Efficiently reducing the wear and friction of ceramic composites by graphene and other 2D filler materials

-final report-

The central idea of our research was to employ thinner graphene nanoplatelets to improve the tribological and mechanical properties of Si_3N_4 ceramic composites. Instead of conventionally used graphene nanoplatelets with typical thickness of over 50 layers, we employed much thinner (below 10 layers), few-layer graphene nanoplatelets (FL-GNPs) obtained by a simple mechano-chemical exfoliation method of milling graphite in presence of melamine. We employed these FL-GNPs as filler material to enhance the tribological and mechanical properties of Si_3N_4 ceramics, at relatively low filler contents (1 - 5 wt %) The most important conclusions and results obtained within this project are listed below:

1. We were able to reduce the wear rate of Si_3N_4 composites employing few layer GNP addition by up to twenty times (from 1.2 $10^{-5}mm^3$ /N m to 5.9 $10^{-7}mm^3$ /N m) for 5 wt% FL-GNP content, compared to monolithic Si_3N_4 ceramics.

2. The steady state friction coefficient of Si_3N_4 composites has been reduced to nearly its half (from 0.8 to 0.43), when using 5 wt% few layer graphene nanoplatelets addition. The addition of 3 wt % of FL-GNPs results in a roughly 15% reduction of the friction coefficient. The addition of 3wt% of conventional GNPs results in a friction coefficient of 0.79, practically identical to that of the monolithic Si_3N_4

3. Using Raman spectroscopy mapping, we have demonstrated the formation of a continuous FL-GNP tribo-film in the wear tracks of 5 wt% FL-GNP composites, evidencing the self-lubricating property of the composites.

4. By employing FL-GNPs as filler material, a 100% increase in the fracture toughness of Si_3N_4 / 3wt% FL-GNP composites (10.5± 0.2 MPa $m^{1/2}$) has been achieved, compared to monolithic Si_3N_4 samples (5.1± 0.3 MPa $m^{1/2}$), and 60% increase over conventional Si_3N_4 / 3wt% GNPs composites (6.6 ± 0.4 MPa $m^{1/2}$). This is the highest fracture toughness achieved for Si_3N_4 composites by graphene addition. For 5wt% filler content, the increase of the fracture toughness was near 50% for both GNP and FL-GNP fillers.

5. The hardness of the composites decreases with increasing filler content. However, composites reinforced with 5wt% of FL-GNP displayed 30% higher Vickers hardness (12.8± 0.2 GPa) than their counterparts comprising conventional 5 wt% GNP filler (9.8 ± 0.2 GPa).

6. We have prepared Si_3N_4 composites with exfoliated hexagonal boron nitride (h-BN) addition, using both conventional and melamine enhanced h-BN exfoliation. We found

that the friction coefficient of the composites with h-BN addition slightly decreased (5 – 18%), compared to the monolithic Si_3N_4. The best results were obtained for 5 wt % h-BN nanoplatelets addition (CoF = 0.65), but the improvement was modest compared to 5wt% few layer graphene addition (CoF = 0.43).

7. The highest fracture toughness increase was achieved with 3wt% FL- h-BN addition, corresponding to 10% increase (5.7± 0.14 GPa) over monolithic Si_3N_4, again much more modest than the best results achieved by us with 3 wt% of FL-GNPs (10.5 ± 0.2 GPa).

8. The Vickers hardness of the composites with h-BN addition has decreased. However, the composites prepared by few layer h-BN addition display 20% higher hardness values than those prepared by thicker commercially available h-BN nanoplatelets.

Graphene nanoplatelets were found much more efficient in improving the tribological properties and fracture toughness of Si_3N_4 composites than h-BN nanoplatelets. The best results have been achieved by thin few-layer graphene nanoplatelets that were prepared by melamine aided exfoliation through ball-milling. This simple additional step in the preparation method result in the best results for reducing the friction coefficient, increasing the wear resistance and fracture toughness of Si_3N_4 composites.

Below we discuss is some details the above outlined results.

Improving the tribological properties of Si_3N_4 composites by few-layer graphene addition

Graphene nanoplatelets (GNPs) have been proposed as one of the most promising filler materials for improving the tribological performance of ceramic composites due to their outstanding solid lubricant properties as well as mechanical and thermal stability. Yet, the addition of GNPs provided only a very limited improvement in the tribological properties of ceramics, particularly concerning the reduction of their friction coefficient. This was due to the difficulties in achieving a continuous lubricating and protecting tribo-film through a high GNP coverage of the exposed surfaces. Within the present project we have developed a fabrication process that can achieve the formation of a continuous tribo-film by efficiently increasing the exfoliation degree of the GNP filler material down to the few-layer (FL) range. This has been achieved by a mechano-chemical exfoliation method, based on the ball milling of graphite with melamine addition to increase the exfoliation efficiency. By employing FL-GNPs as filler material, the wear resistance of Si_3N_4 composites can be highly increased, while the friction coefficient is also significantly reduced, without compromising the other mechanical properties of the composites. We were able to demonstrate the formation of a continuous FL- GNP-based tribo-film, already at 5wt% FL-GNP content.

TEM investigations evidenced that the GNPs prepared by melamine addition are significantly thinner than the conventionally exfoliated GNPs (Figure 1). Based on TEM images, and the detailed analysis of corresponding Raman spectra, we could estimate that the presence of melamine during milling reduces the average platelet thickness below 10 layers, as opposed to 50 -60 layers obtained by ball milling without melamine addition.

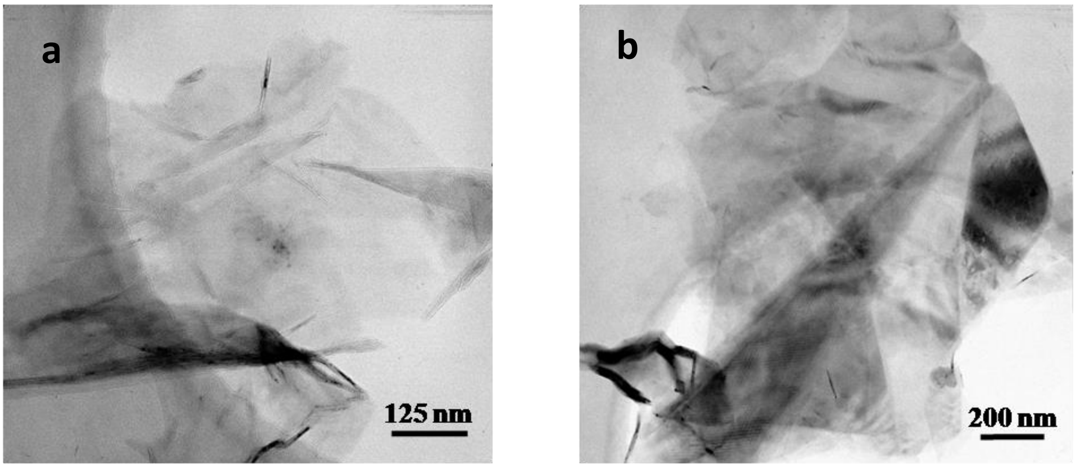

Fig.1. *Transmission electron microscopy images of graphene nanoplatelets exfoliated by mechanical milling. Melamine addition to the milling process results in substantially thinner few-layer GNPs (a) as compared to those obtained by conventional exfoliation (b).*

We have prepared Si_3N_4 composites of different compositions reinforced with both conventional GNPs and ultra-thin few-layer graphene nanoplatelets (FL-GNPs) using the Spark Plasma Sintering method.

Material	App. Density (g/cm^3)	α-Si_3N_4 (%)	β-Si_3N_4 (%)	ZrO_2 (%)	D Si_3N_4 (nm)
Si_3N_4	3.32	38,6	58,7	2,4	274
Si_3N_4/3%GNP	3.28	40,1	54,3	2,1	263
Si_3N_4/3%FL-GNP	3.3	60	33,2	1.1	240
Si_3N_4/5%FL-GNP	3.13	53.2	36,7	2.1	243

Table 1. *The apparent density, phase composition, and average Si_3N_4 grain size of the composites.*

To investigate the tribological properties of the sintered nanocomposites we used a Si_3N_4 ball (D = 6 mm) under dry sliding conditions, with 5N loading and 10 cm/s sliding speed. The addition of 3wt% of conventional GNP exfoliated without melamine addition results in a friction coefficient of 0.79 +/– 0.02, practically identical to that of the monolithic Si_3N_4. The addition of 3 wt % of FL-GNPs exfoliated with melamine addition results in a roughly 15% reduction of the friction coefficient. However, the best results have been obtained with 5 wt % of FL-GNP addition, where the steady state friction coefficient was found 0.43 +/– 0.04, about half of the value for monolithic Si_3N_4. To our knowledge such a substantial reduction of the friction coefficient upon GNP addition has not been reported before in Si_3N_4 or any other ceramic material. We found that the composites prepared with only 5wt% of FL-GNPs are characterized by more than 20 times increased wear resistance, while their friction coefficient is reduced to nearly its half, as compared to monolithic Si_3N_4. (Figure 2.)

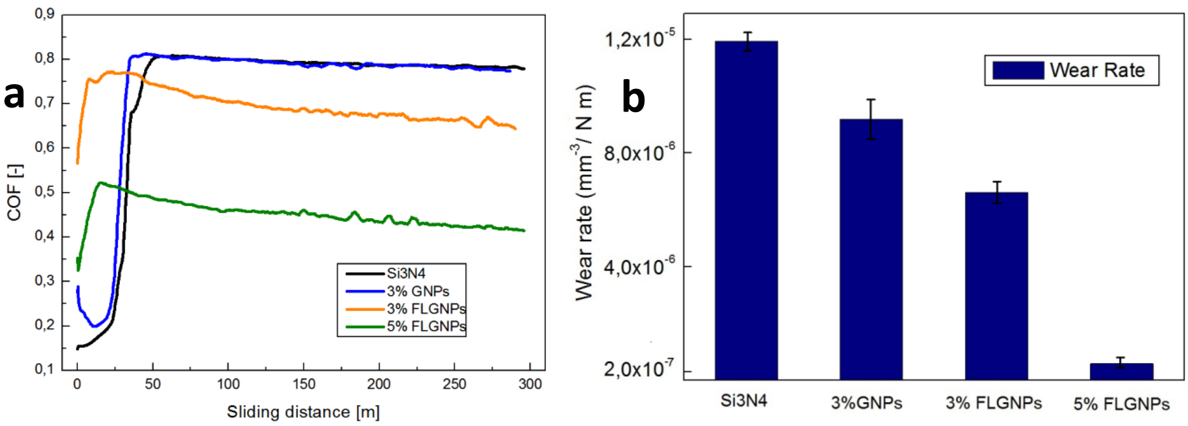

Fig. 2. *a) Friction coefficient of various composites measured under dry sliding conditions with Si_3N_4 ball, at 5N loading, and 10 cm/s sliding speed. Composites with 5wt% of FL-GNP addition display a highly-reduced friction coefficient. b) Wear rate of various Si_3N_4 composites displaying a striking improvement of the wear resistance for composites with 5 wt% of FL-GNP addition.*

We also measured the wear and found that the wear rate of the 5 wt %FL-GNP sample ($5.9\ 10^{-7}$ mm^3/N.m) is about twenty times lower than the wear rate of the monolithic Si_3N_4 ($1.2\ 10^{-5}$ mm^3/N.m). This is a spectacular improvement of the wear resistance. For comparison, composites with 3 wt % of GNP display a 14% reduction of wear rate while for the composites with 3 wt% of FL-GNP a 41% reduction has been measured.

The outstanding improvement in the tribological properties can be clearly observed in the optical images of wear tracks.

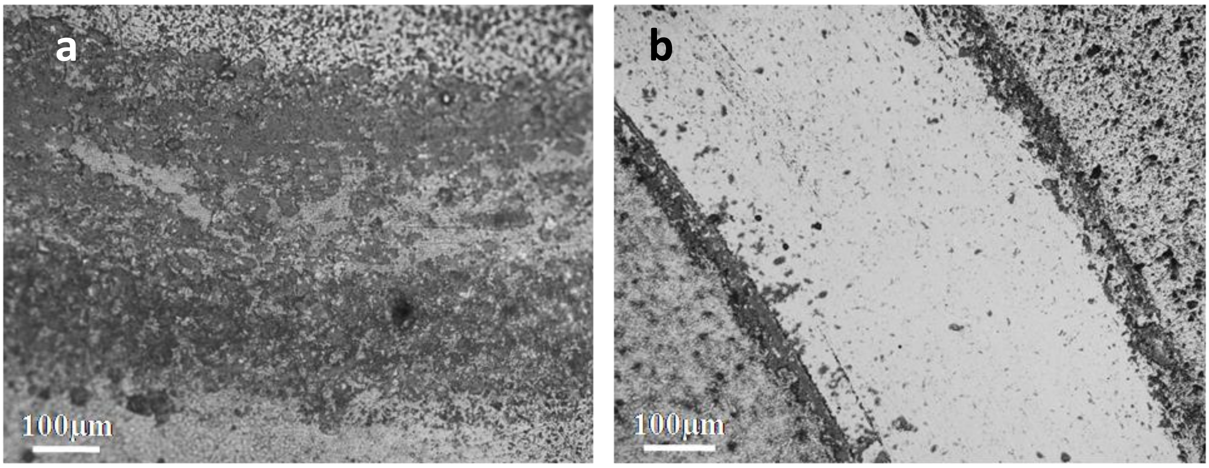

Fig. 3. *Optical microscopy images of wear tracks for a) monolithic Si_3N_4 and b) Si_3N_4/5wt% FL-GNP composite. While abrasion groves are present in high density in monolithic samples, they are almost completely absent for the composites with 5 wt% of FL-GNP addition*

By confocal Raman spectroscopic mapping of the wear tracks we have shown that this outstanding improvement in the tribological properties can be attributed to the formation of a continuous protecting and lubricating tribo-film consisting of FL-GNPs of high structural quality.

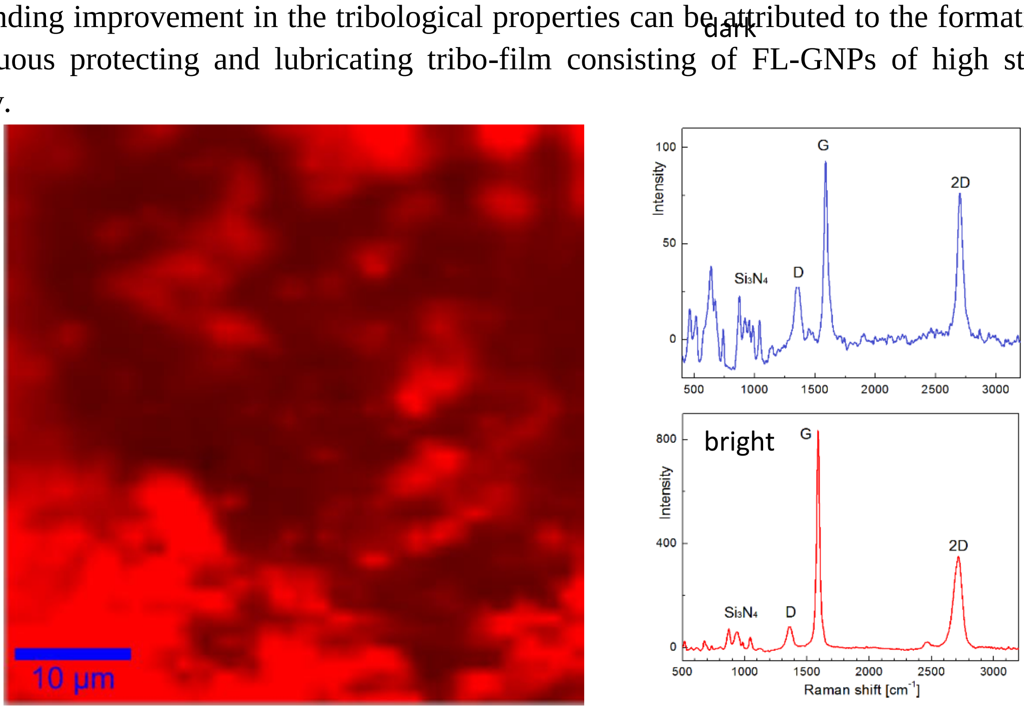

Fig. 4. *a) Raman spectroscopy map of the G peak of FL-GNPs recorded inside the wear track of a Si_3N_4 / 5 wt% FL-GNP sample. The red colour indicates a high G line intensity. b) Characteristic Raman spectra inside the wear track, displaying the main lines of both the FL-GNPs and the Si_3N_4 matrix.*

We have demonstrated that the addition of graphene nanoplatelets with reduced thickness to Si_3N_4 ceramics, remarkably improves the tribological performance of such ceramics. As compared to monolithic Si_3N_4, only 5wt% of few layer graphene nanoplatelet addition can improve the wear resistance by more than 20 times, while reducing the friction coefficient to its half. By confocal Raman spectroscopic mapping of the wear tracks we have shown that this outstanding improvement in the tribological properties can be attributed to the formation of a continuous protecting and lubricating tribo-film consisting of FL-GNPs of high structural quality. There are key technological advantages in developing highly wear-resistant and low-friction ceramic composite materials. Components produced from such materials enable the substantial reduction of losses during operation, as well as a significant increase of their durability.

Improving the fracture toughness of Si_3N_4 composites by few-layer graphene addition

It has already been shown that the addition of graphene nanoplateles to ceramic matrix composites can significantly increase the fracture toughness of ceramic composites, in general, and Si_3N_4-based composites, in particular. The improvement achieved in the fracture toughness of various Si_3N_4/GNP composites strongly varied depending on several factors, such as: filler content, preparation technique, as well as the properties of the GNPs. The highest improvements in the fracture toughness have been achieved when employing chemically derived graphene oxide (GO) as filler material. It has been shown that upon the addition of 4.3 vol.% of GO the toughness of Si_3N_4 composites improved from 4.5 MPa $m^{1/2}$ to 10.4 MPa $m^{1/2}$. By direct comparison, the addition of 4.3 vol.% of conventional unoxidized GNPs yielded a substantially lower toughness value of about 6 MPa $m^{1/2}$. The improvement of the fracture toughness is in general almost double when graphene oxide is employed as filler material instead of unoxidized graphene nanoplatelets. However, it has also been shown that GO is far less efficient in improving the tribological properties of ceramic composites, compared to unoxidized graphene nanoplatelets. Therefore, to obtain Si_3N_4 / graphene composites that are outstanding in both tribological and mechanical applications, it is desirable to prepare composites with unoxidized graphene flakes that are also characterized by high toughness values. We proposed to achieve this by preparing thin unoxidized GNPs with their thickness approaching that of graphene oxide flakes. We prepared thin unoxidized few-layer GNPs by the simple melamine assisted ball milling process discussed above. Our aim was to substantially improve the fracture toughness of Si_3N_4 composites without oxidizing the structure of graphene platelets. Si_3N_4 composites with 3 and 5wt.% of graphene nanoplatelet (GNP) additions were prepared by spark plasma sintering. We used both commercially available GNPs and thinner few-layer graphene nanoplatelets (FL-GNPs) prepared by further exfoliation through ball milling with melamine addition.

The microstructure of the sintered composites has been investigated by Scanning Electron Microscopy (SEM) and XRD measurements. We have acquired SEM images of fracture surfaces of all Si_3N_4 composite samples (see Fig. 5). SEM images clearly reveal that FL- GNPs prepared by melamine assisted exfoliation form much thinner inclusions in the ceramic matrix than the conventional GNPs.

The fracture toughness and Vickers hardness values obtained from micro-indentation measurements are shown in Fig. 6. The micro-indentation tests have been performed on polished sample surfaces parallel with the uniaxial pressing direction applied during the sintering. The fracture toughness of the reference monolithic Si_3N_4 sample was 5.1± 0.3 MPa $m^{1/2}$. For composites reinforced with conventional GNPs, the fracture toughness increased by about 30% and 50% for 3 and 5 wt.% filler content, respectively.

The best results have been obtained for 3 wt.% of FL-GNPs, where the fracture toughness increased by more than 100% to 10.5 ± 0.2 MPa $m^{1/2}$ as compared to the monolithic reference sample. This value equals or even surpasses the highest toughness value previously reported for Si_3N_4 composites.

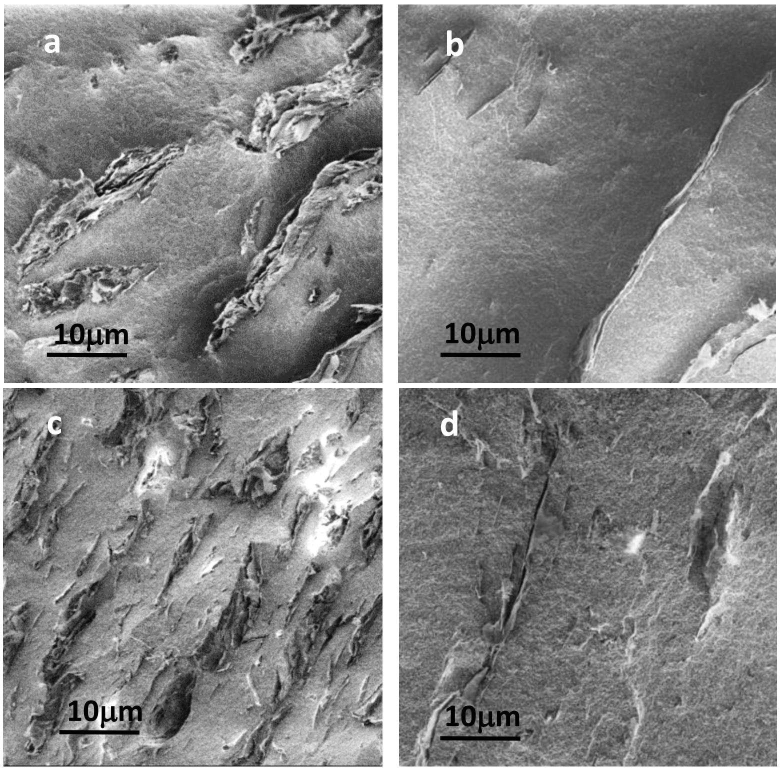

Fig. 5. *Scanning electron microscopy images of fracture surfaces of Si_3N_4 composites with: a) 3 wt.% GNPs; b) 3 wt.% FL-GNPs; c) 5 wt.% GNPs and d) 5 wt.% FL-GNPs.*

However, previously such large improvements of the toughness could only be obtained by employing graphene oxide, while here we achieved this with unoxidized FL-GNPs. The full benefits of using unoxidized graphene platelets can be harnessed in tribological applications, as we have shown previously, as graphene oxide reinforced composites are characterized by a limited improvement of the tribological properties.

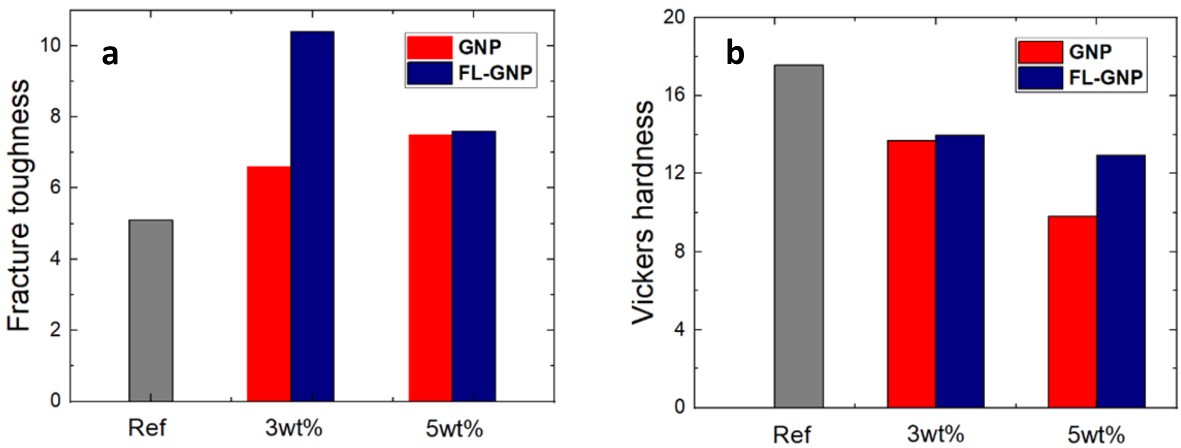

Fig.6 *Fracture toughness (a) and hardness (b) values of Si_3N_4 composites prepared with different type and concentration of graphene nanoplatelet additions.*

We attributed the substantial toughness improvement of our sample, matching those of graphene oxide, to the ability to prepare thin graphene flakes even without oxidizing their structure. Thinner flakes provide much larger contact areas (for the same GNP content), and a more homogeneous distribution within the matrix. Larger contact areas improve the stress transfer between the ceramic matrix and the flakes, while a more homogeneous distribution ensures that crack propagation encounter more often GNPs.

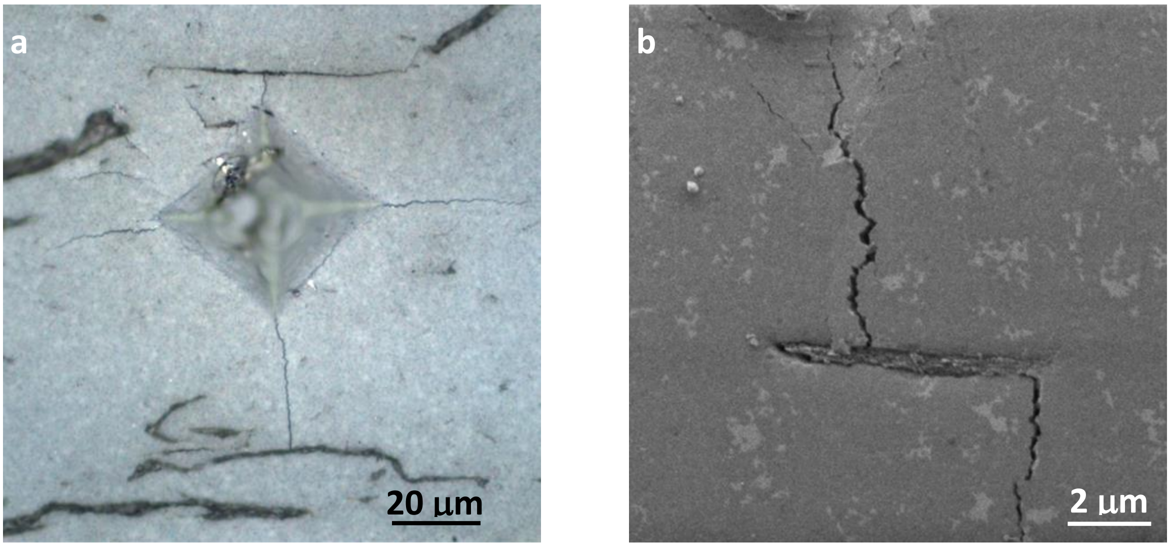

Fig.7. *a) Optical microscopy image of an indentation mark and the resulting cracks evidencing the stopping of crack propagation by FL-GNPs of large lateral size. b) SEM micrograph showing a crack deflection by a shorter GNP.*

When increasing the FL-GNP content to 5 wt.% we found that the toughness of the composites decreases to values similar to that obtained with conventional GNPs. We also note that a pronounced anisotropy in the orientation of the graphene flakes can be clearly observed. The graphene sheets tend to align perpendicular to the direction of the uniaxial pressure applied during the sintering. This results in a twofold anisotropy in the toughness (crack propagation lengths). On one hand, there is a difference between the toughness values measured on sample surfaces (planes) parallel and perpendicular to the pressing direction applied during sintering. As we specified above for 3wt.% FL-GNP samples the toughness value measured in the parallel plane was $K_{IC\parallel} = 10.5 \pm 0.2$ MPa $m^{1/2}$. In the perpendicular plane we measured a lower toughness value of $K_{IC\perp} = 7.8 \pm 0.2$ MPa $m^{1/2}$. Moreover, an in-plane anisotropy in the crack propagation length within the sample surface parallel to pressure direction can also be observed. Cracks propagating perpendicular to the aligned GNP sheets have a much higher chance to encounter graphene flakes than cracks propagating in the direction parallel to the sheets

As concerning the hardness values, we found that by increasing the graphene content the hardness of the composites decreases. The main reason for this is that the graphitic fillers provide softer spots as compared to the Si_3N_4 matrix, and they can also promote pore formation, further softening the composites. However, while this decrease becomes more pronounced with increasing filler content, samples reinforced with 5 wt.% FL-GNPs display 30% higher hardness values than the 5 wt.% GNP samples. A possible explanation for this is that the pore formation near FL-GNP additions is reduced as compared to thicker GNPs, as also indicated by the measured density values (Table 2).

Material	GNP content (wt.%)	Apparent density (g/cm^3)	Fracture toughness (MPa $m^{1/2}$)	Hardness HV1 (GPa)
Si_3N_4	0	3.31	5.1± 0.3	17.5 ± 0.4
Si_3N_4/GNP	3	3.27	6.6± 0.4	13.9± 0.9
Si_3N_4/FL-GNP	3	3.29	10.5± 0.2	13.7± 0.5
Si_3N_4/GNP	5	3.21	7.5± 0.4	12.8± 0.4
Si_3N_4/FL-GNP	5	3.29	7.6± 0.5	9.8± 0.4

Table 2. *The apparent density, fracture toughness and hardness of the investigated composites*.

In conclusion, we found that by employing thinner FL-GNPs as filler material a 100% increase in the fracture toughness of Si_3N_4 / 3wt.% FL-GNP composites (10.5± 0.2 MPa $m^{1/2}$) can be achieved as compared to the monolithic Si_3N_4 samples (5.1± 0.3 MPa $m^{1/2}$), and 60% increase compared to conventional Si_3N_4 / 3wt.% GNP composites (6.6 ± 0.4 MPa $m^{1/2}$). For 5wt.% filler content the increase of the fracture toughness was near 50% for both GNP and FL-GNP fillers. The hardness of the composites decreased with increasing GNP content. However, composites reinforced with 5wt.% of FL-GNPs displayed 30% higher Vickers hardness (12.8± 0.2 GPa) than their counterparts comprising conventional GNP fillers (9.8 ± 0.2 GPa). We attribute the enhanced mechanical properties obtained with thinner FL-GNPs to their higher aspect ratio leading to a more homogeneous dispersion, higher interface area, as well as smaller pores in the ceramic matrix.

Investigating other 2D materials for reinforcing Si_3N_4 ceramics.

We have also proposed within the framework of the current project to prepare Si_3N_4 composites with two-dimensional filler materials other than graphene. Our first choice of such a filler material was molybdenum disulfide (MoS_2). However, due to the relatively low thermal stability of transition metal chalcogenides, we were not able to preserve the structural integrity of MoS_2 nanopaltelets during the sintering process. Therefore, we have switched to hexagonal boron nitride (h-BN) nanoplateltes, which are known for a much higher thermal stability. Indeed, we were able to successfully prepare Si_3N_4 composites with well-preserved h-BN nanoplatelets. For preparing the composites, we used both commercially available h-BN nanoplateltes, and thinner h-BN platelets prepared by us, by ball milling with melamine addition, similar to the preparation of few layer graphene nanoplatelets.

We have investigated the tribological properties of Si_3N_4 / h-BN and Si_3N_4/ FL-h-BN composites using a Si_3N_4 ball (D=6 mm) under dry sliding conditions, with 5N loading and 10 cm/s sliding speed.

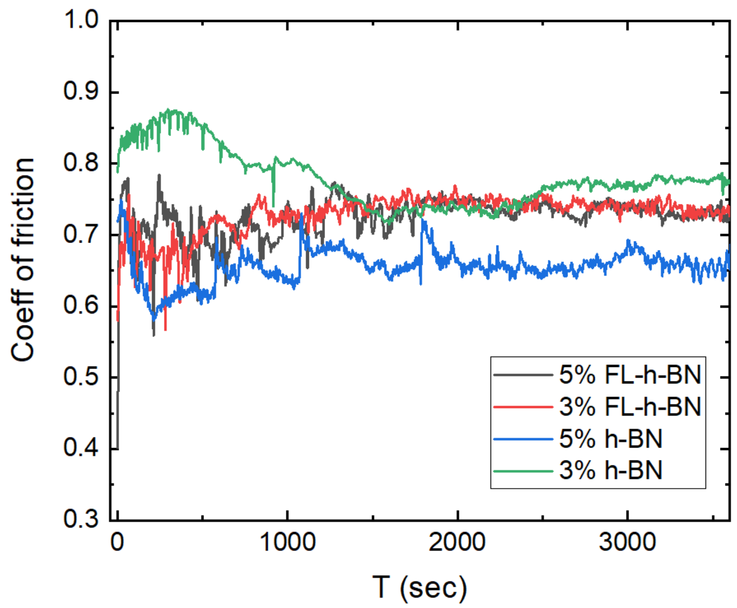

Fig. 8. *Friction coefficient of various Si_3N_4/h-BN composites measured under dry sliding conditions with Si_3N_4 ball, at 5N loading, and 10 cm/s sliding speed. Composites with 5wt% of h-BN addition display the lowest friction coefficient.*

As can be seen in Fig. 8 the h-BN addition only moderately improves the steady state friction coefficient from the 0.8 value of monolithic Si_3N_4. In contrast to graphene, the lowest value of friction coefficient was obtained for the 5wt% h-BN samples instead of FL-h-BN filler. However, from the practical point of view the overall improvement is much less significant than in the case of graphene addition. h-BN nanopaltelet addition is also much less efficient for improving the wear resistance of Si_3N_4 composites as compared to graphene. The best results were obtained for 5wt% FL-h-BN samples (1.1 $10^{-5}mm^3$ /N m) that correspond only to an insignificant wear resistance improvement over the monolithic Si_3N_4 samples. For other samples the wear resistance have been decreased by h-BN addition. Therefore, for improving the tribological properties of Si_3N_4 composites, h-BN has proven much less efficient than graphene. While it can reduce the friction coefficient (by ~ 20%), it does not improve significantly the wear resistance.

Concerning other mechanical properties of h-BN reinforced Si_3N_4 composites, we have performed Vickers hardness and fracture toughness measurements by micro-indentation experiments on a hardness tester (KS Prüfechnik) applying a load of 10Kp for 10 seconds.

HV10 and K_{IC} Si_3N_4 / h-BN				
Sample	Hardness HV1 (GPa)	+/- (GPa)	K_{IC} (Shetty) (MPa.$m^{1/2}$)	+/- (MPa.$m^{1/2}$)
3% h-BN	10.25	0.18	4.86	0.19
5% h-BN	10.51	0.44	4.54	0.16
3% FL-h-BN	12.40	0.46	5.57	0.14
5% FL-h-BN	12.65	0.33	5.13	0.30

Table 3. *Vickers hardness, and fracture toughness of the investigated Si_3N_4/h-BN composites*

As apparent in Table 3, the hardness values decrease significantly compared to monolithic Si_3N_4 (17.5 GPa), yielding values similar to those obtained with graphene nanoplatelets addition (Table 2). However, in this case, thinner FL-h-BN nanoplatelets perform better. Regarding the fracture toughness, in contrast to the substantial improvement achieved with graphene addition, h-BN samples display only a very modest improvement of the fracture toughness (~ 10%), and only in the case of thin FL-h-BN filler phase. Conventional, commercially available h-BN nanoplatelets slightly degrade the fracture toughness of Si_3N_4 composites.

Consequently, employing h-BN as filler material affects the hardness of Si_3N_4 composites in a very similar manner to graphene additions, while it offers some improvement of their fracture toughness, only when added in the thinner few-layer form.

Overall, we can conclude that graphene nanoplatelets have proven far superior to hexagonal boron nitride for improving the tribological and mechanical properties Si_3N_4 ceramics from almost all investigated aspects.