Please cite the Published Version


DOI: https://doi.org/10.1063/1.3552375
Downloaded from: https://e-space.mmu.ac.uk/622524/

Enquiries:
If you have questions about this document, contact rsl@mmu.ac.uk. Please include the URL of the record in e-space. If you believe that your, or a third party's rights have been compromised through this document please see our Take Down policy (available from https://www.mmu.ac.uk/library/using-the-library/policies-and-guidelines)
New Generation of MoS$_x$ Based Solid Lubricant Coatings: Recent Developments and Applications

Julfikar Haider$^a$ and M S J Hashmi$^b$

$^a$School of CEIS, Ellison Building, Northumbria University, Newcastle Upon Tyne, NE1 8ST, UK
$^b$School of MME, Dublin City University, Dublin-9, Republic of Ireland

Abstract. In recent times, there is a growing interest in applying Molybdenum disulphide (MoS$_x$) solid lubricant coatings on components to improve the tribological performance (i.e. lower friction coefficient and wear rate). The tribological performance of MoS$_x$ coating is strongly dependent on coating properties and tribological environment. MoS$_x$ coatings are highly successful in certain applications such as in space/vacuum technology, but its effectiveness is questioned in other terrestrial applications such as in cutting tool industry due to its lower hardness and poor oxidation resistance leading to shorter life. In order to circumvent this drawback, the paper identifies that current research is being concentrated on developing MoS$_x$ based coatings using three different approaches: (1) Metal or compound addition in MoS$_x$ coating (2) MoS$_x$ layer on hard coating and (3) MoS$_x$ addition in hard coating matrix. Although the primary objective is same in all three cases, the third approach is considered to be more effective in improving the tribological properties of the coating. Finally, the potential applications of MoS$_x$ based coatings in different industrial sectors have been briefly outlined.

Keywords: Molybdenum disulphide, Solid lubricant, Coating, Sputtering.

PACS: 81.15.Cd

INTRODUCTION

Molybdenum disulphide (MoS$_x$) is the most appropriate solid lubricant coating in tribological applications, where the traditional liquid lubrication is not suitable (e.g., devices used in space) and where there is a need to fully or partially eliminate liquid lubricant. Sputtered MoS$_x$ coating is an attractive choice due to its low co-efficient of friction (usually in the range of 0.01 - 0.25) and its ability to retain the favourable tribological properties in extreme environments (cryogenic temperature up to a maximum temperature of 300-400 °C in air and up to 800 °C in high vacuum). Sputtered MoS$_x$ coating obtained at optimum deposition conditions can display the lowest coefficient of friction (0.002) among the currently known solid materials under favourable operating conditions (i.e., ultra-high vacuum) [1]. MoS$_x$ coating is also regarded as a true solid lubricant as it can form a sacrificial transfer layer between the two mating surfaces, which helps to reduce friction and wear. Fundamental knowledge, historical development, lubrication mechanism, deposition methods and applications of MoS$_x$ coating have been reviewed by many authors [2, 3].
Pioneering work by Spalvins during late 1960’s has established that sputtering is a remarkable technique for depositing high quality MoS\textsubscript{x} coating [4]. The tribological performance of MoS\textsubscript{x} coating is strongly dependent on tribological environment and coating properties, which are controlled by sputtering conditions as shown in Figure 1.

Coating Properties

Depending on the sputtering conditions, purely amorphous or quasi-amorphous (i.e., poorly crystallized) and crystalline MoS\textsubscript{x} coating can be resulted. The latter one is more favourable for low friction properties. Two types of crystallite orientations are generally observed in sputtered MoS\textsubscript{x} coating: basal planes perpendicular to the substrate (Type I) and (2) basal planes parallel to the substrate (Type II) as shown in Figure 2 [1]. Type I coating is characterised by needle-like topography, high shear strength and loosely packed columnar structure compared to the cluster shape topography, low shear strength and dense non-columnar structure in Type II coating. Furthermore, the exposed reactive edge sites (100) Type I coating easily oxidise in humid environment leading to higher coefficient of friction and poor wear resistance. On the other hand, Type II coating having basal plane (002) parallel to sliding direction can provide low shear strength and hence, low friction and wear result. In addition, the protected edge sites in Type II coating can offer higher resistance to oxidation.

MoS\textsubscript{x} coatings produced by conventional sputtering process (DC or RF) exhibit typical of Type I coating. MoS\textsubscript{x} coating deposited by closed-field unbalanced magnetron sputtering exhibits long life, low coefficient of friction and high resistance to humidity due to a good combination dense non-columnar microstructure, favourable basal plane orientation and excellent adhesion to the substrate. Only a very thin coating of about 0.2 μm is required for effective lubrication [1]. Coating properties do not vary considerably with the thickness within the range from 0.15 to 3.0 μm [5].
MoS\(_x\) coating with higher ratio of basal plane to edge plane (002)/(100) yields lower friction and wear rate and exhibits increased resistance to degradation in reactive environments. It has been shown that negative bias voltage (-50 to -100 V), unbalanced mode of the magnetron, pulsed power supply, deposition rate, deposition pressure and temperature have significant influence on the crystal growth with (002) orientation [5, 6]. The low friction properties of MoS\(_x\) coating are strongly dependent on the stoichiometry (S/Mo ratio = x), which can vary from low to high sulphur content (0.8 < x < 2.2). However, an optimum combination of wear and friction properties can be obtained with a deficiency of sulphur in the coating (x values in the range of 1.2-1.8). The content of crystalline structure increases with increasing the x value, which will improve the lubrication property of MoS\(_x\) coating and a minimum x value of 1.1 is required to maintain the hexagonal crystal structure in the coating [1]. Sulphur deficiency in MoS\(_x\) coating is generally occurred due to resputtering of sulphur atoms from the growing coating by the energetic ion bombardment under low pressure, high negative bias voltage or strong unbalanced condition of the magnetron.

**Tribological Environment**

Operating conditions and environment have profound impact on the durability and friction properties of MoS\(_x\) coating. Under ultra high vacuum and dry nitrogen environments MoS\(_x\) coating exhibits super-lubricant properties with coefficient of friction as low as 0.002 [7]. The super low friction properties of MoS\(_x\) coating in vacuum could be related to the specific structural properties (e.g., stoichiometry, crystallinity etc.), development of transfer film on the matting counter face and friction induced basal plane orientation during sliding leading to very low interfacial shear strength. It has also been demonstrated that friction coefficient and wear rate increase with the increasing relative humidity level during wear testing. However, the rate of increasing friction coefficient and wear with the relative humidity is much higher in random/edge oriented MoS\(_x\) coating than basal oriented MoS\(_x\) coating due to the fact that random-oriented MoS\(_x\) coating oxidises more easily [6].
ADVANCES IN MOS\textsubscript{x} BASED COATINGS

MoS\textsubscript{x} coating exhibits low friction and long life in vacuum or inert environment, it struggles to provide the same in terrestrial environment due to its low hardness and susceptibility to oxidation. To address this issue, research is being undertaken on developing MoS\textsubscript{x} based coatings using three different approaches (Figure 3).

![Architectures of MoS\textsubscript{x} based coatings](image)

**FIGURE 3.** Classification of MoS\textsubscript{x} based coating architectures.

### Metal or Compound Addition in MoS\textsubscript{x} Coating

Efforts have been devoted to improve the tribological properties of pure MoS\textsubscript{x} coating by incorporating metals (Au, Pb, Ti, Cr etc.) or compounds (e.g., PbO, SbO\textsubscript{x}) into the coating in the form of composite or multilayer structure [8, 9, 10]. It has been evidenced that the improvement comes through structural modifications such as formation of densified structure, tribologically favoured basal oriented structure, higher hardness and preferential oxidation of metal protecting the MoS\textsubscript{x} from oxidation during wear. A 5-20% concentration of metal/compound in MoS\textsubscript{x} coating could give optimum tribological properties. Ti is most frequently used as an inclusion in MoS\textsubscript{x} coating due to its good adhesive properties and compatibility with MoS\textsubscript{2}. The metal-doped MoS\textsubscript{x} coating has showed potential improvement over pure MoS\textsubscript{x}, but lifetime is still limited owing to the soft MoS\textsubscript{x} matrix.

### MoS\textsubscript{x} Layer on Hard Coating

In this architecture, MoS\textsubscript{x} coating is deposited on top of hard coatings (e.g., TiN, CrN, TiCN, TiAlN, DLC, Si\textsubscript{3}N\textsubscript{4}) [10, 11]. This double layer approach can enhance the performance of the coating in tribological applications by the combined effect of friction reducing MoS\textsubscript{x} top layer and hard and load bearing under layer. The solid lubrication property of MoS\textsubscript{x} coating could be fully developed by a strong support from the underneath hard coating. The hard coating layer could be produced either in the form of multilayer or graded structure and the soft layer on top of that either as pure MoS\textsubscript{x} or MoS\textsubscript{x}/Ti [10]. Although soft MoS\textsubscript{x} coating could be removed very quickly, the lubrication effect could still be maintained for extended periods of time.
**MoS\textsubscript{x} Addition in Hard Coating Matrix**

Recently, combined hard-solid lubricant coatings have been produced by adding MoS\textsubscript{x} into hard coating matrix (TiN, TiAlN, TiSiN, TiB\textsubscript{2}, CrN, CrB\textsubscript{2} etc.) [12, 13]. These coatings can provide both high wear resistance and low friction coming from the hard and soft parts respectively. Again, the low friction properties can be maintained throughout the entire lifetime of the coating as MoS\textsubscript{x} is uniformly distributed across the whole thickness of the coating. MoS\textsubscript{x} concentrations from 7-11% are suggested to achieve optimum tribological properties. TiN+MoS\textsubscript{x} coating deposited by closed-field magnetron sputtering demonstrated a significant reduction of coefficient of friction (~ 45%) and wear rate compared to pure TiN coating as shown in Figure 4.

![Coated samples](image)

**FIGURE 4.** Comparison of wear rates among TiN, TiN+MoS\textsubscript{x} and MoS\textsubscript{x} coatings.

**APPLICATIONS OF MOS\textsubscript{x} BASED COATINGS**

Pure MoS\textsubscript{x} coating is most commonly used in space/vacuum applications. Lately, it has been reported that significant improvement in tool life (2-5 times) could be achieved in milling, drilling, punching, hobbing etc. with MoS\textsubscript{x} based coatings either as a top layer on hard coatings (TiN, TiAlN etc.) [14] or in a composite form (e.g., TiN-MoS\textsubscript{2}) [12]. Figure 5 shows MoST (MoS\textsubscript{2}/Ti) coated circular saw and hob for machining applications. The MoS\textsubscript{x} based coatings allow improved chip flow with a lowered coefficient of friction, reduced cutting force, heat generation and built-up edge formation in the cutting tool. Hence, improved tool performance, higher productivity and better workpiece quality result. MoS\textsubscript{x} based coatings have also found applications in plastic moulds, extrusion dies, stamping tools etc. and in automotive parts such as pistons and piston rings.
CONCLUDING REMARKS

Sputtered MoS$_x$ coating has come a long way since its first successful use in space applications. Technological improvement in sputtering process such as the development of closed-field unbalanced magnetron has contributed towards the deposition of MoS$_x$ coating with improved properties and longer life. Nevertheless, such improvement is still not satisfactory for terrestrial applications. Therefore, new generation MoS$_x$ based hard and solid lubricant coatings has been developed by modifying coating structure and architecture in order to broaden the application range. Coating companies have already started commercial production of MoS$_x$ based coatings (MoST™ by Teer Coatings Ltd., UK and MolyGlide® by Guhring, Germany). In future, a widespread use of MoS$_x$ based coatings can be anticipated.

REFERENCES