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Investigation of crystalline and amorphous MoS_2 based coatings: Towards developing new coatings for space applications

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ABSTRACT

The study focus on understanding what governs the tribological behavior of dry lubricated contact to find out the keys to develop new coatings for space applications. Firstly conducted on sputtered columnar MoS_2 coatings and amorphous MoS_2+Ti coatings, experiments show that contamination modulates the 3rd body rheology and helps controlling the 3rd body generation (particle size and amount). To dissociate the role of both Ti and the coating microstructure in the tribological behavior of the coatings, a sputtered amorphous MoS_2 coating is studied. The study confirms the beneficial impact of the addition of a controlled amount of contamination on their tribological behavior. It also brings some recommendations to design coatings for space applications in terms of microstructure, addition of metal and gaseous dopant, etc.

1. Introduction

Since the beginning of space exploration the duration of missions has progressively increased from several minutes to several years reaching 15 [1,2] to 30 years [3]. High reliability and great precision to within a few μm [2] or μrad [4] are now also required for space equipment such as satellites with no possibility for maintenance after launching [5]. Furthermore, mechanisms are required to be assembled and tested on Earth. Assembling is done in clean rooms with controlled humidity rate ((55 ± 10)%) and temperature (22 ± 3 °C) [6]. Once assembled, every single mechanism, even one shot mechanisms, have to be tested to certify that they will handle launch stresses and then properly function once in space [7–11]. Mechanisms are tested either in vacuum, air, or dry N_2 environments. Specific equipment, such as those operating under cryogenic conditions, is tested under both realistic working conditions and standard laboratory conditions (clean rooms) [12]. Although the number of micro-, nano-, and pico-satellites [13–15] is growing, most satellites can still not be fully tested in a vacuum chamber due to their size [16]. That means that during testing operations, their constituting mechanisms and even onboard devices are exposed to clean room environments. Ground operations can amount to as high as 30% of the total mechanism's working lifetime [17]. Finally, prior to launching mechanisms can be stored for up to several years [3], and thus see extended periods of exposure to clean room environments. Consequently, during their ground lifetime, mechanisms are surrounded by contaminants of different nature (organic, ionic, etc.) [18–20]. Once in space, the satellite can take several years to reach its final destination [16,17,21]. Then, during its mission components in relative motion (mainly rolling or sliding) can execute up to hundreds of millions of cycles throughout their lifetime [19,22]. As with the case on Earth, mechanisms will interact with their surrounding environment in which both pressure and composition vary depending on the orbit [10,18, 23–26]. Moreover, the near surrounding environment of the satellite can strongly differ from the orbit atmosphere due to outgassing of the material constituents of the mechanisms [10,25,26].

Consequently, developing dry lubricants meeting the requirements of such increasingly complex applications is very challenging because numerous mechanical and physicochemical environments, which are not necessarily reproducible on Earth, must be taken into account. Through the years, many different materials have been developed and tested in an attempt to address these requirements. Considering only lamellar solids based coating materials, the following can be encountered:

1.1. *Coatings comprised of single lamellar solids*

MoS_2 and WS_2 are the most widely encountered although MoS_2 is the most widely used since WS_2 does not appear to have a better behavior than MoS_2 [27,28] apart from at elevated temperatures as reported by Zabinski [29]. They both provide low friction and long wear life in vacuum but high friction and short life in air [27–29]. Recent studies of Colas et al. [30,31] discussed the literature on MoS_2 and compared it with their experimental results. They

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showed that depending on vacuum level, and consequently on contamination, wear life of MoS_2 can be extended if a reasonable amount of contaminants is present in both the coatings and the environment. That raised the questions of the vacuum level to use for ground test operations, material selection tests, and above all a potential nondetrimental, see beneficial, effect of reasonable internal and external contamination. Materials such as $MoSe_2$, WSe_2, $NbSe_2$, NbS_2, $TaSe_2$, TaS_2, $MoTe_2$, and WTe_2 were also studied [32–38]. $MoSe_2$, WSe_2 and $MoTe_2$ are found to have good tribological properties (low friction and long life) and both $MoSe_2$ and $MoTe_2$ are more thermally stable than MoS_2. Like MoS_2 and WS_2, $NbSe_2$, $MoSe_2$ and WSe_2 exhibit sensitivity to humidity but also exhibit low load carrying capacity; As for WTe_2, it is prone to adhesion and its friction coefficient in vacuum > 0.2. It appears that the electronic structure of Nb and Ta does not ensure low friction in comparison to Mo and W based materials [19]. $MoSe_2$ and NbSe2 exhibit good electrical conductivity and $NbSe_2$ was tested for electrical sliding contact applications [32]. W, Nb and Mo selenides were not widely used because of their high cost [39]. However, interest seems to be recently renewed [40–42]. Finally a lubricant with potential for vacuum application was graphite fluoride CF_x $(0 < x < 1.2)$ [39,43–45]. Some attribute its good friction properties to the fact that the addition of fluorine to graphite increases the graphite interlayer distance [39]. However, it has mainly been tested in dry and moist air [45–48] and exhibit promising lubrication characteristics. CF_x has not often, or perhaps ever, been used due to its high cost [39]. However, like for the selenides, interest has been renewed recently [49,50].

1.2. Codeposited coatings

Codeposition of metals with MoS_2 is known since the early 1970s [51]. Since then, almost every metals which can be deposited using vacuum deposition techniques (Cr, Au, Ag, Ti, Ni, Ta, Zr, etc.) [39,51–63] have been tested. In all cases, the aim was to find a solution to the MoS_2 sensitivity to humidity while both increasing its load carrying capacity and maintaining its extremely good friction behavior in vacuum. However, most studies with metallic dopants were conducted in dry or humid air and in dry N_2 environments. The latter was considered as vacuum equivalent [52] although concerns on this have been raised [53,64]. Indeed, it has recently been demonstrated that dry N_2 environment is not equivalent to vacuum especially because it induced dramatic changes in the tribological behavior of MoS_2+Ti coatings [31]. Nonetheless, all those studies have shown that

- Homogeneous distribution of the doping metal throughout the coating appears preferable to a multilayered structure because it does not improve, and might even decrease, the tribological properties of the coating [54–56]. However, multilayered structures worked well for WS_2/MoS_2 multilayered coating whose wear rate was threefold lower as compared to the individual coatings of MoS_2 and WS_2 [27,28].
- An optimal concentration of doping metal exists which depends on the metal itself [51,54–62]. For the same metal, that concentration depends on the environment [59] and on the contact stress [57].
- The higher the concentration of doping atoms, the more the coating becomes amorphous [60–62].
- The coating hardness increases with its densification [54,56,59–61].
- The load carrying capacity increases with the metallic doping [54,56,61].

Vacuum experiments were conducted with Au/MoS_2 [55] and MoS_2+Ti [31,53] coatings. Compared to MoS_2, the tribological behaviors of the former were good, see better than MoS_2, under vacuum of 10^{-4} Pa whereas the tribological behavior of the latter was mediocre (extremely short wear life and high friction) in vacuum ranging from 10^{-3} Pa to 10^{-6} Pa. The inclusion of Ti inside MoS_2 coatings reverses the tribological behavior of MoS_2 by dramatically improving its behavior in both dry N_2 and humid air environments. Colas et al. [31] showed that the origin of this dramatic improvement was due to migration and segregation of Ti inside the contact leading to the creation of a bi-phasic 3rd body with specific rheology. Ti presumably acts as a reactive agent protecting MoS_2 from oxidation and allows it forming a 3rd body phase close, in composition (Mo+S+O) and both morphology and ductility, to the unique 3rd body created under ultrahigh vacuum from MoS_2 coatings. Such elementary selection phenomenon has also been encountered in newly developed MoSeC coatings with the carbon [65]. After friction the carbon was more concentrated outside or at the periphery of the friction track while $MoSe_2$ oriented layer was created in the center of the track.

1.3. Nanocomposite coatings

Nanocomposite coatings are composed of a matrix filled with nanoparticles (ceramics, metals, dichalcogenides, etc.). Their mechanical and tribological properties depend on the nature of the fillers, their contents and dispersion in the matrix, the size of particles and on how they are bonded together and/or to the matrix [39,66–70]. Those new coating possibilities have given rise to new concepts such as super-tough and adaptive nanocomposites [67–70]. The aim of adaptive nanocomposites, also called “Chameleon nanocomposites”, is to adapt themselves to the stresses and environmental conditions (atmosphere, contact stresses, thermal cycling and so forth) undergone by the contact. This is done by modifying the structure and composition of the extreme surface of the coating, for example, by the migration of material like silver (Ag) or gold (Au) at high temperature through micro-cracks from the bulk to the surface of the component in order to resist stress, or by the formation of a thin film of WS_2 and MoS_2 in vacuum or dry nitrogen (N_2), or DLC in humid environment. When a thin film forms in one environment but is unsuited for the following one, it is removed and another film better suited for the second environment is formed. This phenomenon can be compared to what occur with some codeposited coatings [31].

Consequently, numerous different coatings can be encountered and choosing one material among them, or developing and adapting a coating to a specific application becomes challenging. More particularly questions remain as to the effect of the coating microstructure, the mechano-physico-chemical role of its constituents and its external or external contaminants, etc. Moreover, comparing results from one study to another is very difficult as tribological behavior depends on the mechanical properties (stiffness, degrees of freedom) of the mechanism (tribometer, mechanical joints, etc.), the type of test (oscillatory and continuous sliding, etc.), etc. [71–73]. Furthermore, the increasing possibilities of creating new coatings and the renewed interest in previously tested material might endanger the analysis of the studies. The risk is to turn experimental results into data bank made from different tests without necessarily having all information allowing rightful comparisons. Especially as comparisons typically focus on friction coefficient values and wear rates and not on the underlying mechanisms governing them.

In previous studies [30,31], the authors considered the tribological issue of dry lubricated contacts in a global view, i.e. by simultaneously considering both physico-chemistry and mechanics during both real-time experiments and post-mortem analysis. A complete tribological investigation procedure has thus been developed and presented [30]. The 3rd body concept [74–76] was extended from solid flows to include gas flows inside the contact. The resulting