The M-ERANET „Grace" project was oriented to the development of advanced $Si_3N_4$/ graphene and SiC/graphene ceramic composites which are characterized with superior wear resistance as well as mechanical and chemical properties making them suitable to a wide range of industrial applications.

In this project the focus was set on non-oxide ceramics, silicon carbide (SiC) and silicon nitride ($Si_3N_4$). Alumina ceramics ($Al_2O_3$) which are still used for sliding parts and face seals in some technical applications, have been be studied to a smaller extend (for comparison).

MTA EK was a WP leader in WP3. „WP 3 Development of ceramic nanocomposites" (month 1- 30)
*Objectives: Graphene/ceramic composites (SiC, $Si_3N_4$, and $Al_2O_3$) with different types of graphene and various graphene contents (1-10 wt.-%) have been prepared for WPs 5-8. Different sintering methods have been used. The research tasks of MTA EK were the followings:*

- ✓ T3.1 Optimization of the homogeneous distribution of graphene in different ceramics by optimizing the milling parameters (rpm, milling time, milling type, etc. wet or dry milling). (MTA EK)
- ✓ T3.2 Development of the optimum powder quality for the SPS and for HIP process. (MTA EK, FCT, IMR SAS)
- ✓ T3.3 Comparison of various sintering methods regarding to the homogeneous distribution of graphene and the final microstructure of the composites on a fundamental (MTA EK) and technological (FCT) level
- ✓ T3.4 – T3.6 Sample preparation for different tests: (i) experimental characterisation in WP5 (TTK, FCT), tribological evaluation in WP6 (FCT) and system integration in WP7 (FCT)
- ✓ T3.7 Microstructural analysis. (MTA EK)

The influence of the 6 different types of graphene and their contents on the ceramic processing, especially sintering and densification was investigated (Tab. 1, Fig. 1).

| Nr. | Type | Preparation |
|---|---|---|
| 1 | MLG | graphite milled by high efficient attritor milling |
| 2 | BG-Grade C | commercial graphene |
| 3 | BG- Grade M | commercial graphene |
| 4 | MG-CO2-48h | milled in $CO_2$ for 48h by ball milling |
| 5 | TRGO-600 | thermally (at 600°C) reduced graphite oxide |
| 6 | G | graphene coating from furfurylalcohol |

***Tab. 1.*** *Different graphene types.*

One of most interested graphene type, multilayered graphene (MLG) was prepared by attritor milling technique. 10 hours intensive milling at 2500 rpm in ethanol of 1 and 5 micrometer sized graphite powders resulted MLG with 15-20 layers (Fig. 1.1). This MLG was used as additive phase for nanocomposite manufacturing. Other 5 graphene types were prepared by Freiburg University (Fig. 1.2-1.6).

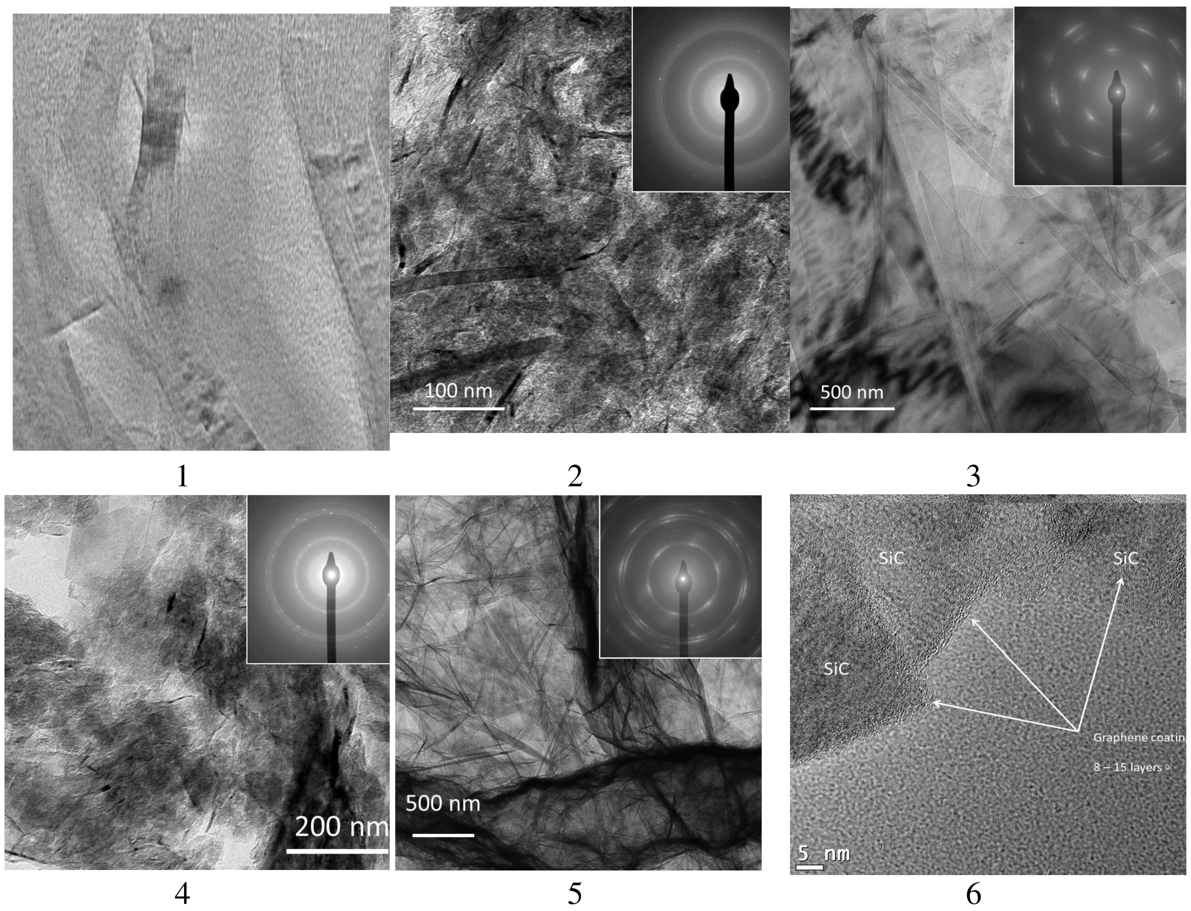



***Fig. 1.*** *TEM images of different graphene additions.*

All of the $Si_3N_4$ / graphene and SiC/graphene powder mixtures as base materials for composite preparation were prepared in MTA EK. Attrition milling was used for $Si_3N_4$ and SiC grain size decreasing and homogenization of graphene addition.

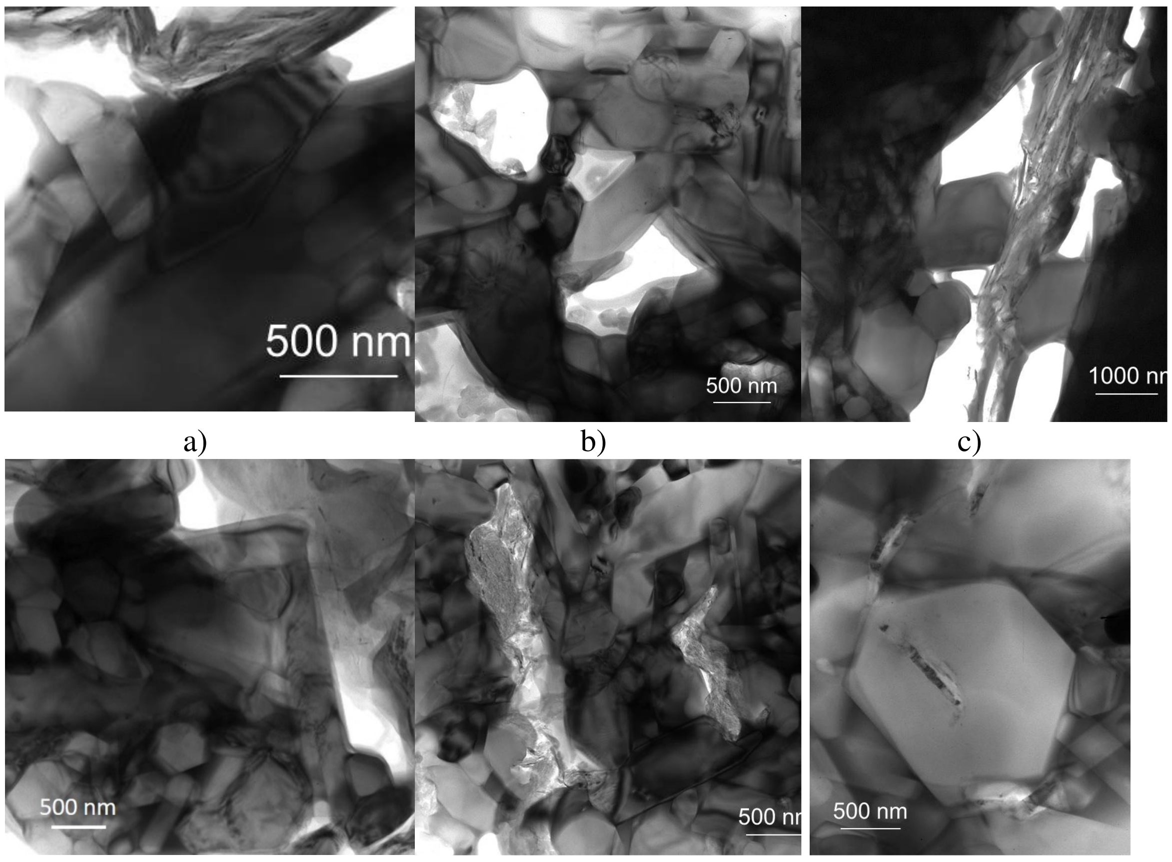
After milling process, 3 different sintering was used for composite development; hot isostatic pressing (MTA EK, TEM micrographs presented in Fig. 2), spark plasma sintering (FCT, IMR) and hot pressing (FCT, IMR).

One special focus was also be set on the spark-plasma-sintering technology (SPS and SPS/FAST)

that are available at FCT and IMR SAS. This method allows fast and energy-efficient sintering of ceramic materials. One precondition is that the green bodies must be electrically conductive and homogeneous to get high-quality, uniformly densified ceramic components.

The $Si_3N_4$ and SiC reference samples without graphene were sintered by all 3 sintering techniques.

Our previous work showed that dense and pore-free microstructures may be sintered by low graphene addition (1-5wt%). The same results was found in pre-tests at FCT partner, that pressure-less sintering of SiC with up to 3 wt.-% TRGO yields sufficient densification. Based on this observation, the consortium decided to continue the experiments with ceramic composites with the graphene addition between 2-3 wt% for densifications by SPS and HIP sintering.



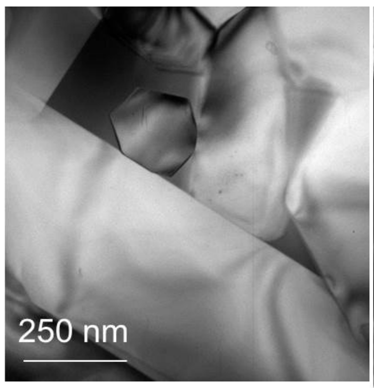

a) b) c)

d) e) f)

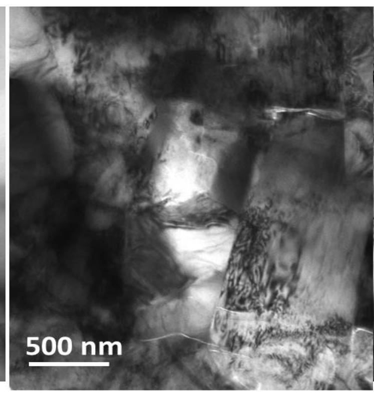
***Fig. 2***. *$Si_3N_4$/ 3 wt% graphene composites sintered by hot isostatic pressing. a) MLG, b)BG-Grade C, c) BG- Grade M, d) TRGO-600, e) MG-CO2-48h, f) G.*

The main result of optimization of composite composition was that hot pressing (HP) is a one of promising sintering technology for higher graphene content in ceramic matrices (Fig. 3). We prepared the composites with 1wt%, 3wt%, 5wt% and 10wt% MLG. Structure and morphology of samples were studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), selection area electron diffraction (SAED). Elemental composition of samples was measured by energy dispersive X-ray spectroscopy (EDS) and X-ray spectroscopy (XRD). The tribological behavior of composites in different environments was investigated and showed the decreasing character of wear at increased MLG content. This new approach is very promising, since ceramic microstructures can be designed with high toughness and provide improved wear resistance at low friction.

In all composites, densities between 97 and 100 % were obtained (Fig. 3). The alpha-$Si_3N_4$ to beta-$Si_3N_4$ phase transformation was completed during hot pressing. The structural investigations and phase analysis measurements confirmed the presence of MLGs in all composites after the HP sintering process. The presence of very fine nanostructured zirconia on the silicon nitride grains is the effect of high efficient milling process. HV values decreased with increasing of MLG content from 18.86 GPa to 9.69 GPa. The small increase to 18.86 GPa of HV at 1wt% MLG content in comparison to 17.01 GPa reference $Si_3N_4$ might be attributed to smaller grain sizes. The results show that improved tribological properties, more stable frictional behaviour and a significant increase of the wear resistance at MLG contents beyond 5 wt% can be achieved. The results were submitted to high impacted Journal of European Ceramic Society and were presented in several international conferences.




a)

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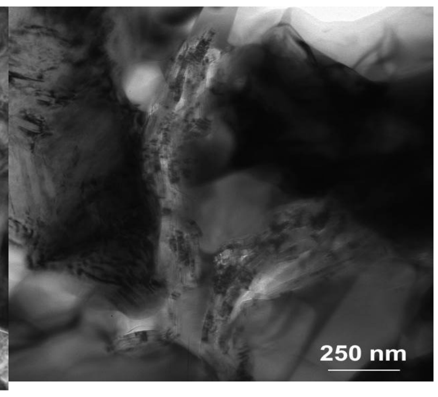


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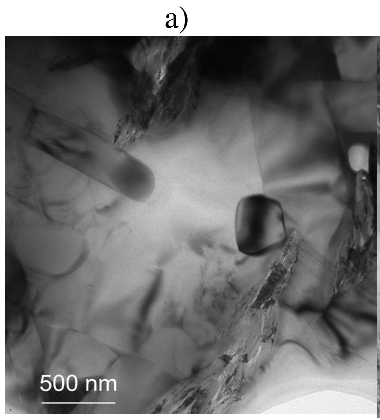


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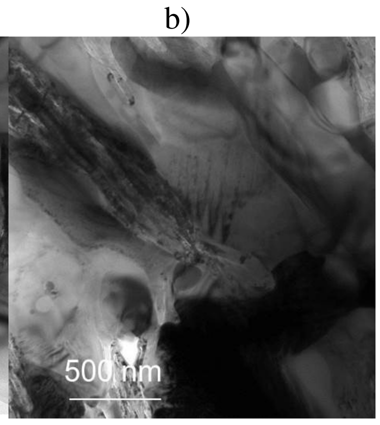
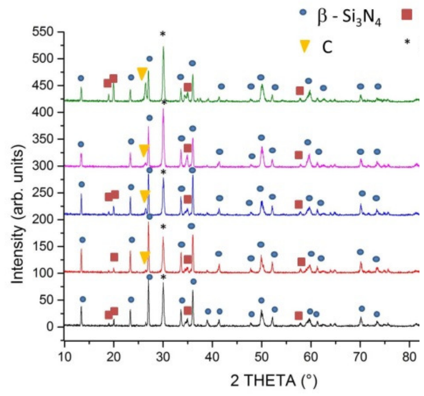



e)




f)

***Fig. 3.*** *$Si_3N_4$/ MLG compsoites sintered by hot pressing sintering. a) 0 wt% MLG, b) 1 wt% MLG, c) 3 wt% MLG, d) 5 wt% MLG, e) 10 wt% MLG, f) XRD measurements.*

a)

b)

c)

***Tab. 2.*** *Real photos of $Si_3N_4$ / graphene composites. a) HP, b) HIP and c) SPS*

**DENSITY (g/cm³) of different sintered $Si_3N_4$ / graphene composites**

| $Si_3N_4$/ 3 wt% graphene | HIP | SPS |
|---|---|---|
| TRGO – 600 | 2.516 | 3.164 |
| furfurylalcohol | 3.201 | 3.212 |
| BG- Grade C | 2.412 | 3.099 |
| BG- Grade M | 2.675 | 3.176 |
| MLG | 2.589 | 3.174 |
| MG-CO2-48h | 3.029 | 3.140 |
| reference | 3.225 | 3.231 |

| $Si_3N_4$/ graphene | HP |
|---|---|
| 0 wt% | 3.41 |
| 1 wt% | 3.36 |
| 3 wt% | 3.37 |
| 5 wt% | 3.42 |
| 10 wt% | 3.33 |

***Tab. 3.*** *Comparison of densities of sintered samples by 3 different sintering techniques.*

**HARDNESS (HV, GPa) of different sintered $Si_3N_4$ / graphene composite**

| $Si_3N_4$/ 3 wt% graphene | HIP | SPS |
|---|---|---|
| TRGO – 600 | 7.84 ± 1.51 | 15.0 ± 1.40 |
| furfurylalcohol | 17.45 ± 0.68 | 17.15 ± 1.14 |
| BG- Grade C | 4.02 ± 0.28 | 13.42 ± 0.28 |
| BG- Grade M | 8.86 ± 1.63 | 13.56 ± 3.08 |
| MLG | 5.82 ± 0.38 | 13.68 ± 0.49 |
| MG-CO2-48h | 11.58 ± 0.70 | 14.17 ± 0.35 |
| reference | 15.02 ± 0.50 | 17.76 ± 0.73 |

| $Si_3N_4$/ graphene | HP |
|---|---|
| 0 wt% | 17.01 ± 0.57 |
| 1 wt% | 18.86 ± 1.10 |
| 3 wt% | 16.16 ± 1.55 |
| 5 wt% | 13.37 ± 0.28 |
| 10 wt% | 9.69 ± 0.24 |

**TOUGHNESS ($K_{IC,}$ $MPa \cdot m^{1/2}$) of different sintered $Si_3N_4$ / graphene**

| $Si_3N_4$/ 3 wt% graphene | HIP | SPS |
|---|---|---|
| TRGO – 600 | | 3.83 ± 0.23 |
| furfurylalcohol | 8.74 ± 1.31 | 4.55 ± 0.10 |
| BG- Grade C | | 6.11 ± 1.2 |
| BG- Grade M | 6.60 ± 1.49 | 3.76 ± 0.51 |
| MLG | 7.49 ± 1.28 | 4.55 ± 0.38 |
| MG-CO2-48h | 6.30 ± 0.27 | 4.15 ± 0.18 |
| reference | 5.9 ± 0.21 | 4.98 ± 0.69 |

| $Si_3N_4$/ graphene | HP |
|---|---|
| 0 wt% | |
| 1 wt% | |
| 3 wt% | 6.84 ± 0.79 |
| 5 wt% | |
| 10 wt% | |

***Tab. 4.*** *Comparison of mechanical properties of sintered samples by 3 different sintering techniques.*

Today SiC or $Si_3N_4$ are standard materials for components and tools that are exposed to severe tribological, thermal or corrosive conditions. The main aim of our work in this project was to develop novel, highly efficient tribological systems on the basis of ceramic/graphene nanocomposites as well as to prove their superior quality and to demonstrate their suitability for technical applications e.g. for slide bearings and face seals in aqueous media. Our current knowledge in the field of ceramic nanocomposites shows that is possible to make ceramic materials with improved mechanical and tribological properties by incorporating graphene into the $Si_3N_4$ and SiC structure.

Sliding tests of composites –pins against SiC rings were performed to characterize the friction and wear behaviors. Sliding tests were performed for 20h under water lubrication at room temperature.

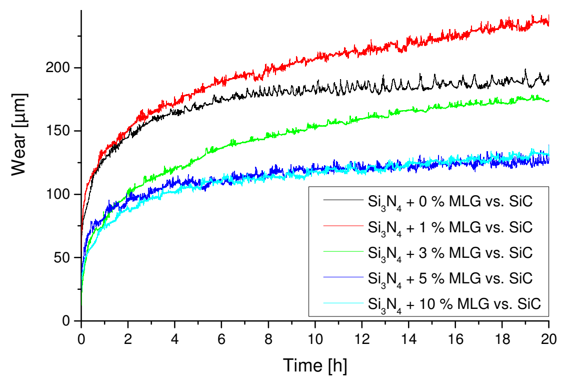



***Fig. 4.*** *Tribological properties of hot pressed $Si_3N_4$/ MLG composites.*

The results showed that improved tribological properties, more stable frictional behaviour and significant increase of the wear resistance at MLG contents beyong 5 wt% can be achieved.

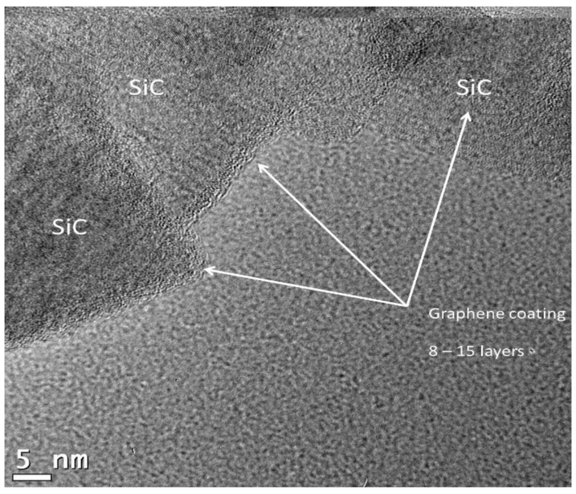
Conclusion:

The main aim of GRACE projekt was the development of $Si_3N_4$/graphene and SiC/graphene komposites for tribological application in aqueous environments. All composites were prepared by high efficient attritor milling and 3 different sintering methods; spark plasma sintering (SPS), hot isostatic pressing (HIP) and hot pressing (HP). It was showed that in the case of SPS and HIP, the optimal structure and tribological properties were observed at lower graphene content 2-3 wt%. On the other hand, HP is suitable for sintering higher graphene addition until 10 wt% without porosities. During the project, the sintering parameters for 3 different methods were optimalized. It was demonstrated that ceramic composites for aqueous media applications have been developed and the graphene additive played an active role in the formation of tribo film and reduced the friction coefficient of the composite.

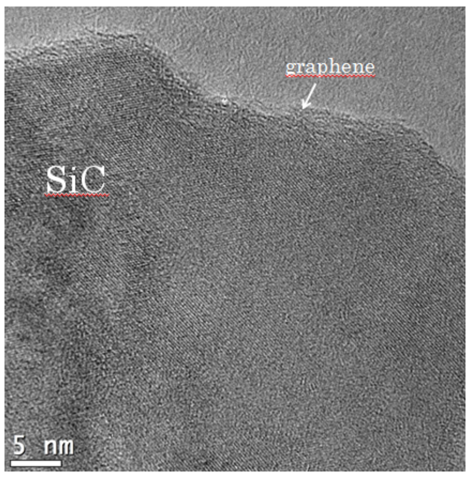
The last part of our work was the production of novel ceramics in high volumes (in kg) for sintering of industrial sized parts and for real parameter testing in FCT and Eagleburgmann companies. 2 kg $Si_3N_4$ milled powder with necessary sintering additives ($Y_2O_3$, $Al_2O_3$) was produced for HP sintering and tribological testing. MTA EK prepared by attritor mill and studied 12 different SiC/graphene (FCT partner), 8 various graphene and SiC/graphene samples (University Freiburg) by TEM and EDS.

During the project the consortium prepared the international patent concerning the 2 different material systems and their preparation steps and properties. Thanks to this decision of industrial partners, we had a very strict limit which scientific results were published and which were patented.

The consortium is working on international patent of SiC/graphene composite preparation for industry. EagleBurgmann company (one of project partners) is leading this patent procedure.




Graphene coated SiC with glucose as carbon source




Graphene coated SiC with furfurylalcohol as carbon source

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