Tribological Properties of Composite Multilayer Coating

Daniel Woldegebriel Gebretsadik¹, Jens Hardell^{1,*} Ihsan Efeoğlu², Braham Prakash¹

¹*Division of Machine Elements, Luleå University of Technology, Luleå SE-971 87 Sweden*

²*Atatürk University, Faculty of Engineering, Department of Mechanical Engineering, 25240-Erzurum, Turkey*

*jens.hardell@ltu.se

ABSTRACT

The use of surface coatings is emerging as one of the most important approaches in reducing friction and wear in various tribological applications. Even though single layer coatings have a wide range of applications, the performance of the single layer alone may not always be adequate to meet the desired tribological property requirements. Hence, coatings consisting of multi-layers to meet different property requirements in demanding applications are required. In this study, the tribological properties of a graded composite multilayer coating with a specific layer sequence of MoS₂:Ti/MoS₂:TiBN/TiBN/TiB₂/Ti deposited on tool steel substrate have been investigated at temperatures of 40°C and 400°C respectively.

The experimental results from the tests at 40°C have shown that the friction coefficient value ranges between 0.02 and 0.034. It was found that the deposition parameters influenced the friction and durability of the coatings. Higher substrate bias was found to result in higher friction and the coating deposited at high substrate bias and low N₂ flow showed the lowest durability. The friction coefficient and durability of the coatings were found to be highly dependent on temperature. At high temperature, the friction coefficient increases almost three fold and the durability decreases significantly.

Keywords: composite multilayer coating; high temperature; friction and wear

1. INTRODUCTION

The use of surface coatings is emerging as one of the most important approaches in reducing friction and wear in various tribological applications. For instance, self-lubricating coatings such as MoS₂-Ti are advantageous in reducing friction, especially in applications in which moving machine assemblies operate in vacuum and at elevated temperatures. Wear resistant coatings such as TiB₂ are important in improving the wear

resistance of a material. Even though single layer coatings have a wide range of applications, the performance of the single layer alone may not always be adequate to meet the desired tribological property requirements. Hence, coatings consisting of multi-layers to meet the requirements in demanding applications can be a possible solution. For example it has been previously reported that co-sputtering of MoS₂ with Ti has resulted in a dense coating with good friction and wear properties [1-3]. Fox et al. [1] have described the development of these MoS₂-Ti coatings and also compared the performance of

Table 1. Properties of the hardened tool steel substrate.

Material	C	Mn	Cr	Si	P	S	Ni	Mo	V	HV	Sa [μm]
Tool steel	0.31	0.9	1.35	0.6	max 100 ppm	max 40 ppm	0.7	0.8	0.145	426	0.052

different compositions of these coatings. They found that addition of a Ti interlayer improved adhesion of the coating to the substrate and incorporation of Ti in the MoS_2 coating reduced friction and enhanced the life of the coating. The objective of this study was to investigate the tribological properties of a composite multilayer coating with the specific layer sequence of $\text{MoS}_2\text{:Ti/MoS}_2\text{:TiBN/TiBN/TiB}_2\text{/Ti}$. The reason behind this particular sequence was to create a coating with a hard and wear resistant layer (TiB_2) and a combination of friction reducing layers (self-lubricating) in the form of $\text{MoS}_2\text{-Ti}$ and TiBN . Possible applications for such a coating could be forming tools where wear resistance and controlled friction is highly desired.

2. EXPERIMENTAL WORK

This section describes the materials, deposition method, tribological test and analysis techniques used in this study.

2.1. Materials and specimens

The substrate material was a pre-hardened hot forming tool steel which was ground and polished prior to deposition using a #1200 grit SiC abrasive paper followed by polishing using α -alumina with a particle size of $0.05\ \mu\text{m}$. Initial surface roughness, hardness and chemical composition of the substrate material are given in Table 1. The coating was deposited in the specific layer sequence $\text{MoS}_2\text{:Ti/MoS}_2\text{:TiBN/TiBN/TiB}_2\text{/Ti}$. The description of different layers of the coating is given in Figure 1.

Figure 1. Schematic showing the layer sequence of the multilayered composite coating.

Each layer in the multilayer coating provides certain properties. The $\text{MoS}_2\text{-Ti}$ and TiBN have a self-lubricating effect. TiB_2 is to improve wear resistance and the Ti interlayer is to improve the adhesion between the coating and the substrate. The coating was a graded composite multilayer coating in which there is no sharp interface between the layers. The grading of the coating avoids high interfacial stresses and significantly improves adhesion of the coating [4].

The substrate specimens were discs ($\varnothing 24\ \text{mm}$ and $7.9\ \text{mm}$ thick). An AISI 52100 grade bearing steel ball ($\varnothing 10\ \text{mm}$) was used as the counterbody in the tribological tests.

2.2. Deposition technique

The multilayer coating was deposited by a Closed-Field Unbalanced Magnetron Sputtering unit (CFUBMS) from Teer Ltd. This technique involves bombardment of the target by energetic ions in the plasma. The bombardment process results in sputtering of target atoms and the sputtered target atoms condense on the substrate. It makes use of magnetic fields parallel to the target so that the ionizing electron-atom collision occurs. It has high ionization efficiency and gives dense plasma in the target region hence it gives higher sputtering rate and higher deposition rate [4]. For deposition of multilayer coatings a multi-source magnetron sputtering is used to control the sequence of the layers. Figure 2 shows a schematic representation of a CFUBMS.

Figure 2. Schematic of the CFUBMS unit.

Table 2. Deposition parameters.

<i>Run No</i>	<i>Nitrogen flow (%)</i>	<i>Substrate</i>	
		<i>Biased dc (-V)</i>	<i>Pulse (kHz)</i>
1	3	50	50
2	3	100	100
3	3	150	150
4	5	50	100
5	5	100	150
6	5	150	50
7	7	50	150
8	7	100	50
9	7	150	100

For the deposition of the test specimens, one Ti, two TiB₂ and one MoS₂ target was used.

The Taguchi method with L9 array is used for deposition of coatings on the test specimens. It allows four parameters to be varied though three parameters were varied in this study. During the deposition of the coating, nitrogen flow (%), substrate bias (-V) and pulse (kHz) were the three parameters varied and the target current and working pressure (0.2 Pa) were kept constant for each run. The different coatings were designated as Run1, Run2... Run9. Table 2 shows the values for the deposition parameters used for each run and Table 3 shows the target currents.

Table 3. Target currents used for the different layers.

<i>Multilayer composite</i>	<i>Targets</i>			
	<i>TiB₂</i>	<i>Ti</i>	<i>TiB₂</i>	<i>MoS₂</i>
	<i>Current (A)</i>			
Ti	0.05	3	0.05	0.05
TiB ₂	0.05	0.05	1.5	0.05
Ti:BN	2	1	2	0.05
Ti:BN:MoS ₂	1.5	1	1.5	0.5
MoS ₂ Ti	0.05	0.5	0.05	1

2.3. Characterisation techniques

The adhesion of the coating was analysed by CSM Revetest scratch adhesion tester and its composition and structure were analysed by XRD and SEM/EDS techniques. The SEM/EDS technique was also used to analyse the specimens after the tribological tests.

The tribological properties were studied using an Optimol SRV high-temperature reciprocating

friction and wear tester. This machine utilises an electro-magnetic drive to oscillate an upper specimen (bearing steel ball) against a lower stationary specimen (coated disc) under normal load which is applied by means of a spring deflection mechanism. The lower specimen block incorporates a cartridge heater which enables tests to be performed at temperatures up to 900°C. A computer control system enables accurate control of the applied load, temperature, stroke length and frequency of the oscillatory movement during the tests. The test parameters are given in Table 4.

Table 4. Test parameters utilised in the tribological tests.

<i>Test parameter</i>	<i>Value</i>
Load	50 N ($P_{\text{cont}} = 1.7 \text{ GPa}$)
Load ramp	0 – 100 – 0 N ($P_{\text{cont @ 100N}} = 2.2 \text{ GPa}$)
Stroke length	1 mm
Frequency	50 Hz
Temperature	40°C and 400°C
Duration	10 min
Relative humidity	25-30%

2.4. Test procedure

All test specimens and specimen holders were thoroughly cleaned in petroleum spirit in an ultra-sonic cleaner, thereafter rinsed with ethanol and dried in air prior to tribological tests.

After mounting the specimens in their respective holders the lower disc specimens were heated to the desired temperature after which the tribological tests were performed.

3. RESULTS AND DISCUSSION

The obtained results from this study are presented and discussed in this section.

3.1. Characteristics of sputtered coating

The adhesion of the coating was evaluated by using a CSM Revetest scratch adhesion tester with a Rockwell-C indenter having a 200 μm radius. The composition of the coating was found to affect the adhesion and Figure 3 shows the load at which complete removal of the coating

occurred for the different compositions. As seen, Run 3 shows the poorest adhesion. All coating compositions showed similar failure mechanisms.

Figure 3. Average failure load from scratch adhesion tests.

The structure of the coating was analysed by XRD and the results are shown in Figure 4. The XRD pattern of the coating shows peaks around $2\theta = 12.0^\circ$ which belongs to the MoS_2 (002). MoS_2 (002) has its basal plane orientation parallel to the substrate surface which is preferable in tribological applications since it provides low friction [5]. Less pronounced peaks were found for Run 6 and 7. Peaks responsible for h-BN appear around $2\theta = 37.0^\circ$ and a prominent peak appears for Run 3. Hexagonal BN is a soft phase with a graphite type structure and has low friction coefficient. The lamellar structure allows easy deformation and prevents severe wear failure of the TiBN layer [6].

TiB_xN_y (100) peak appears at about $2\theta = 34.7^\circ$ in the XRD spectra and the sharpest peak is found for Run 3. For TiB_xN_y , B atoms are incorporated into the TiN lattice [7]. The possible peak for TiB_2 (100) is close to the TiB_xN_y . Since the TiB_2 deposition time was very short, there is a possibility of diffusion of nitrogen into the TiB_2 phase during the growth of TiBN base structure, the peaks of TiB_2 and TiB_xN_y may overlap.

The surface hardness of the tool steel discs increased after deposition of the multilayer coating. Test specimens from Run 2 and Run 7 exhibited a hardness of 764 and 746 $\text{HV}_{0.01}$

respectively. The lowest hardness was found for Run 6 (578 $\text{HV}_{0.01}$). The hardness of the coating is usually affected by the nature and proportion of the phases present in each layer and the nature of the phases in each layer could be affected by different factors such as the amount of nitrogen which determines the proportion of phases in the TiBN and the soft h-BN or the amount of Ti in the MoS_2 -Ti.

The hardness of the coating from different runs was also found to be dependent on the temperature to which the specimens were exposed, Figure 5. The hardness values are for the complete system (coating and tool steel substrate).

Figure 5. Hardness of the different coating compositions before and after exposure to 400°C.

The hardness was measured for all specimens before and after exposure to the two test temperatures. Specimens which were exposed to 400 °C for approximately 20 min were found to have lower hardness compared with the hardness for specimens at room temperature. The reason for the decrease in hardness could be related to the appearance of metallic Ti phase. Published research has shown that there is a decrease in hardness of a TiBN layer due to appearance of metallic Ti phase when it is annealed at 400 °C for 30 min [5]. Moreover, there is also the possibility of diffusion of N at higher temperature which may alter the hard TiB_2 phase into TiBN, which is less hard than the TiB_2 .

Figure 4. XRD spectra of the composite multilayer coatings.

3.2. Friction properties

The friction properties of the graded multilayer coatings were studied under various conditions. The coefficient of friction was found to be dependent on time. At the very beginning of the test the friction coefficient was as high as 0.07 but as the test progressed the coefficient of friction decreased and stabilised. The increase in friction coefficient before steady state is due to the energy needed in re-orienting the crystallites of MoS₂ on the top surface [5]. The coefficient of friction vs. test duration is shown in Figure 6. Friction coefficient values between 0.02 and 0.034 were obtained. Figure 7 shows the average steady state friction coefficient values for all nine runs. These were obtained as the average value of friction of two tests after the initial running-in period, i.e. steady state friction.

Figure 6. Coefficient of friction as a function of time for all nine different coating compositions at room temperature.

Figure 7. Average steady state friction for the different coating compositions at 40°C.

The lowest average coefficients of friction were obtained for Runs 2 and 4. Run 2 presented a very rapid running-in whereas Run 4 had a high initial friction which was gradually reduced and ended up at a very low level.

The coatings deposited at higher substrate bias have shown higher friction coefficients under constant load conditions. Considering the specimens prepared at the same nitrogen flow (i.e. Run 1, 2, 3 or Run 4, 5, 6 or Run 7, 8, 9), the friction coefficients are found to be comparably higher for coatings prepared at higher substrate bias (-150 V) than those prepared at lower substrate bias (-50 and -100 V). Since the most important layer for the low friction is the top MoS₂-Ti layer, the dependence of the friction coefficient could be explained by noting the effect of substrate bias on the S/Mo ratio. Bülbul et al. have shown that as the substrate bias increases the S/Mo ratio decreases. This is due to the fact that an increased ion bombardment from the plasma facilitates resputtering of S by increasing atom mobility [8]. Furthermore, the morphology of a coating is known to be dependent on the temperature of the substrate during deposition which is directly affected by the substrate bias. The increase in substrate bias increases the homologous temperature (T/T_m) where T is the substrate temperature and T_m is the melting temperature of the coating and favours formation of fully dense grain structures [4]. There is no obvious influence of the pulse on the friction coefficient of the coating.

3.3. Load dependence of friction coefficient

The friction coefficient was found to decrease when the normal force increases and lowest friction coefficients were found at a load of 100 N as can be clearly seen in Figure 8. For Run 3 the coating fails at lower load levels. At lower loads the surface contact is not complete and slip does not take place between fully conformal lamellae but as the load increases the surface contact increases and slip takes place between fully conformal lamellae so that the friction coefficient decreases [5]. A minimum friction coefficient value of 0.019 was found for all coatings except for Run3, Run5 and Run7. The minimum friction coefficient values for the different coatings at 100 N are given in Table 5.

3.4. Friction characteristics at high temperature

The frictional behaviour of the coating has also been found to be dependent on temperature, Figure 9. One feature of the friction coefficient curve is that there is no steady range. The friction and wear properties of the coatings at room temperature and at 400°C respectively show two basic differences. First, the friction coefficient increases significantly by three to four times when the temperature is increased from 40°C to 400°C. Secondly, the life-time of the coating decreases significantly at 400°C. These differences arise mainly from the structural changes induced by the increase in temperature. At high temperature, there is oxidation of the top layer resulting in the formation of abrasive oxides such as molybdenum dioxide which is abrasive in nature [5]. As a result, the proportion of the MoS₂ on the surface decreases which consequently increases the friction. The increase in friction and the presences of abrasive oxidation products at high temperature lead to rapid wear and result in shorter life time of the coating.

3.5. Durability of coating

Many factors such as coating thickness, adhesion of the coating and presence of defects in the coating affect the durability of the coating. The value of the substrate bias used during the deposition of the coating usually affects the overall performance of the coating. Previous studies have shown that even though high negative substrate bias increases the energy of the bombarding ions, it leads to defects and increased residual stress in the film [4]. It is likely because of this reason, the coating from Run 3, which was deposited at a substrate bias of -150 V, failed at an early stage of the test. In contrast, for Run 1 and Run 4, the multilayer coatings deposited at lower substrate bias (-50 V) have shown better durability. At room temperature, the longest durability was recorded for Run 1 (1933 s) and the lowest durability was for Run 3 (111 s). For the coatings deposited at 3

Figure 8. Frictional behaviour during load ramp.

and 5% N_2 flow, the durability deteriorated as the bias voltage increased. But the coatings deposited at a 7% N_2 flow have shown an opposite behaviour. In Figure 10, the durability of the multilayer coatings at 40°C and 400°C respectively has been compared. Failure of the coating was considered to occur when friction exceeded 0.2. As mentioned earlier, the durability of the coating at lower temperature is superior compared to that at high temperature. The longest durability for the coatings at 400°C was found to be 141 s which was for Run 1. The increase in temperature is accompanied by chemical and structural changes which in turn affect the friction and wear properties significantly. At high temperature, there is formation of abrasive oxidation products on the top layer which will contribute to the increase in friction and wear of the coating. The durability of the coating is dependent on the life time of the self-lubricating layer. The underlying layer is the hard and brittle

TiB_2 . More importantly, the XRD pattern shows the presence of a (100) TiB_2 which has inferior tribological properties than that of (001) TiB_2 . Hence, once the top layer, with lubricating property, is removed the lower layer is susceptible to rapid removal due to wear.

Figure 10. Durability at 40°C and 400°C for the different coating compositions.

Figure 9. Coefficient of friction as a function of time for all nine different coating compositions at 400°C.

Table 5 Minimum friction obtained during load ramp tests for the different coating compositions.

Run No	Run1	Run2	Run3	Run4	Run5	Run6	Run7	Run8	Run9
Min. friction at 100 N	0.019	0.019	0.022	0.019	0.024	0.019	0.023	0.019	0.019

4. CONCLUSIONS

Tribological studies have been carried out on nine compositions of a graded multilayer coating with a layer sequence of MoS₂-Ti/MoS₂:TiBN/TiBN/TiB₂/Ti. The salient conclusions from these studies are as follows:

- The deposition parameters of the coating, as well as the test parameters such as contact pressure and temperature during tribological tests have been found to influence the tribological behaviour.
- High substrate bias and low nitrogen flow during deposition of the coating resulted in the lowest durability.
- Increased substrate bias (-150 V) resulted in increased friction of the coating.
- No obvious influence of pulse frequency has been found.
- Friction increased by 3 – 4 times as the temperature was increased from 40°C to 400°C.

5. ACKNOWLEDGEMENTS

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