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Enhanced tribological performance of tungsten carbide functionalized surfaces via in-situ formation of low-friction tribofilms

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ABSTRACT

An innovative in-situ method of generating tungsten disulphide (WS_2) tribofilms was proposed in this study. It was found that the WS_2 tribofilms formed via a tribochemical reaction between tungsten carbide particles embedded in a steel surface and an extreme pressure lubricant additive led to low friction and significantly improved anti-wear properties in humid air. The presence of the WS_2 tribofilms was detected by X-ray Photoelectron Spectroscopy and their chemical surface composition was discussed. The friction behaviour was influenced by the rate of WS_2 tribofilms formation, EP additive concentration and normal load applied. Moreover, it was found that the WS_2 tribofilms were crucial for significant reduction in friction and negligible wear of WC-functionalized steel surfaces.

1. Introduction

The importance of reducing friction and wear in modern machinery is crucial and needs to be emphasised due to economical, energy efficiency and long-term reliability standpoint. Moreover, due to increasing demands towards tribological performance, the design of mechanical systems is constantly connected with the challenge of reducing friction during operation while simultaneously sustaining higher loads for longer duty cycles. This implies crucial tribological stress to the system, forcing engineers to identify novel wear protection techniques and develop innovative lubrication approaches. Among them, there is a growing interest for the development of tailor-made materials and coatings with self-lubricating properties. Transition metal dichalcogenides (TMD) are one of the most promising compounds for friction reduction. The paradigmatic example for tribological applications is molybdenum disulphide (MoS_2), whereas it has been reported in some works that tungsten disulphide (WS_2) could perform better due to its higher thermal resistance. Furthermore, the oxides formed (WO_3) reduced friction and were slightly more protective than MoO_3 [1–3].

The most widely used method to obtain TMD films is by a conventional magnetron sputtering. This leads inevitably to a disordered structure and, therefore the main drawbacks of TMDs include low tribological performance in oxygen or moist environments, low hardness as well as low load carrying capacity [4–6]. In order to overcome theses drawbacks, several approaches have been tried in alloying TMD coatings to increase their density with the double aim of impeding their oxidation and increasing their mechanical strength [7–10]. Among the metals used for alloying were Ti [11], Al [12], Au [13], Pb [14], Ni [7], and Cr [15] with titanium being the most successful from a commercial standpoint. However, all films obtained by the above-mentioned technique exhibit two general properties: prevalence of the TMD phase (maximum quantity of the alloy was about 20 at%) and limited interaction between the TMD phase and the alloying element [16]. Therefore, the main issues remain and magnetron sputtered TMDs are mainly restricted to vacuum applications [17].

Another concept presented in the literature referred to the deposition of carbon containing TMD coatings (C-TMDs) [3]. The goal was to obtain composite coatings that will incorporate the good properties of both materials and thus avoid the above mentioned drawbacks [18,19]. Furthermore, another study on deposition of C-TMDs by co-sputtering dealing with nanolayered structured coatings, that contained tungsten disulphide and carbon layers in the nanometre scale, has been reported in the literature [20]. However, the outcome of those films registered only moderate performance. The sliding properties of Mo–Se–C coatings incorporating two different carbon contents have also been investigated in different sliding environments [21]. It was found that the friction increase of Mo–Se–C coatings in humid air was mainly due to the increase in shear strength of the $MoSe_2$ structure caused by the presence of water molecules in the sliding interface.

TMDs tribofilms can be also formed in-situ by tribochemical reactions on contacting surfaces during the sliding process. Grossiord et al. studied the friction reduction mechanisms of molybdenum

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dithiocarbamate (MoDTC) under boundary lubrication. MoDTC are molybdenum and sulphur containing compounds, which form by electron transfer mechanisms MoS_2 single sheets during the friction process by degradation of the MoDTC molecule. The overall data demonstrated the responsible mechanism for the observed friction reduction of MoDTC was the effect of sliding between single layers of MoS_2 [22].

Several attempts have been reported in the literature to form either wear protective or low-friction tribofilms by tribochemical reactions between extreme pressure (EP) or Anti-Wear (AW) additives and DLC coatings [23–27]. They essentially relied on the decomposition of sulphur and molybdenum-containing friction modifiers for the formation of MoS_2 tribofilms under boundary lubrication. However, a new mechanism was found by Podgornik et al. who noticed that in case of WC-doped hydrogenated DLC/steel combination, the EP and AW additives reacted with exposed steel surfaces, and together with the transferred coating material formed a new tribofilm that was responsible for the improved tribological properties of the system [28]. In this first attempt, it was found that the combination and the type of additives had a pronounced effect on the tribological behaviour of the DLC coated surfaces but no direct reaction between additives and the DLC coating could be detected. Moreover, DLCs were also able to provide improved protection against failure of contact surfaces, thus extending the life-time of the components for up to 5 times in the case of lubricant loss, or when the lubrication was purposely starved [24,29]. A subsequent study using similar EP additives showed the in-situ formation of a WS_2 tribofilm proved by XPS [30,31]. However, the tribofilm was detected only on the steel counter-surface and not on the DLC coatings, and it was considered instrumental in reducing the friction for up to 50%. Nevertheless, the low friction state required the consumption of both W from the DLC-doped coating and S from the additive and led to accelerated wear [29–31]. The reaction rate was influenced by the additive concentration used.

Taking into account all of the above, it is beneficial to develop a new concept of generating TMDs in the contact zone to provide low friction in various sliding environments, while ensuring wear resistance. This concept should be straightforward and not rely on rare elements or expensive methods. On this basis, we propose a simple, cost-effective yet innovative in-situ method of generating WS_2 tribofilms. This has been accomplished via a tribochemical reaction occurred during the sliding process between surface embedded tungsten carbide (WC) particles and a sulphur-containing EP lubricant additive. The WC particles were embedded into steel samples using a novel surface treatment technology called machine hammer peening (MHP) [32,33].

To the best of our knowledge, this is the first successful attempt to generate in-situ WS_2 tribofilms on surfaces through tribochemical reactions between WC particles and EP lubricant additives in humid air.

2. Experimental section

2.1. Sample preparation

The disc substrates used in this study were chromium–nickel austenitic stainless steel (AISI 304) and the ball material was AISI 52100. A tungsten carbide powder of grain size 0.8 μm was selected for embedding into the steel disc substrates. The powder was applied on the surface using a suspension in mineral oil with a viscosity of 46 mm^2/s recorded at 40 °C. Afterwards, the surface was exposed to a MHP treatment using an electromagnetic actuator system (accurapuls), attached to a five-axis machining centre C20U (Hermle), according to a previously described procedure [32,33]. After the MHP process, the samples were ultrasonically cleaned in water with 2% Universal Ultrasonic Cleaning Solution (EM80) in order to remove the remaining oil. Using this technology, a homogeneous layer of tungsten carbide grains can be embedded onto the surface [34]. The WC particles were applied only onto the disc surfaces and the balls remained uncoated. For comparison purposes, hammered steel samples, without the WC embedded particles were tribologicaly tested as reference samples, also.

2.2. Chemicals

The lubricants used in this investigation were poly-alpha-olefin oil (PAO 8) as the base oil, and sulphurized olefin polysulphide (40% of sulphur content) as the EP additive, and were obtained from OMV (Vienna, Austria). The fluids were blended into mixtures using additive concentrations of 0.5%, 1.5% and 3% by weight and were evaluated against additive-free PAO 8, employed as the reference lubricant. The physical properties of the lubricants (viscosity and density) were measured using a Stabinger viscometer SVM 3000 from Anton Paar GmbH (Graz, Austria) and are listed in Table 1. The viscosity index was determined according the ASTM D2270-04 standard. It should be noted that the viscosity and density values are relatively similar for all lubricants, therefore it is expected that they will not have a significant impact on overall tribological behaviour of the mixtures.

2.3. Tribological investigations

The tribological evaluation was conducted with a SRV® tribometer (Optimol Instruments Prüftechnik GmbH, Munich, Germany) using a ball-on-disc configuration in oscillating reciprocating motion. New specimens were used for each test and were cleaned in an ultrasound bath using two different solvents (toluene and petroleum ether) for ten minutes, before and after the tribological experiments. The lubricant quantity (0.2 ml) was adjusted using a pipette to ensure fully immersed tribocontacts for the entire duration of the experiment. The coefficient of friction (COF) was monitored as a function of time, normal load and additive concentration. At least three repetitions were performed for each test condition and the results were averaged. The SRV rig parameters and the properties of the tested specimens are listed in Table 2.

2.4. Surface analyses

The topographies of the worn surfaces were analysed using a white light confocal microscope (μsurf, NanoFocus AG, Oberhausen, Germany). The volume of the wear scars acquired on both tribo-pairs (ball and disc) was calculated with MATLAB software, as previously described in our earlier works [35,36]. In brief, an ideal surface was defined as the reference surface. The surface selected was spherical for the ball and plane for the disc, respectively. The programme calculated the wear volume by substracting the value between the reference surface and the measured (worn) surface, thus providing the volume of the removed material.

Table 1
Physical properties of the lubricants.

Sample	Viscosity (mm^2/s)		Viscosity index (VI)	Density at 15 °C (g/cm^3)
	40 °C	100 °C		
PAO 8 (additive-free)	45.5	7.9	146.2	0.83
PAO 8+EP4 (3.0%)	44.9	7.8	145.4	0.84
PAO 8+EP4 (1.5%)	45.1	7.9	146.0	0.83
PAO 8+EP4 (0.5%)	45.3	7.9	146.1	0.83