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Ł. MAJOR[1*], D. KOPP[2], B. MAJOR[1], J.M. LACKNER[2]

CHARACTERIZATION OF THE SELF-DRY-LUBRICATION AND SELF-HEALING EFFECTS ON NANO- AND ATOMIC SCALE IN Zn/MoS_2/GRAPHITE/Zn COATINGS DEPOSITED BY ATMOSPHERIC PRESSURE PLASMA SPRAYING ON ULTRA-LIGHT CONSTRUCTION POLYMERS

In order to increase the resistance of the polyamide 11 (PA 11) surface to sliding wear, the economical low-temperature atmospheric pressure plasma deposition (APPD) technique was used to produce innovative thick Zn/MoS_2/graphite/Zn coatings with self-dry-lubrication and self-healing functions [1]. The specific problem was concern on structure characterization in nano- and atomic scale of these effects. The self-dry-lubrication was possible thanks to the possible breaking of weak van der Waals' bonds both in graphite and MoS_2 structures. The effect was described as a result of the shifting of atomic layers in both MoS_2 and graphite layers within the same phase and at their boundaries while the self-healing effect occurred in the form of closing micro-cracks in the structure of the coatings and rebuilding van der Waals' atomic bonds.

Keywords: Polymer substrates; APPD coatings; self-healing; wear; SEM/TEM microstructure

1. Introduction

Recent advancements in polymers and polymer composites, particularly for bearing materials, have underscored their potential as lightweight alternatives to traditional metals in modern engineering [2-4]. However, a key challenge remains their high friction coefficients under unlubricated conditions. Polyamide 11 (PA11) is widely used in applications such as screws, bearings, and gears, owing to its favorable physical and tribological properties, including high strength, low density, and chemical resistance [5,6]. Nonetheless, PA11's susceptibility to oxidation, which leads to material degradation, highlights the need for advanced stabilization technologies [6-10]. To improve the tribological performance of PA11, ceramic coatings are often employed. However, conventional vacuum-based coating processes can be cost-prohibitive for thicker layers [11-15]. A more economical and scalable alternative is the Atmospheric Pressure Plasma Deposition (APPD) method, which allows the deposition of thick layers (>100 µm) without the need for a vacuum chamber [16,17]. In this research, an innovative multilayer Zn/MoS_2/graphite coating was applied to PA11 surfaces, incorporating self-lubricating and self-healing functionalities. These coatings, approximately 200 µm thick, were deposited using the APPD technique, which offers substantial benefits such as eliminating the requirement for vacuum chambers, faster deposition rates, and reducing the risk of surface degradation. Furthermore, APPD is an energy-efficient and cost-effective process, making it highly suitable for sustainable development practices. This study proposes the use of APPD to apply MoS_2/Graphite/Zn coatings on PA11, significantly enhancing its wear resistance. Molybdenum disulfide (MoS_2), known for its low friction properties [18,19], is combined with graphite [20], another effective lubricant, while zinc (Zn) serves as a binder. The key features of these coatings include high adhesion, low friction, dry self-lubrication, and self-healing capabilities.

2. Materials and methods

2.1. Coatings deposition

This powder includes MoS2 from OKS 100 (>97.7 wt.% of purity), graphite MOS C80 from Tribotecc® (>87.8 wt.% of purity) and zinc from ECKART® (>95.6 wt.% of purity). The final feedstock composition consists of 50 wt.% of MoS2, 25 wt.% of graphite and 25 wt.% of Zn. The three-component powder was

[1] INSTITUTE OF METALLURGY AND MATERIALS SCIENCE, POLISH ACADEMY OF SCIENCES, 25 REYMONTA STR., 30-059 CRACOW, POLAND
[2] JOANNEUM RESEARCH FORSCHUNGSGESELLSCHAFT MBH, INSTITUTE FOR SENSORS, PHOTONICS AND MANUFACTURING TECHNOLOGIES, RESEARCH GROUP LASER AND PLASMA PROCESSING, LEOBNER STRASSE 94, 8712 NIKLASDORF, AUSTRIA

* Corresponding author: l.major@imim.pl

homogenised for 15 min. with a TURBULA® 3D shaker mixer after which complete homogenisation was achieved. The exact particle size distribution of the solid powders was determined with a Bettersizer 2600 BT-802, which disperse the solid powders in ethanol (≥96%). Grains with an average diameter of 10 um accounted for 9.332%. Grains with an average diameter of 50 um accounted for 28.47% and grains with an average diameter of 90um accounted for 57.67%. The powder fractions, designated as V4, were carefully optimized to enhance adhesion properties to the substrate and cohesion properties between the matrix material (ZnO) and the dry lubricants (MoS_2, graphite), aiming to produce low-friction, wear-resistant coatings. The resulting coatings were subjected to micromechanical wear tests using a ball-on-disc contact method. The test parameters are provided in the accompanying table.

2.2. Micromechanical tests (wear test)

TABLE 1

Tribometer setup in rotational mode (UMC Bruker) [1]

Wear track diameter	Linear speed	Number of cycles	Distance	Applied force	Hertzian stress
20 mm	100 mm*s^{-1}	20000	1256 m	1 N (const.)	68.5 MPa

2.3. Microstructure characterization

Microstructural characterization of the MoS_2/Graphite/Zn coatings was conducted using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM analyses were performed using in-lens detectors (Trinity) on a DualBeam SCIOS II microscope (ThermoFisher). The same microscope was also utilized for the preparation of thin foils for TEM analyses. The DualBeam microscope, in addition to an electron column for imaging, is equipped with an ion column that uses a gallium (Ga+) ion beam for precise preparation of thin foils from the specific points of interest for TEM analysis. This preparation process is fully automated using the AutoTEM 4 software. TEM analyses were carried out in bright field mode (TEM BF), high-resolution mode (HRTEM), and using the scanning and transmission technique (STEM). Phase analysis was conducted using selected area electron diffraction (SAEDP) and HRTEM techniques, while qualitative chemical composition analysis was performed using energy dispersive X-ray spectroscopy (EDS). These analyses were conducted on the THEMIS (200 kV) FEG microscope (ThermoFisher).

3. Results and discussion

The coating should have self-lubricating and self-healing properties. So to prove it as well as in order to precisely characterize the changes in the microstructure of the coating caused by mechanical load, I conducted observations on three selected areas of the coating along the wear track. A change in microstructure was noted, depending on the applied load, ranging from minimal at the edges of the track to maximum at its center. The focused gallium ion beam technique combined with high-resolution SEM microstructure analysis allowed for the precise identification of places from which thin foils were subsequently obtained for TEM analysis and cross-sectional analyzes were performed. The first area was near the wear path, but from observation of the surface topography there was nowear (Fig. 1).

The coating was composite. The large, bright areas is zinc, while the darker areas is MoS_2 or graphite. Looking at the cross-section of the coating, an area of large grain zinc, layered graphite and also layered MoS_2 were identified (Fig. 1b). Detailed microstructure characterization on the cross-section was done by TEM BF. It has been identified that in each of these three phases, even though the thin foil was prepared not from the wear path but from an area close to it, active wear mechanisms and structural changes were found. Kinking deformation was characterized in the MoS_2 region (Fig. 2).

Kinking deformation is another deformation mode which is less common when compared with slip and twinning but is important for materials with high plastic anisotropy [21]. The for-

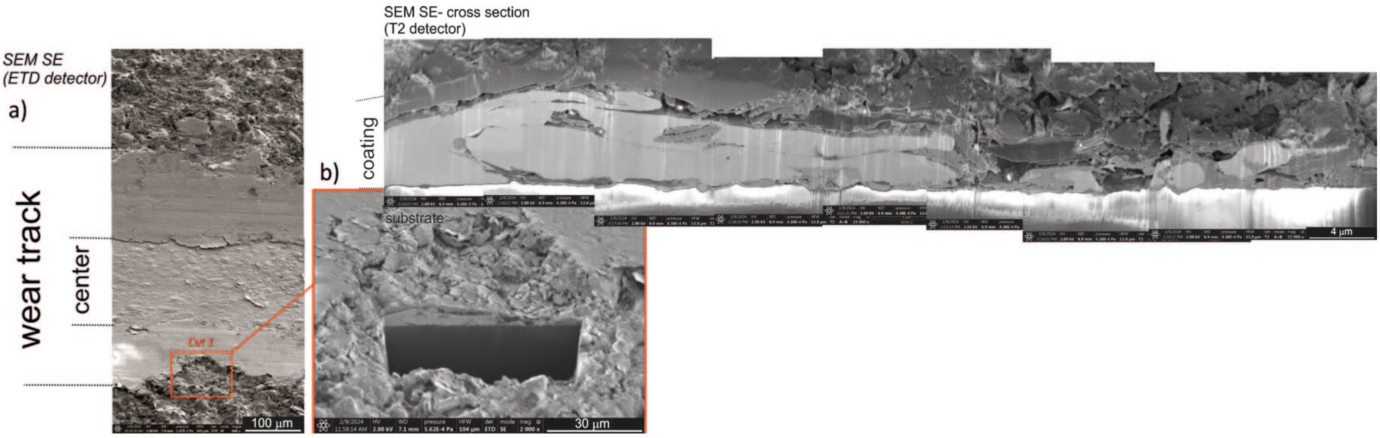

Fig. 1. Topography image done by SEM (SE) of wear track with indicated area for the following TEM characterization; a). plan view of the wear track; b). cross-section of the wear track

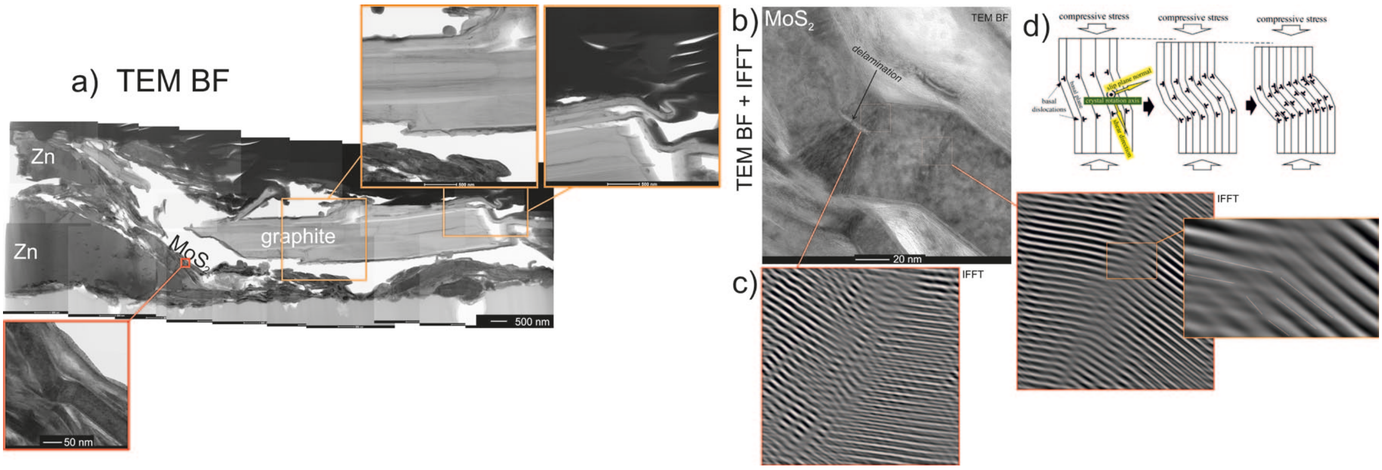

Fig. 2. The cross- section analysis of the coating close to the wear track done; a) TEM BF of the coating on the cross-section; b). TEM BF image of the kinking deformation mechanism; c). IFFT image; d). scheme of the kinking deformation

mation of deformation kink bands is found in many anisotropic materials. The model suggests cooperative initiation and/or operation of the basal dislocations, followed by arrangements of basal dislocations which align perpendicular to the slip plane. This process is believed to be the basic process for deformation kink band boundary. The crystal structure of molybdenum disulfide (MoS_2) takes the form of a hexagonal plane of S atoms on either side of a hexagonal plane of Mo atoms. These triple planes stack on top of each other, with strong covalent bonds between the Mo and S atoms, but weak van der Waals forcing holding layers together. When it comes to the graphite phase area and the wear process taking place there, wear mechanisms wear also present (Fig. 3). Graphite has a giant covalent structure in which: each carbon atom forms three covalent bonds with other carbon atoms. The carbon atoms form layers of hexagonal rings. There are no covalent bonds between the layers. Neighboring planes are weakly bonded together through van der Waals forces. The van der Waals bond is hence responsible for the softness of graphite and for the fact that is a very good lubricant. As a result of the load caused by the external force applied during the wear process, these bonds are broken, which leads to delamination. In this way, several-layered graphite bands are created (Fig. 3).

These bands can be deformed through the kinking deformation mechanism (Fig. 3(d), (e)). This mechanism was previously described using the example of MoS_2. Analysis of the area closer

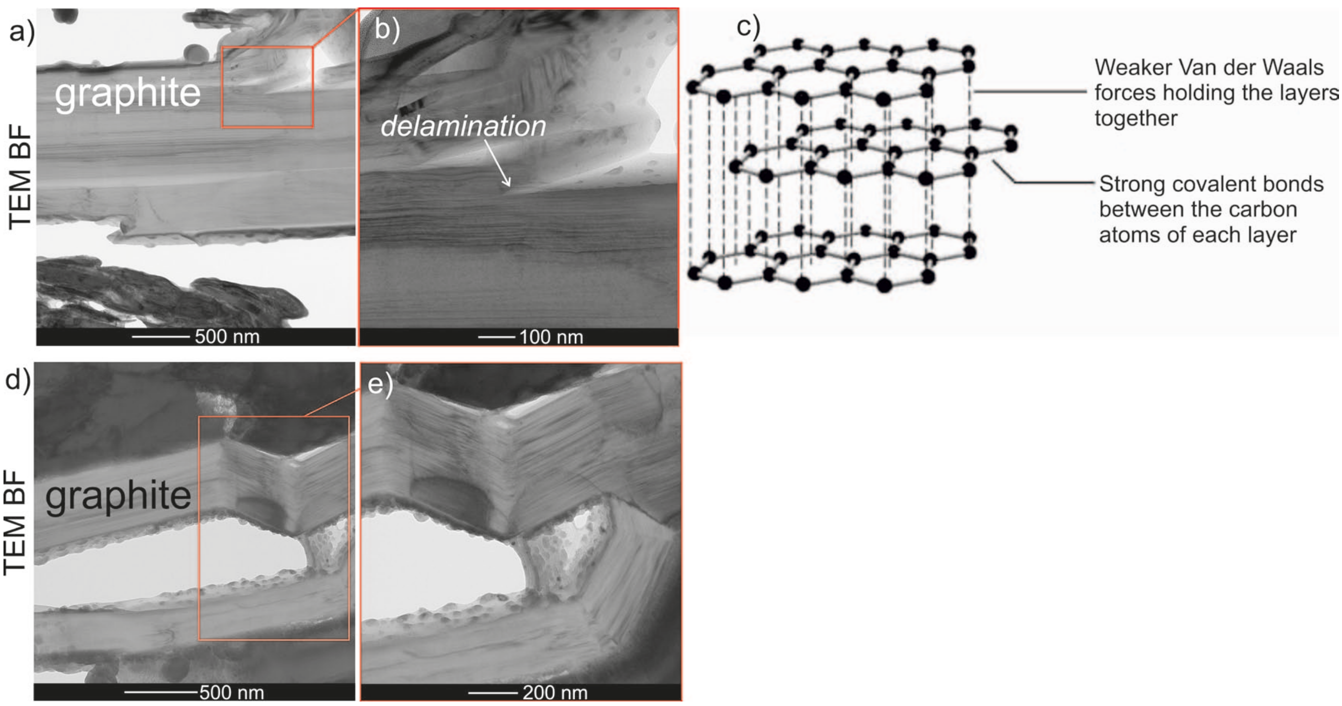

Fig. 3. Microstructure characterization of the wear mechanism in the graphite phase; a). TEM BF image of the wear mechanism in the graphite phase; b). higher magnification; c). scheme of the graphite atomic layers arrangement; a). TEM BF image of the kinking deformation in the graphite phase; b). higher magnification of the kinking deformation effect

to the wear center showed structural changes in the coating in the cross-section (Fig. 4).

The self-healing mechanism of the coating structure is already visible. Compared to the previously characterized cross-section (Fig. 1), the coating in this area has a more layered structure. Its structure is more fine (Fig. 4(b)). This was created by cracking the zinc along basal slip planes, more or less evenly spaced from each other (Fig. 5). As a result of the applied force, the cracking process occurred relatively quickly due to the very limited range of plasticity.

Subsequently, the cracks enlarged and bands of MoS_2 or graphite were inserted into these areas of the cracks between the zinc fragments which was proven by qualitative analysis of chemical composition (Fig. 6).

An alternating arrangement of zinc and the lubricating phase (in this case MoS_2) was created.

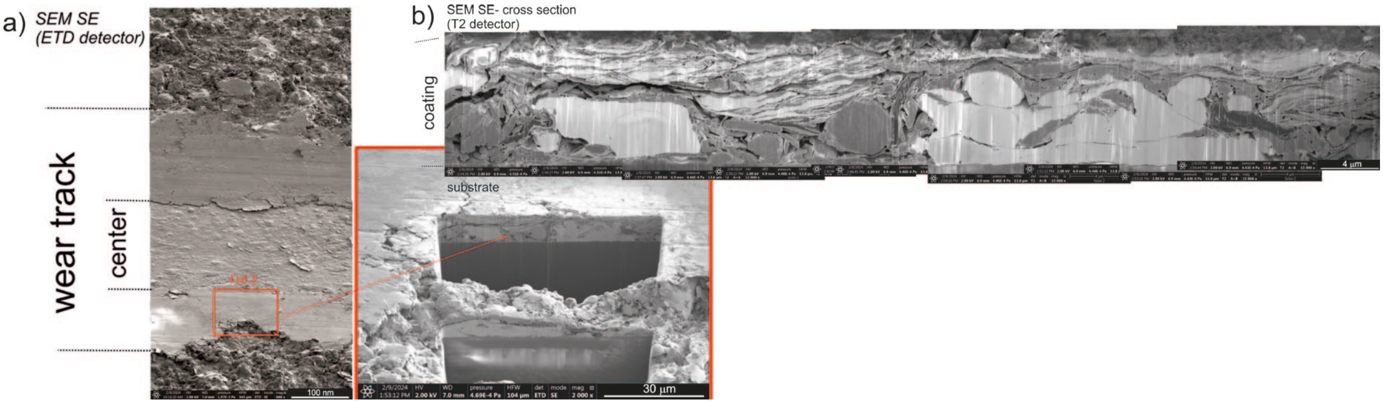

Fig. 4. a). Topography image of wear track with indicated area for the following TEM characterization; b). cross section characterization done by SEM (SE)

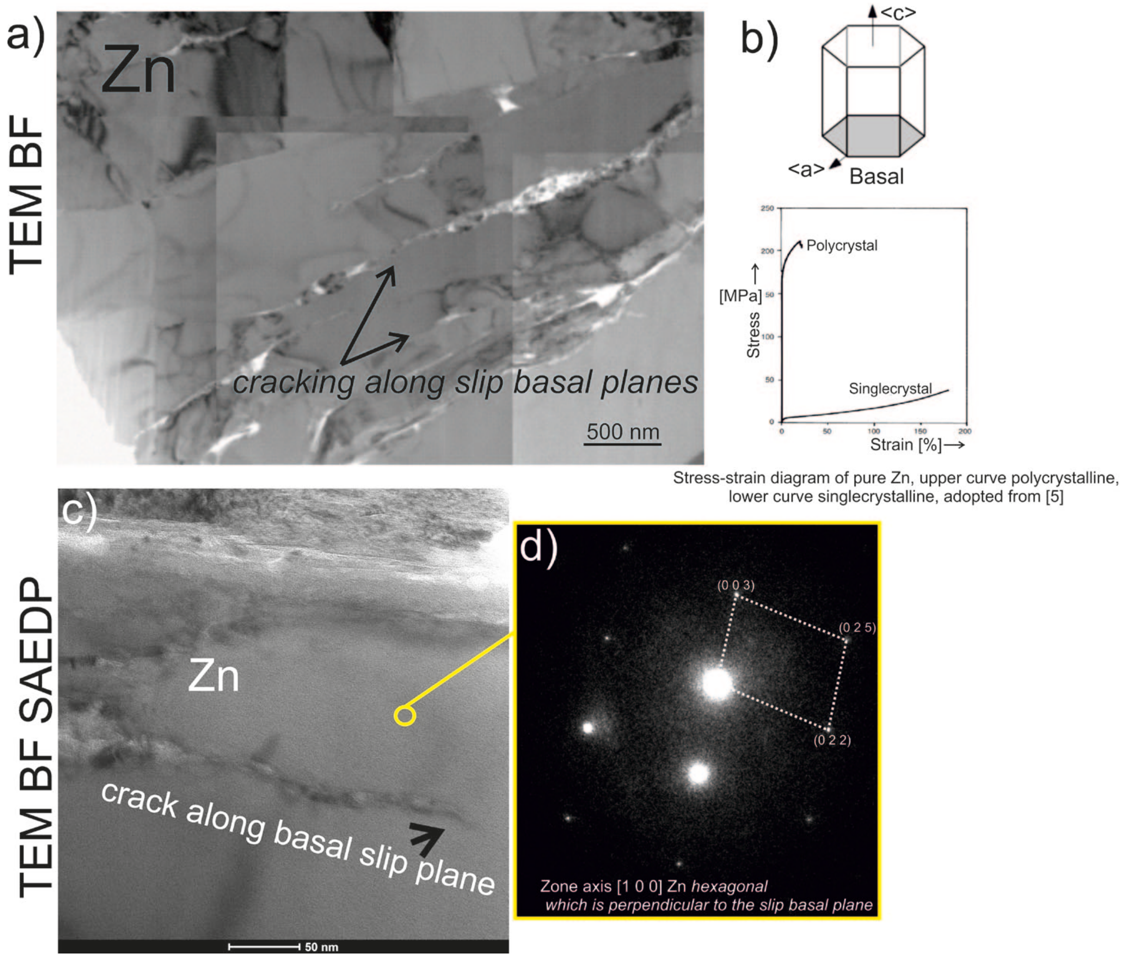

Fig. 5. Microstructure characterization of the cracking process in the Zn phase in the uploading process during wear done by TEM BF; a). TEM BF image of the cracking process in Zn phase; b). scheme of crystallographic planes along which cracking appeared and illustration of the tensile test of polycrystalline Zn as well as single crystalline phase; c). TEM BF of the cracks (higher magnification); d). SAEDP of the Zn phase

The relatively high magnification showed a very good quality of adhesion of MoS_2 to Zn. This connection was created during the coating wear process. This is the self-healing effect of the structure (Fig. 7).

In the case of MoS_2, the formation of a thin layer directly adhering to the metal surface occurs not only as a result of physical adsorption (as in the case of graphite), but also through chemisorption, caused by the chemical reaction of sulfur ions with metal atoms (Fig. 7b). After creating this layer, the unevenness cavities are then filled with molybdenum disulfide molecules until slip begins to occur between the MoS_2 layers. The lubricating effects are the same as for graphite lubrication. This creates slippage, i.e. a self-lubricating effect. The last location analyzed was the center of the wear path. Looking at the cross-section, there is little material left. Cross-sectional analysis was performed using a TEM (Fig. 8). At the initial stage of the wear process, the zinc grains were large enough to produce diffraction from a single grain (point diffraction) (Fig. 5), while at the final stage (wear center), its structure was fragmented enough to produce ring diffraction (Fig. 8).

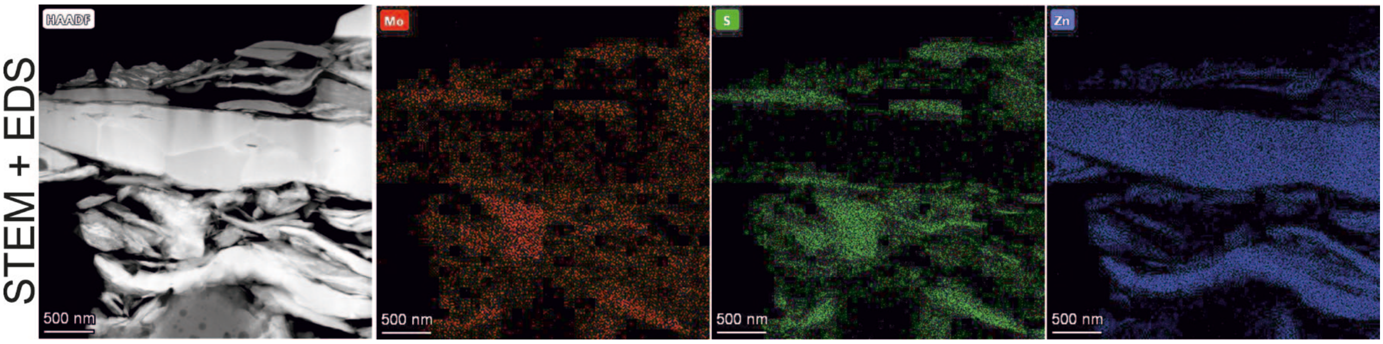

Fig. 6. Qualitative chemical analysis of the coating on the cross-section done by STEM and EDS

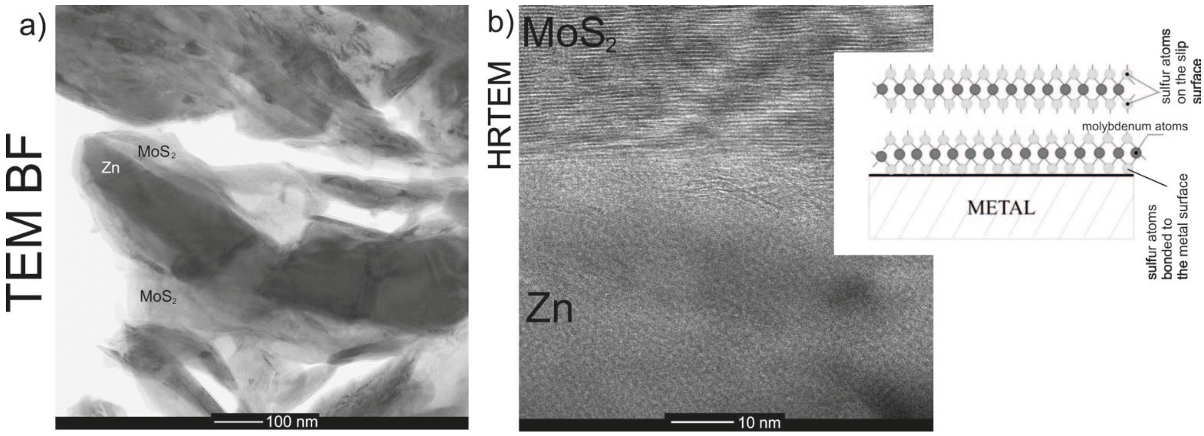

Fig. 7. Microstructure characterization of self-healing effect on the cross-section; a) TEM BF image; b) HRTEM image together with the scheme of the atomic layers arrangement in the MoS_2

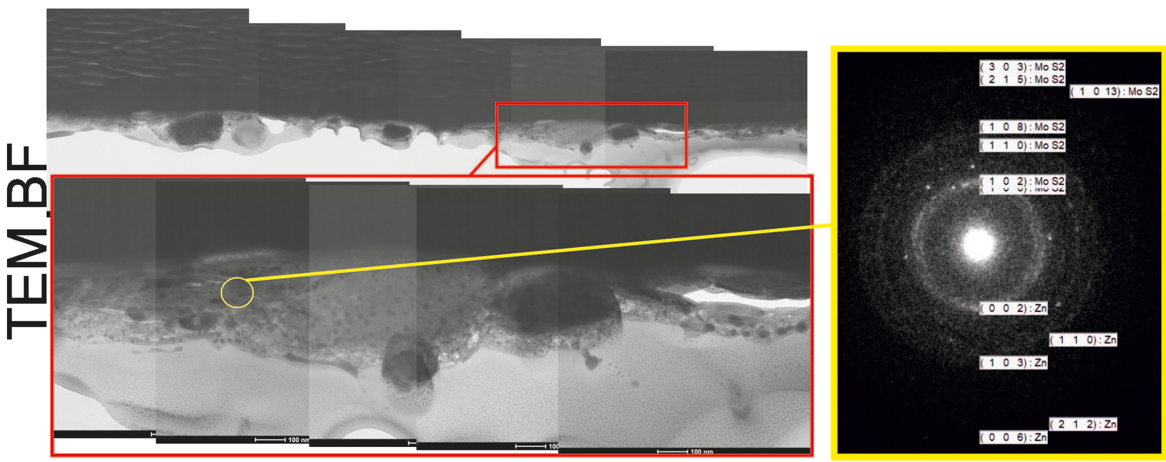

Fig. 8. Microstructure characterization of the coating from the center of the wear path on the cross-section done by TEM BF; a). TEM BF image of the coating on the cross-section; b). SAEDP

Qualitative analysis of the chemical composition of EDS showed strong fragmentation of the structure. The metallic and lubricating strands are relatively thin but still provide a self-lubricating effect (Fig. 9).

The layered arrangement was confirmed by high-resolution images. The layered arrangement of zinc and the lubricant phase is visible. In the case of the lubricant phase, the number of component layers was already small at this stage (Fig. 10).

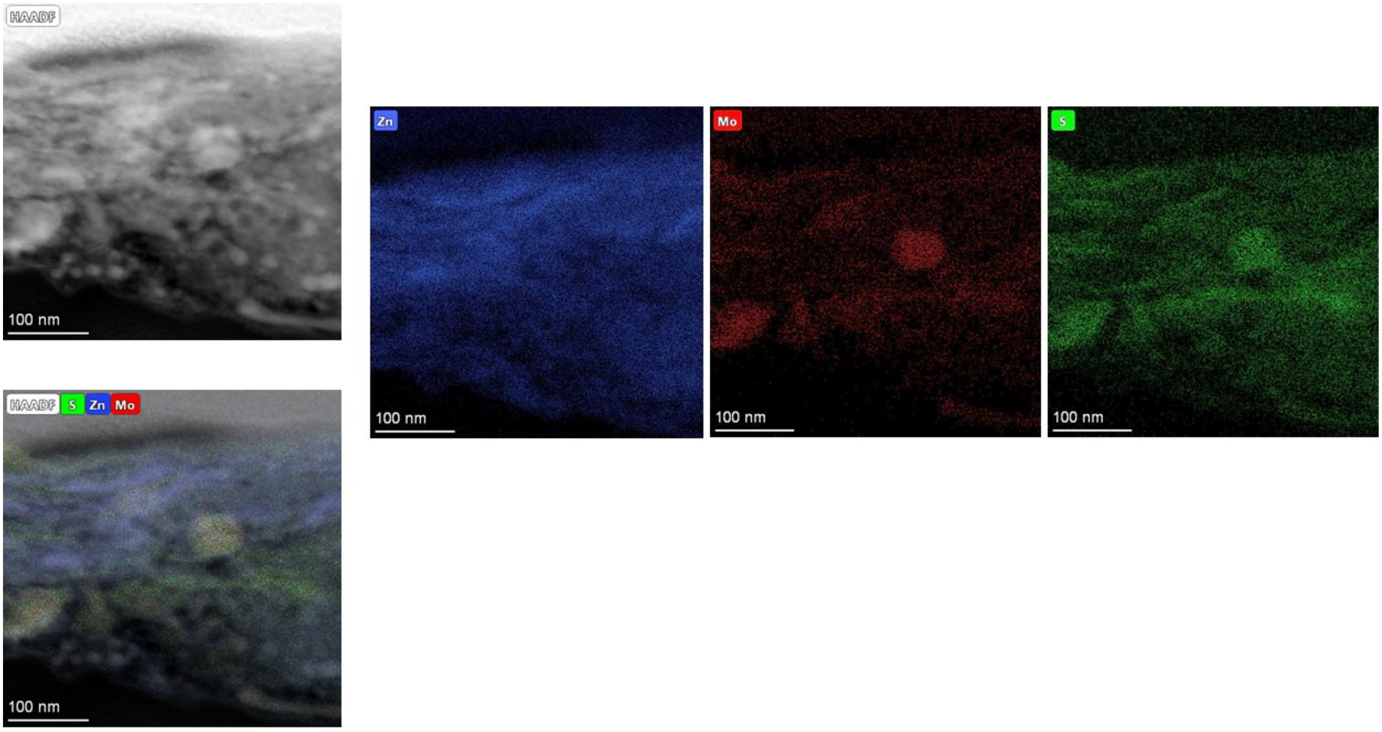

Fig. 9. Qualitative chemical analysis of the coating from the center of the wear path done by STEM and EDS

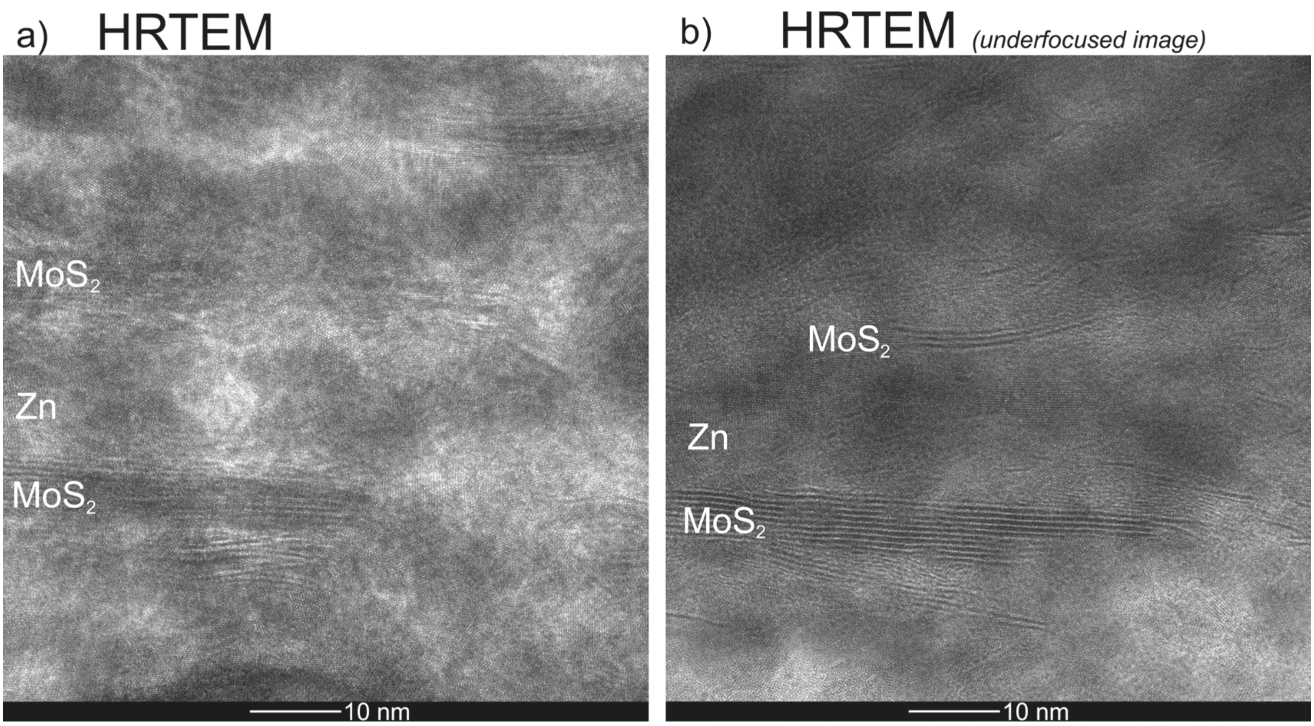

Fig. 10. The HRTEM analysis of the coating from the wear center on the cross-section

3. Conclusions

This study examines the structural dynamics of MoS_2 and graphite under mechanical stress, highlighting key findings that impact material performance. A significant observation is the kinking deformation in both materials, which enhances their structural adaptability under stress. The role of van der Waals bonds is crucial, as these weak interactions facilitate the slippage of layers, vital for their lubrication properties. As stress increases, the materials exhibit a transition to a finer, multi-layered structure, showcasing their microstructural adaptability. Zinc's cracking along basal slip planes adds insight into the wear mechanism. Notably, a self-healing effect is observed, where cracks allow the insertion of MoS_2 or graphite bands, preserving material integrity under cyclic loads. The research also highlights the strong chemisorption of MoS_2 to metal surfaces, unlike graphite's physical adsorption. This enhances the self-lubricating properties of MoS_2. Additionally, the transfer of coating material to the counter-sample surface demonstrates the material's sustained lubricating capabilities. In conclusion, this study provides valuable insights into the deformation, bonding, and self-healing mechanisms of MoS_2 and graphite, confirming their effectiveness as solid lubricants in various applications.

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