and embedded in Si_3N_4 based matrix were clearly identified in all parts of sandwich structure after HIP sintering. A large number of ZrO_2 grains were located between the Si_3N_4 particles. The cross-section study revealed the presence of the multilayered graphene addition between the rod-like Si_3N_4 particles. The size of the MLG addition ranged between 100 nm and 600 nm, and their thickness ranges from 5 nm to 30 nm. The size of silicon nitride rods is about 300 nm in width and 800-1200 nm in length. Elemental analysis revealed 89 at%, 92 at% and 85 at% of carbon at different spots. It indicates that the natural MLG particles were kept without sever oxidation during the whole manufacturing process.

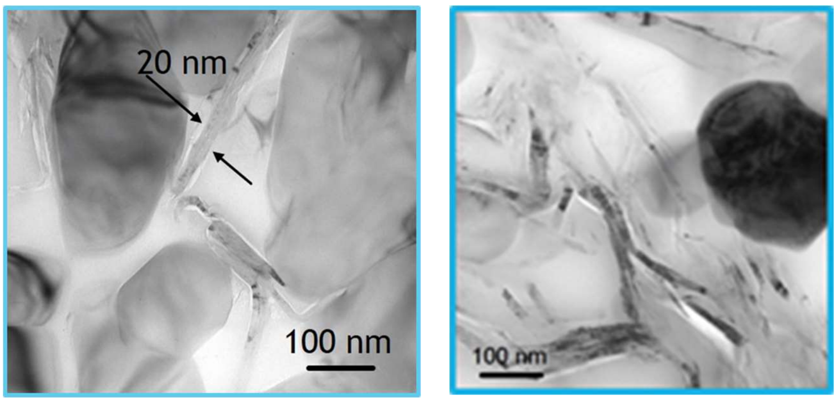

Fig. 6. The TEM micrographs of the Si_3N_4 – ZrO_2 with 5 wt% MLG and Si_3N_4 – ZrO_2 with 30 wt% MLG composites

4. In the case of base Si_3N_4-ZrO_2 composite, only beta-Si_3N_4 and Y-doped zirconia phases can be identified by X-ray diffraction. This proves that the commercial alfa-Si_3N_4 powder transformed completely to beta-Si_3N_4 during the hot isostatic pressing at 1700C, 20 MPa nitrogen gas pressure for 3 h dwelling time. In the case of composite with 5 wt% MLG, the phase transformation from alfa to beta-Si_3N_4 was completed. The alfa-Si_3N_4 particles dissolved in the existing liquid phase and subsequently, new beta-Si_3N_4 nuclei were formed. However, in the case of 30 wt% MLG, the phase transformation was partial; alpha-Si_3N_4 crystalline phase could be identified as well adfter sintering. On the other hand, amorphous carbon phase was also detected between 15 and 25 theta for composites with 30 wt% MLG. The ratios of identified ceramic phases in Si_3N_4-ZrO_2 composite were around 61% beta-Si_3N_4, 39% Y doped ZrO2 for Si_3N_4-ZrO_2 base composite, 58%beta-Si_3N_4, 42% ZrO2 were characteristic at composite with 5 wt% MLG and 51% alpha-Si_3N_4, 16% beta-Si_3N_4, 33% ZrO_2 was identified the composite with 30 wt% MLG.
5. The sandwich structures enhanced the mechanical properties compared to reference ceramic with 30 wt% MLG. The position of the layer with higher graphene content, high ratio of alfa/beta phase of Si_3N_4 and higher porosity had crucial effect on the final mechanical properties. The hardness decreased from ~6.51 GPa to 0.5 GPa with increasing of MLG addition from 5 wt% to 30 wt%, increasing of porosity of the final microstructure and content of alpha-Si_3N_4. The same tendency was observed for bending strenght values. The highest bending strength belonged toreference with 5 wt% MLG compared to 8 times lower value for reference with 30 wt% MLG. The sandwich structure 5-30-5 wt% MLG enhanced the mechanical properties compared to reference ceramic with 30 wt% MLG. The position of the layer with higher graphene content, high ratio of alpha/beta phase of Si_3N_4 and higher porosity have crucial effect on the final mechanical properties. The mechanical (bending) test confirmed that sandwich structure with 5-30-5 wt% MLG showed 2 or 3 times better properties than sandwich structure with 30-5-30 wt% MLG. The main effect on mechanical properties had the layer with 30 wt% MLG and it regulated the mechanical behaviour of final sandwich ceramic.
6. Testing of the sandwich structures by scratch measurements in dry conditions reflected the inherent character of references, thus the layer with 5 wt% MLG resulted friction coefficient ~0.5 and the layer with 30 wt% MLG ~0.7. No tribofilm formation was observed during tribological testing of composites.

In conclusion in this project novel mechanically robust ceramic/CNT and ceramic/graphene multifunctional composites with enhanced functional properties, mechanical, electrical, thermal and tribological properties have been developed with optimized microstructures based on the conventional powder technology. The realized composites show improved multifunctional properties compared to the state of the art functional ceramics. The norms for optimizing the properties of the synthesized ceramic composites could be established based on the systematic studies on synthesis parameters, microstructure and functional properties. The in-situ characterization on the microstructure and properties essentially contribute to the understanding of the relationship among synthesis parameters, microstructure and properties. A clear vision of how to design new generation layered ceramic/graphene composites with even more functionalities and improved properties is presented by completed project. In summary 10 publications (open access) and one book chapter (Elsevier) all showing the NKFIH contract number (NN 127723) have been published. The results have been presented in 10 international and two national conferences.