SHORT TERM SCIENTIFIC MISSION: FINAL REPORT

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Elisabetta Serpini, from the University of Modena and Reggio Emilia - Sup&rman lab, visited the Advanced Materials Group at the Czech Technical University in Prague for a three-months period (November 2016-January 2017) in the context of the COST Action MP1303. Given the mutual interest of the two groups on Transition Metal Dichalchogenides (TMDs) as solid lubricants, particularly Molybdenum Disulphide, as highlighted in the last COST meeting in Riga (July 2016), an STSM was proposed as a kick start for a more extensive collaboration between the two groups.

The Lab. Sup&rman led by Prof. Sergio Valeri has a longstanding experience in the growth of films for tribological applications and in their chemical characterization by means of XPS and Auger techniques [1,2]. Now the group is focusing on thin self-lubricating films and their interaction with different atmospheres [3]. The research group led by Prof. Tomas Polcar at the Department of Control Engineering, Faculty of Control Engineering in Prague has large theoretical (MD simulations) experience on solid lubricant coatings, especially TMDs [4,5].

The purpose of this mission was dual. On one hand, there was the tribological investigation of MoS2 coatings produced in Modena with the magnetron sputtering technique. The coatings were deposited on Silicon substrate to minimize the effect of substrate on the tribological characteristics of the coatings themselves (single crystal Si is atomically flat and does not favor interdiffusion of species to or from the coating). They were 200nm thick as the Modena group was interested in thin films. Given the deposition parameters, the coatings were expected to be nanocrystalline. This was verified by means of FIB and SEM analysis.

The tribological tests were aimed to investigate the role of load and speed on coefficient of friction at different levels of relative humidity, namely ambient humidity (RH=20-25%) and vacuum. Vacuum measurements were performed on a custom-built vacuum tribometer. Additionally, we wanted to investigate the role of load and speed on oxides formation and on MoS2 recrystallization, provided we saw such a phenomenon as suggested by the Molecular Dynamics simulations performed by the Praga group, through Raman spectroscopy.

A reduction in coefficient of friction with increasing load (1 to 7N) was indeed observed, as could be expected from a similar work by Polcar et al. on a composite MoS2 coating [4], both in humid air and in vacuum. The coefficient of friction was usually lower in vacuum than in humid environment for every load considered (ranging from 0.08 to 0.2), even though the test performed in humid air at the highest load (7N) displayed a coefficient of friction (0.08) comparable to the values obtained in vacuum (in between 0.02 and 0.1). The effect seems to be more pronounced in humid environment. A trend with increasing speed (0.1 to 0.5m/s) is not as easily identifiable, for this reason tests were performed only in humid environment (as previous trend with load was more pronounced in such environment) and not in vacuum.

Raman spectra were acquired on both tracks and counterpart, for all the tests performed. Great care was put into identifying the correct acquisition parameters, since it is well known that MoS2 readily oxidizes at high laser power, especially if using red laser [6]. In our case the laser employed was a green laser, nevertheless often we were required to use an especially low intensity in order not to modify the material, of course at the expense of signal intensity. Raman spectra were acquired on all the virgin coatings employed and on MoS2 single crystal for comparison.

As a general rule, the transfer material present on the counterpart for all tests performed in humid environment oxidizes more readily than in the case of vacuum. This suggests a different reactivity of the material, but whether it is due to different crystallinity/crystal orientation or different chemical composition/presence of adsorbates is not clear. Also, the wear rate was greatly accelerated with respect to vacuum, and even though the coefficient of friction did not exceed 0.3, Raman could not identify MoS2 peaks inside the wear track if not in traces. For this reason, calculation of wear rate was almost meaningless and mainly the pile up at the wear track borders was analyzed with Raman. Generally speaking, no traces of oxide (MoO3) were found in the wear tracks (sides). Some traces were found on the counterpart in the presumed contact area, but very sparingly. Also, part of the tribolayer, giving rise to Raman signal, was present on the counterpart even after cleaning with ethanol.

In vacuum the wear rate was such that even at the highest load most of the wear track was still covered with residual film giving rise to Raman signal. In this case there was a clear trend of increasing wear with increasing applied load. Additionally, it was possible to utilize higher intensity while analyzing the counterpart, leading to higher signal intensity. Signal coming from oxides was found neither in the residual films nor on the counterpart, if not in traces in this last case.

One of the preliminary conclusions we were able to reach at this point was that oxidation of MoS2 was not the main mechanism of failure of the coatings: oxides were seldom present, even in the humid environment case. This is consistent with and integrates previous results obtained in Modena.

Analysis of Raman spectra also gives information about the level of crystallinity of the MoS2 coating [7]. The single crystal, when probed with a green laser, exhibits two sharp peaks at 383 and 408 cm^{-1}; in the case of sputtered films, there is an additional broad peak around 223 cm^{-1}, which is commonly associated to defects of the crystalline structure, and the peak at 383 cm^{-1} is broader as well. In previous works, it was shown how annealing of an almost amorphous film can improve the crystalline quality of the film, corresponding to a sharpening of the 383 cm^{-1} peak and the disappearance of the 223 cm^{-1} peak.

Raman spectra collected on all tracks and respective counterparts have been catalogued and compared with those acquired from the virgin coatings. All the virgin coatings exhibited the broad peak around 225 cm^{-1}. Unfortunately, despite the fact that all the coatings were deposited utilizing the same parameters, some differences in the Raman spectra are present, indicating a slightly different crystallinity which renders the comparison of data more difficult. From a visual comparison with the spectra acquired on the tracks/counterpart, it is evident that the 223 cm^{-1} component decreases with sliding and the 383 cm^{-1} peak becomes slightly sharper, which could indicate a re-crystallization of the coating due to sliding. This result can represent a nice proof of the effect of re-crystallization with sliding, which has already been shown with MD simulations by the group in Prague. This effect is visible in all set of tests performed, but it is more evident in the case of “less crystalline” virgin coatings. A more detailed analysis of the Raman data (estimation of position, width, area and intensity of peaks) is currently still in progress.

In the last part of the STSM, different systems have been studied with Atomic Force Microscopy, namely single crystal MoS2, MoS2 flakes obtained with the scotch-tape method and deposited on Silicon substrate, and MoS2 coatings with the same characteristics as the ones studied with the tribometer (200nm thick, deposited on Si substrate).

The AFM has been operated in LF mode in order to obtain information about friction at the nanoscale. The AFM employed offered the possibility to vary the relative humidity inside the measuring chamber in a continuous way, from dry environment (obtained by fluxing nitrogen inside the chamber, corresponding to a few % of RH) to 100% RH.

The first set of experiments has been performed using a Si tip treated with a hydrophobic coating. While measuring lateral force on single crystal MoS2, RH has been progressively varied from 100% to ambient value and vice versa. The results suggest that for single crystal friction does not depend on the level of relative humidity. Lateral force vs applied load graphs were obtained as well.

On a 200nm thick MoS2 coating, lateral force vs applied load graphs were obtained. The slope of these curves (coefficient of friction) is the same for low humidity (RH=15%) and high humidity (RH=80%) and its value is higher than the single crystal case by an order of magnitude.

MoS2 flakes of different thickness were studied (5nm and 40nm). For the thick flake, the coefficient of friction exhibited the same characteristics as that of the coatings; it was the same order of magnitude and did not change whether the tests were performed in high RH or in nitrogen atmosphere. On the thin flake, the coefficient of friction was extremely low in nitrogen atmosphere, comparable to the single crystal (bulk) case. In high humidity the shape of the lateral force vs applied load curve deviated slightly from linearity at low load, but the slope of the curve at higher loads is still similar to the one obtained for the nitrogen case. This could mean that humidity influences thin flakes more than thick ones when low load are applied due to capillarity.

The dependence of friction on flake thickness was also investigated. In order to obtain self-consistent measurements, scans over large areas (50x50 μm^2) were performed in order to obtain data from many different flakes. All tests were performed in nitrogen atmosphere. Despite the large errors, it seems that a slightly increasing trend with increasing flake thickness has been identified.

After these preliminary results, a nanoshaving experiment was conducted on MoS2 coating in nitrogen atmosphere. Several 5x5 μm^2 scans were performed at higher load as they were intended to perform the actual nanoshaving, followed by a low load 15x15 μm^2 overscan. From the overscan it was possible to estimate and monitor the evolution of the depth of the hole created and the difference in friction with respect to the virgin coating. This process was repeated several times, until the depth of the hole stabilized after several cycles.

Measurements were performed also with a different AFM operated inside a glovebox, which also offered the possibility to heat the sample in controlled atmosphere. Unfortunately, the system was very difficult to operate and the results obtained were scarce and unreliable. For this reason, tests inside a glovebox were not pursued any further.

Some of the previous measurements were repeated using an untreated silicon tip to determine the role, if any, of the chemical properties of the tip on the system. One of the main results was that, again, at high relative humidity friction was higher for thin flakes with respect to thicker ones. This behavior seems intrinsic to flake thickness and not dependent on tip characteristics.

Additionally, surface potential maps were obtained on thick, composite flakes having different thicknesses (“subflakes”) in different areas. Data are currently under investigation.

The nanoshaving experiment performed on the MoS2 coating was repeated with the untreated tip, again in nitrogen atmosphere. Results similar to the ones obtained with a coated tip were observed, indicating that similar results are to be expected in the same environment, regardless of the chemical characteristics of the tip. Further, this could suggest that, at least for the MoS2 coating, the chemical characteristics of the tip do not influence the results because the tip is coated with MoS_2 as soon as sliding starts.

To validate this hypothesis, all the AFM tips utilized during the measurement campaign were analyzed with SEM. All of them resulted somehow modified. The tips utilized for sliding on the coatings resulted coated themselves as well, not only on the very tip, but also on their sides. This could validate the previous hypothesis, but as decisive proof chemical analysis of the transfer material and further tests (stopped at the very beginning of sliding to see if transfer material is already present) are needed. In the case of flakes, some of them are often attached to the AFM tip, both at the very tip and at its sides. Very rarely some material is (seemingly) attached only to the tip sides. In the case of single crystal, the tips result damaged.

Data analysis of all the AFM measurements is still in progress. Preliminary results seem promising and hopefully will lead to a few publications, both as standalone material and as validation of MD simulations. The same can be said for macroscopic tests performed with the tribometers. Additional work needs to be performed on both fronts. Macroscopic tests can be carried on in Modena on thicker MoS_2 coatings and/or rougher substrates like steel. The most interesting results obtained with the AFM need to be repeated and refined, and possibly also expanded. For all these reasons, Prof. Valeri's and Prof. Polcar's groups will continue and deepen the collaboration, and future exchange visits are being planned.

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