MASTER'S THESIS

Tribological Properties of Composite Multilayer Coatings

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Preface

This thesis is written for the partial fulfillment of my MSc studies in materials science and engineering at the division of Engineering Materials under the AMASE programme which is a joint European programme.

I would like to express my deepest gratitude to my supervisor Professor Braham Prakash at the division of Machine Elements for his fruitful advice and friendly approach throughout my project work. I am also very grateful to my co-supervisor Mr. Jens Hardell for his invaluable support, encouragement and continuous support in my research. I am thankful to Mr. Lennart Wallström for his support throughout my stay at LTU. I am also thankful to Professor Ihsan Efeoglu for his support in preparation of test specimens from Atatürk University, Turkey. I would like to express my appreciation to my colleagues for their helpful discussion during my research.

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Daniel W. Gebretsadik
Luleå, July 2009

</div>

Abstract

Deposition of surface coatings is one of the important approaches in improving the friction and wear properties of surfaces. For instance, self-lubricating coatings such as MoS_2-Ti are advantageous in reducing friction. These self-lubricating coatings outperform liquid lubricants in several applications such as vaccum and high temperatures. Wear resistant coatings such as TiB_2 are important in reducing wear rate of a material. Even though single layer coatings have a wide range of application their tribological performance may not be sufficient. Hence, coatings that consist of different properties can be prepared as multilayer coatings. These coatings can have different sequence of layers depending on the intended application of the material.

In this study, the tribological properties of a graded composite multilayer coating with specific sequence of MoS_2:Ti/MoS_2:TiBN/TiBN/TiB_2/Ti deposited on tool steel substrate was investigated. The coating was deposited by a Closed-Field Unbalanced Magnetron Sputtering technique. The friction and wear properties of the coating were studied at 40 °C and 400 °C with the help of a high-temperature reciprocating friction and wear tester and wear scars were also analyzed with Scanning Electron Microscope with incorporated Electron Dispersive Spectroscopy. The hardness of the coating was also studied with the help of micro-hardness tester.

The experimental results for the tests done at 40 ^{0}C have shown that the friction coefficient value ranges between 0.02 and 0.034. It has been found that the friction coefficient values were different depending on the deposition parameters used and the coatings deposited at higher substrate bias were found to result in higher friction. The durability of the coating was also found to be dependent on the deposition parameters and the specimen deposited at -150 V substrate bias and 3 % N_2 flow has 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 by three folds and the durability decreases significantly. The SEM images of the wear scars have shown that the wear is an adhesive wear type. The hardness of the tool steel surface was also improved with the deposition of the multilayer coating.

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1. Introduction

1.1 Tribology

Most of materials in Industrial application and day to day life involve activities that cause friction and wear. Formally, tribology is defined as the science and technology of interacting surfaces in relative motion and of related subjects and practices. It includes the field of friction, lubrication and wear. Many industries suffered a great loss of manufacturing process due to collapse of manufacturing machines due to wear and fail of lubrication. Friction is main cause of wear and energy dissipation. Improving friction can make substantial savings. It is obvious that enormous amounts of the world's resources are used to overcome friction in one form or another. Lubrication is an effective means of controlling wear and reducing friction. Hence, for the survival of a machine wear and friction must be decreased and/or controlled carefully [1].

1.2 Techniques to improve friction and wear properties of a surface

The tribological properties of a material such as friction and wear can be improved with different techniques such as making use of selected surface coatings. Surface coatings can be of different types. One of the surface coatings types that improve the friction property of a surface are self-lubricating coatings.

A solid lubricant (self-lubricating) is generally defined as a material that gives lubrication under essentially dry conditions, to two surfaces in contact moving relative to each another. The usage of self-lubricating surface coatings has enormous advantages compared with the traditional fluid lubricants such as oils. For instance, liquid lubricants have limitations that hinder their use in certain conditions. They can not be used in certain applications because of the difficulty in applying them, sealing problems, weight or other factors. At high temperatures, liquid lubricants decompose or oxidize. At higher temperature liquid lubricants becomes less viscous and their performance deteriorate. Under corrosive environments liquid lubricants are decomposed or contaminated which is not the case in most solid lubricants. In some cases they could also be poisonous. Hence, under different conditions such as high temperature, high vacuum and corrosive conditions self-lubricating coatings are chosen. The most known solid lubricants are MoS_2 and graphite [2].

1.3 Self-lubricating and wear resistant Surface coatings

There are different surface coatings with distinct properties that can be used to improve the friction and wear behavior of a surface. These coatings can be deposited on the surface of a substrate with different deposition techniques such as CVD and PVD. In the following pages different types of surface coatings that are constituents of the multilayer coating in the specimen of interest are discussed.

1.3.1 MoS$_2$-Ti Coating

MoS$_2$ is one of the most known surface coating which has a self-lubricating property with an improved friction and wear resistance. Many research findings have been published on the MoS$_2$ surface coating and its tribological properties. Investigation of MoS$_2$ based coating gives a very low friction coefficient which arises from the 'easy shear' planes of the lamellar structure, Figure 1. Actually, the coefficient of friction is dependent on the surrounding environment and the applied load [3, 4]. More over its tribological properties are also affected by the pre-treatment of the substrate such as surface characteristics, mechanical properties and physical-chemical properties of the substrate [5].
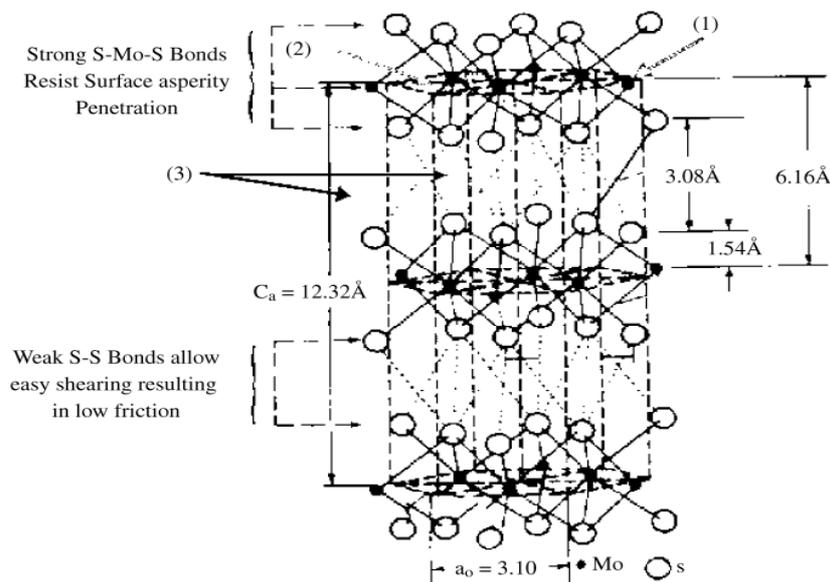
Figure 1. MoS$_2$ structure responsible for low friction [6]

Figure 2 shows the difference in the amount of wear fragments on uncoated steel and MoS_2 coated steel.
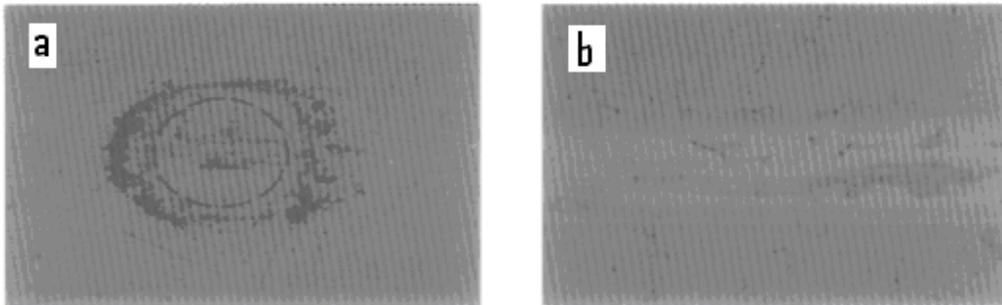
Figure 2. Optical images of wear scars on (a) the steel pin (b) the MoS_2 coated steel plane [3].

The tribological properties of MoS_2 can be improved by co-deposition of titanium. Investigations on the properties MoS_2-Ti coatings have been made in many studies. Some published research findings show the effect of addition of the Ti on the mechanical properties of the coating. For instance, the properties of the MoS_2 coatings deposited by magnetron sputtering on tool steel is found to be improved by co-deposition of small amount of Ti metal. The results show that the tribological properties of MoS_2Ti coating becomes much more wear resistant and higher load bearing properties compared with pure MoS_2 coating. In other studies it has been shown that MoS_2-Ti has good adhesion and lower friction coefficient in humid air than those of pure MoS_2 coatings [7].

The amount of Ti in MoS_2-Ti coating has an influence on the tribological properties. The structure of the coating has been found to be dependent on the amount of Ti. For instance, pure MoS_2 coating is amorphous but with a Ti concentration of 15.3% and 19.5% gives a composite microstructure consisting of crystalline MoS_2 phase and amorphous MoS_2. The degree of crystallization of the MoS_2Ti coatings increases with titanium content. Figure 3 shows X-ray diffraction patterns of MoS_2Ti coatings with different titanium content.
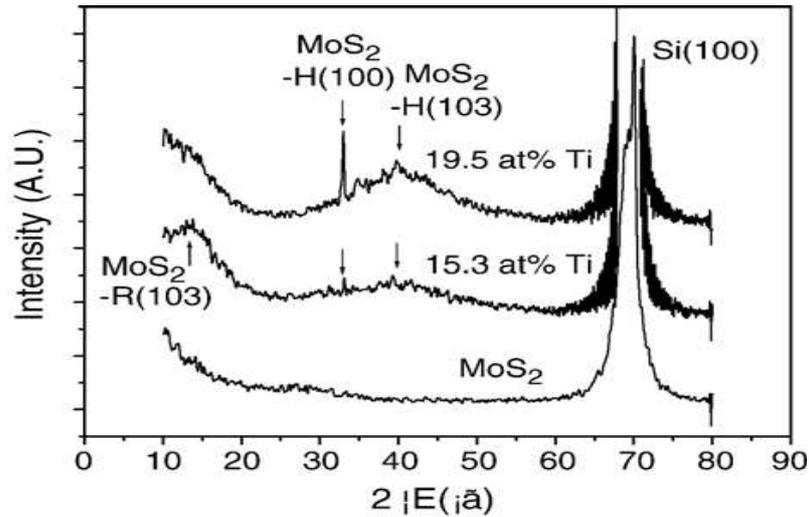
Figure 3. X-ray diffraction patterns of MoS$_2$Ti coatings with different titanium content [7].

The MoS$_2$-Ti coating exhibits high hardness. Figure 4 shows the effect of Ti content on the hardness and Young's modulus of the MoS$_2$Ti coating.
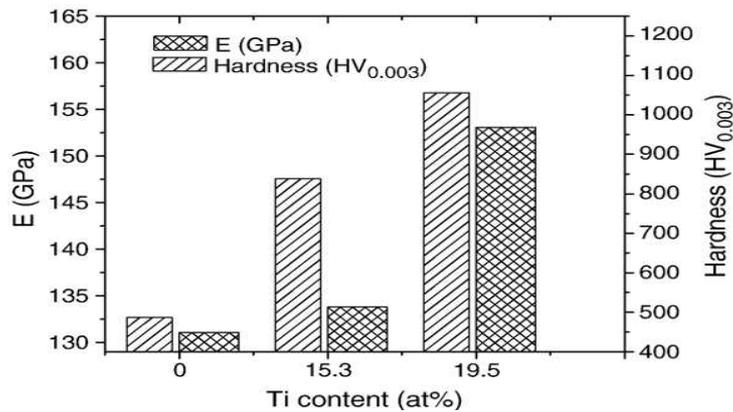
Figure 4. Hardness and elastic modulus of MoS$_2$Ti coatings with different Ti content [7]

In others studies on the hardness of the MoS$_2$-Ti deposited by magnetron sputtering ion plating system indicated that it has a hardness between 1000 and 2000 VHN and this hardness were not due to a superlattice or multilayer formation [8]. The evidence indicated that the Ti is present within the MoS$_2$ lattice, Figure 5, and the responsible reason for the hardness is assumed to be the strain produced within the lattice. Hence, MoS$_2$-Ti coatings posses improved tribological performance which makes it chosen for many industrial applications [9].
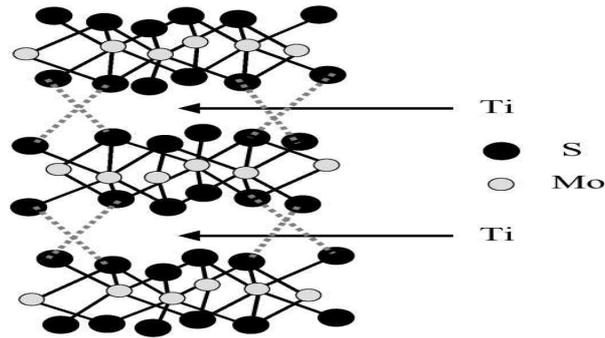
Figure 5. The probable place of the titanium atoms in the MoS$_2$Ti structure [8].

1.3.2. TiBN coatings

TiBN coating is one of the important coatings with attractive tribological properties. Many investigations have been made so far on TiBN coating. It is consisting of three phases, namely, TiB$_2$, TiN and BN and their proportion is dependent on the amount of the constituent elements used during deposition of the coating. Hence, the properties of the coating are affected by the amount Ti, B, and N.

For instance, Garcia-Gonzalez et al studied different samples of TiBN coatings deposited by dc reactive sputtering technique. The results show that the TiBN coating consisted of three phases, TiB$_2$, TiN and BN. As the flux of nitrogen increase the proportion of the two crystalline BN and TiN phases increases, Figure 6. TiB$_2$ is found to be amorphous. The variation in the hardness values of the samples is due to changes in structural and chemical compositions as the nitrogen flux changed [10].
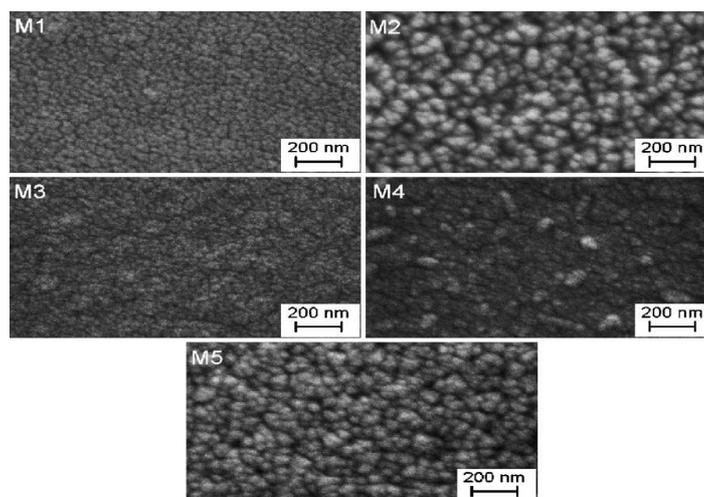
Figure 6. SEM image showing effect of N$_2$ flux on the structure of TiBN coatings [10].

The deformation mechanism is dependent on the nature of the TiBN coatings. For nanocomposite coatings with grain size of 10 nm and less the deformation mechanism is governed by the process that occurs around a grain boundary. Unlike conventional materials, dislocations do not exist in nanocomposite materials since the grain boundaries do not allow the formation of dislocations. The deformation mechanism is governed by sliding of grain boundaries [11].

The amount of boron was also found to have an impact on the properties of the TiBN coatings [12]. Figure 7 shows how the hardness of TiBN coating varies with boron content. This change is due to the grain refinement and increased phase fraction of TiB_2.
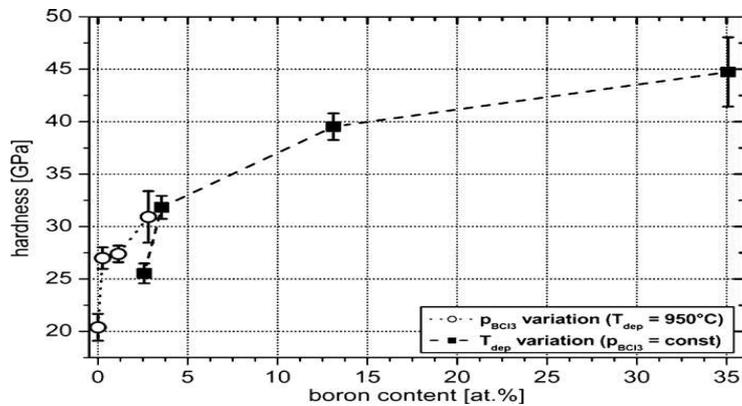
Figure 7. Effect of boron content on hardness of TiBN coatings [13].

The boron content of the TiBN coating was also seen to affect the friction coefficient. For the coating with 3.5 at.% boron the value of the friction coefficient was 1.1. This is due to high surface roughness often combined with a coarse, loosely-bonded surface structure hence wear debris during sliding can be formed easily so that the friction coefficient increases. When the boron content increases to 13.1 at.% B, a friction coefficient of 0.93 was obtained. For 35.1 at% boron content friction was found to be 0.47 and 0.26 after 47,730 and 106,000 cycles, respectively [13].

1.3.3 TiB$_2$ Coating

TiB_2 is one of the common coatings used to improve performance of a tool. Published literatures on the TiB_2 coating have shown that it is a super-hard coating and is brittle in nature. For instance, a stress free TiB_2 coating prepared by magnetron sputtering has exhibited a hardness of 50 GPa and a Young's modulus value of 600 GPa [14]. In another study of the TiB_2 coating

prepared on cemented carbide substrates using direct current magnetron sputtering, hardness and Young's modulus was found to be very high and it has very high abrasive wear resistance [15]. The way the TiB_2 coating fails depends on the substrate bias used during deposition of the coating as sown in Figure 8.
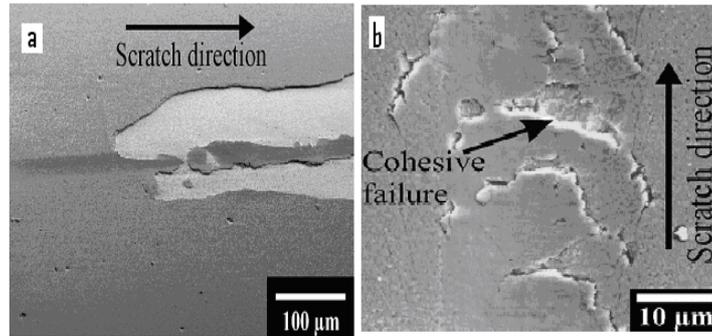
Figure 8. SEM images showing typical TiB_2 coating failure mode for substrate bias of -110V and 0V, respectively, in the scratch test: (a) an adhesive failure and (b) a cohesive failure [15]

1.3.4 Ti interlayer Coating

It has an HCP crystal structure and an elasticity modulus of 107 GPa. It has a good corrosion resistance and has the highest strength-to-weight ratio. The metal forms passive and protective oxide layer. Usually in multilayer coatings titanium is used as interlayer to improve the adhesion of the coating to the substrate.

1.4 Multilayer coatings

Even though single layer coatings have a wide range of application their tribological performance may not be sufficient. Multilayer coatings show an improved tribological properties compared with single layers. Multilayers can be prepared by sequentially depositing the individual layers with thicknesses up to a few tenth of a micrometer using, for example, multisource evaporation and sputtering techniques. This second generation of tribological coatings is generally constituted by a combination of basic materials like MoS_2-Ti, TiBN, TiB_2 and so on. Structural characterizations of multilayer coatings are carried out by viewing the film in cross-section in order to observe the individual layers [16, 17].

Different studies have shown that multilayer coatings have advantages over singlelayer coatings and can combine the attractive properties of different materials in a single protective layer. The introduction of a number of interfaces parallel to the substrate surface can deflect

cracks or provide barriers to dislocation motion, increasing the toughness and hardness of the coating [18]. The fracture toughness and wear resistance are larger when the number of the layers increases [19].

The main reason for using multilayer coatings is not only for improving the wear but also other specific properties. For instance the different layers could have different purposes. One of the interlayer can increase toughness and resistance to corrosion and oxidation, while the top layer can provide low friction and wear. The other advantages of combining several structures and compositions within one coating include achievement of various individual physical properties, such as enhancing adhesion, controlling the residual stress within the coatings, preventing crack formation under severe operating conditions and increasing hardness and toughness by allowing layers or phases to slide over each other when they deflect under load [20].

There is very little published literature on multilayer coatings made of $MoS_2Ti/TiBN/TiB_2/Ti$. But there are some literatures which deal with multilayer coatings of different components. For instance, multilayer coating of TiN and a thin MoS_2 film was proven to have superior tribological properties, especially in metal cutting and forming operations as compared to TiN or MoS_2 alone [20]. Investigation on a single layer and multilayer coating of TiN and TiN/Ti/TiNO has revealed that the tribological properties of the multilayer is more attractive than the single layer. The resistance to micro-abrasive wear in the multilayer coatings is 1.9 times higher than that for monolayer coatings and the friction coefficient for both types of coatings were the same [21]. Y.L Su has shown that TiN/TiCN/TiN has a better wear resistance than the binary-layer TiN/TiCN and the single-layer TiN coating. This enhanced resistance is attributed to the thermal and fatigue cracks reduction for multilayer coatings. The primary wear mechanism, for binary-layer TiN/TiCN coated and multilayer TiN/TiCN/TiN coating, is adhesive wear. However, for a single-layer TiN coating thermal and fatigue cracks accelerate the wear process. These results confirm that multilayer coatings provide improved tribological properties compared with a monolayer coating [22].

Hence, from the results of different studies made on multilayer coatings it is possible to predict that the $MoS_2Ti/TiBN/TiB_2/Ti$ multilayer coating will have improved tribological properties than the single layer coatings alone.

2. Objectives

The main objective of this project is to study the tribological properties of the graded $MoS_2:Ti/MoS_2:TiBN/TiBN/TiB_2/Ti$ multilayer coating deposited by Closed-Field Unbalanced Magnetron Sputtering on a tool steel substrate.

Specific objectives

- To measure the friction coefficient value for the multilayer coating deposited under different deposition parameters.
- To determine the dependence of the friction coefficient on the applied load.
- To determine the durability of the multilayer coatings.
- To study the performance of the coating at high temperature.
- To determine the wear mechanism for the multilayer coating.

3. Experimental work

3.1 Material and specimens

The test specimens analyzed were graded multilayer coatings consisting of MoS_2-Ti, TiBN, TiB_2, and Ti. The coating was deposited on tool steel substrate. Each of the layers in the multilayer coating has their own purpose. The MoS_2-Ti and TiBN have a self-lubricating effect. TiB_2 is to improve wear property and the interlayer Ti 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 top layer was made of the MoS_2Ti. Figure 9 shows the exact sequence of the coating.
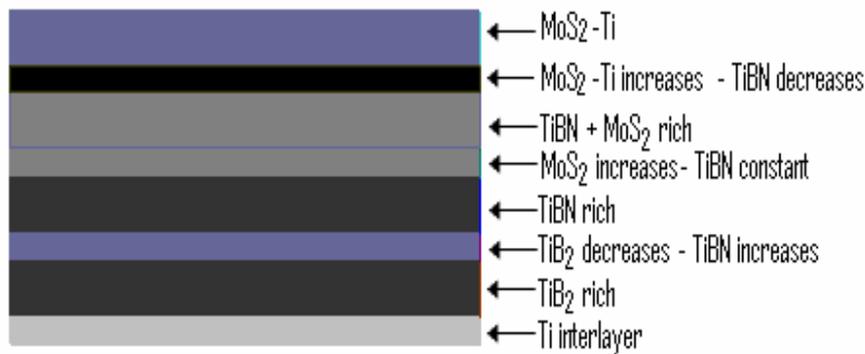
Figure 9 Schematic representation of the multilayer coating.

3.2 Experimental technique

3.2.1 Deposition Technique

The multilayer coating was deposited by Closed-Field Unbalanced Magnetron Sputtering (CFUBMS). This technique involves bombardment of the target by energetic ions in the plasma. The bombardment process causes the 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 [23]. For

deposition of multilayer coatings a multi-source magnetron sputtering is used to control the sequence of the layers. Figure 10 shows a schematic representation of a CFUBMS. For the deposition of the test specimens, one Ti, two TiB_2 and one MoS_2 targets was used.
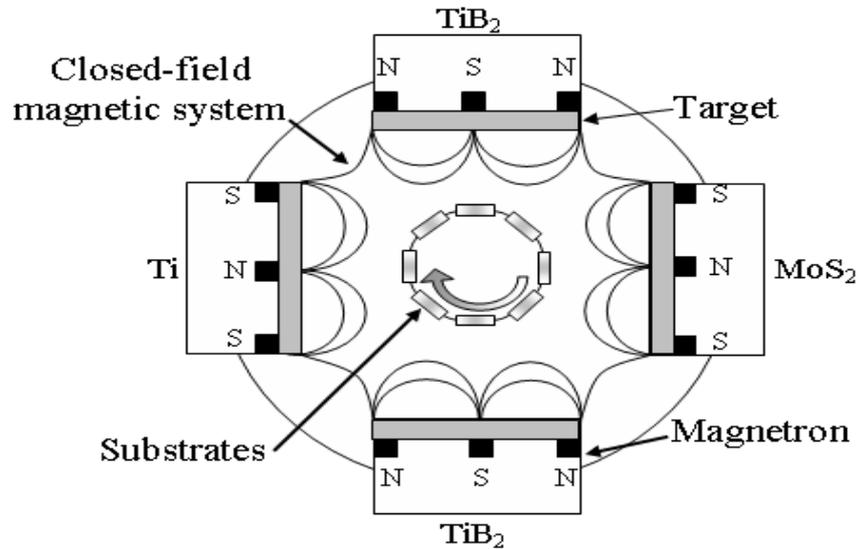
Figure 10. Schematic representation of the CFUBMS

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 test specimens were designated as Run1, Run2... Run9. Table 1 shows the values for the deposition parameters used for each run.

<div align="center">Table 1. Values of deposition parameters used.</div>

Run No	Nitrogen flow (%)	Substrate			Targets*			
		Biased dc(-V)	Pulse (KHz)		TiB_2	Ti	TiB_2	MoS_2
				Multilayer composite		Current (A)		
1	3	50	50	Ti	0.05	3	0.05	0.05
2	3	100	100					
3	3	150	150	TiB_2	0.05	0.05	1.5	0.05
4	5	50	100					
5	5	100	150	TiBN	2	1	2	0.05
6	5	150	50					
7	7	50	150	$TiBN:MoS_2$	1.5	1	1.5	0.5
8	7	100	50					
9	7	150	100	MoS_2Ti	0.05	0.5	0.05	1

3.2.2 Characterization Techniques

The SRV (Schwingung Reibung Verschleiβ) reciprocating friction and wear tester was used throughout this investigation. In the test chamber of this machine the upper specimen slides back and forth against the test specimen mounted on the lower specimen holder. The lower specimen can be heated with the help of a heating cartridge to the desired temperature. The machine is interfaced with computer software and allows setting the test parameters such as temperature, load, stroke length, frequency and test duration. Figure 11 shows a schematic representation of the SRV reciprocating friction and wear tester.

Scanning Electron Microscope (SEM) incorporated with electron dispersive spectroscopy (EDS) was used to obtain images of the wear scars and to perform the elemental analysis on the surface and wear scars. It is a type of electron microscope which helps in imaging the samples surface by scanning it with a high energy beam of electrons. It is advantageous due to its large depth of focus and variable magnification. The hardness of the coating is one of the basic mechanical properties to be studied. The hardness of the coating was studied with a micro-hardness tester.
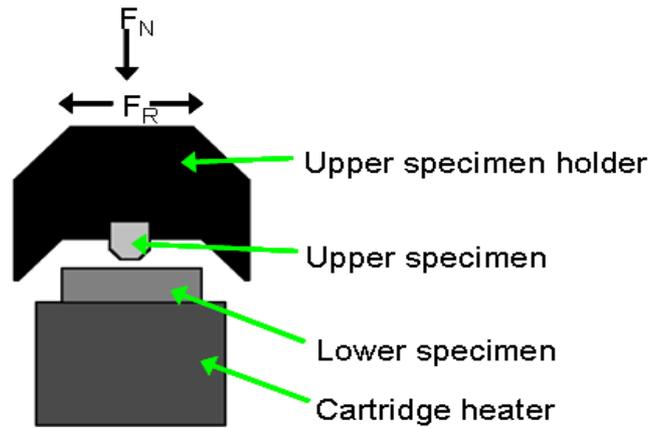
Figure 11 Schematic representation of SRV reciprocating friction and wear tester

3.3 Test parameters

The friction property was studied by varying different parameters and the upper specimen used throughout this investigation was steel ball of 10 mm diameter. To study the dependence of friction coefficient on the load, a load ramp test was done by varying the normal force from 0 to 100 N during the test duration keeping all other parameters constant. The durability of the coating was studied by setting a cut-off friction coefficient value of 0.2 and running the test until the coating failed while the other parameters kept constant. The performance of the coating was also studied at 400 ^{0}C. Table 2 and 3 show the test parameters used in this study.

Table 2. Test parameters used in the friction test.

Test Parameters	Values
Load ramp	50 N
Temperatures	40, 400 ^{0}C
Stroke length	1mm
Frequency	50 Hz
Duration	10 min

Table 3. Test parameters used in the load ramp test.

Test Parameters	Values
Load ramp	20, 40, 60, 80, 100, 80, 60, 40, 20 N
Temperatures	40 ^{0}C
Stroke length	1mm
Frequency	50 Hz
Duration	10 min

3.4 Test procedures

All tests were made in a manner that increases the accuracy and precision of the experimental result. The test chamber was cleaned at higher temperature to avoid a contamination of the specimens and specimen holders. The specimens and the specimen holders were also cleaned using an ultrasonic cleaner in petroleum spirit and the specimens were rinsed with ethanol and dried in air. The cleaning was made for every test specimen before and after the test. The test was made by mounting the test specimen on the lower specimen holder and the upper specimen (steel ball) in the upper specimen holder and heating the test specimen until the set temperature value was achieved. After the specimen was heated up to the desired temperature the test was done for duration of 10 min.

4. Results and discussion

4.1 Characteristics of sputtered coating

The coatings were graded multilayer coating in which there are no sharp interfaces. Figure 12 shows a cross-section of the graded multilayer coating. The grading of the composition avoids high interfacial stresses and significantly improves adhesion of the coating [23].
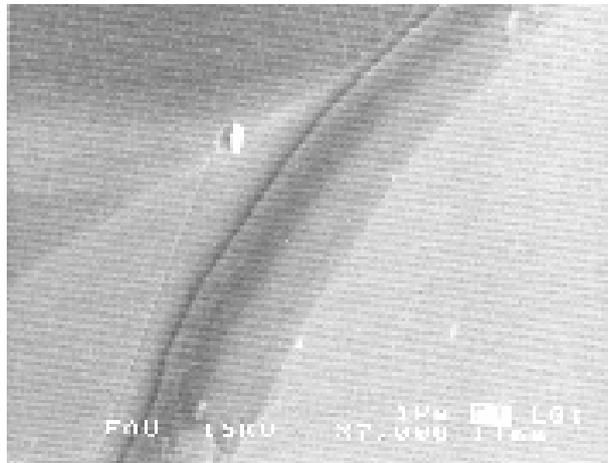

Figure 12. SEM image of the graded multilayer coating deposited by CFUBMS.

The XRD pattern of the coating in Figure 13 shows peaks around $2\Theta=12.0$ which belongs to the MoS_2 (002). MoS_2 (002) is with basal plane orientation parallel to the substrate surface which makes it preferably chosen in tribological applications [24]. Less pronounced peaks were found for Run 6 and 7. Peaks responsible for hexagonal BN appears around $2\Theta=37.0$ and pronounced peaks appear 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 [25].

$TiB_xN_y(100)$ peak appears at about $2\Theta=34.7$ in the XRD spectrum and the sharpest peak belongs to Run 3. For TiBxNy B atom is incorporated into the TiN lattice [26]. The possible peak for TiB_2 (100) is near to the TiB_xN_y. Since the TiB_2 deposition time was very short and it is possible that nitrogen has diffused to TiB_2 phase while the TiBN base structure was growing.
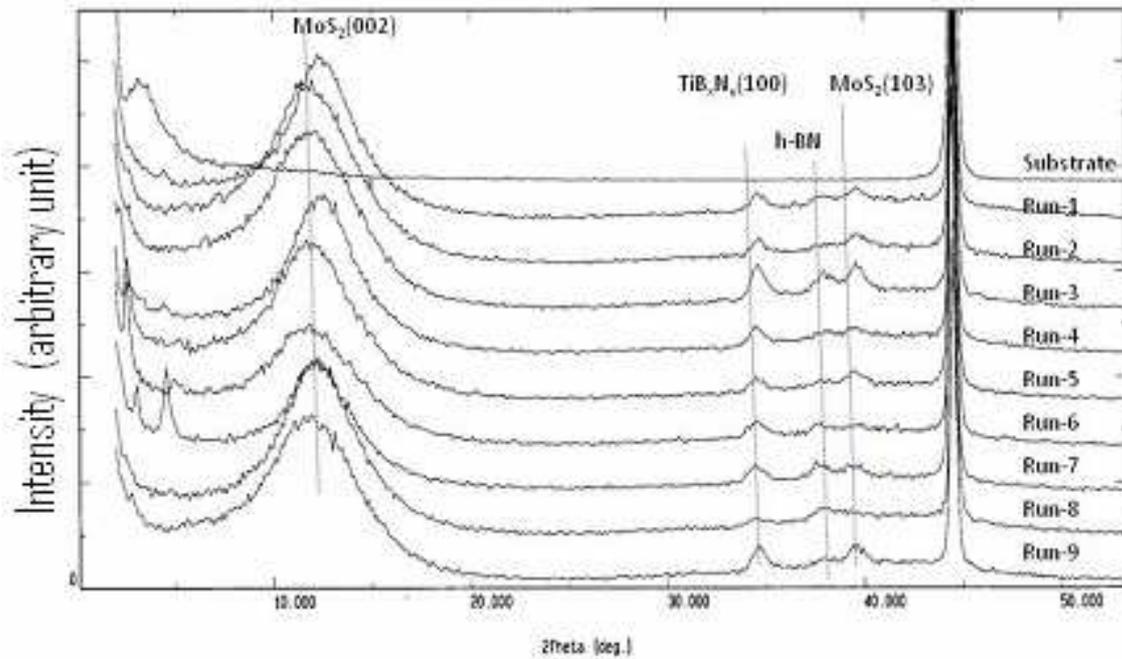
Figure 13. XRD pattern of the graded multilayer coatings.

4.2 Friction properties

The friction properties of the graded multilayer coating 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 went on the coefficient of friction decreases and becomes steady. The increase in friction coefficient before the steady range is due to the energy needed in re-orienting the crystallites of MoS_2 on the top surface [24]. The coefficient of friction vs test duration is shown in Figure 14. For comparison purpose the coefficient of friction for the pure tool steel substrate is also shown.

Figure 14. Coefficient of friction for tool steel substrate at 40 and 400 °C and coatings at 40 °C.

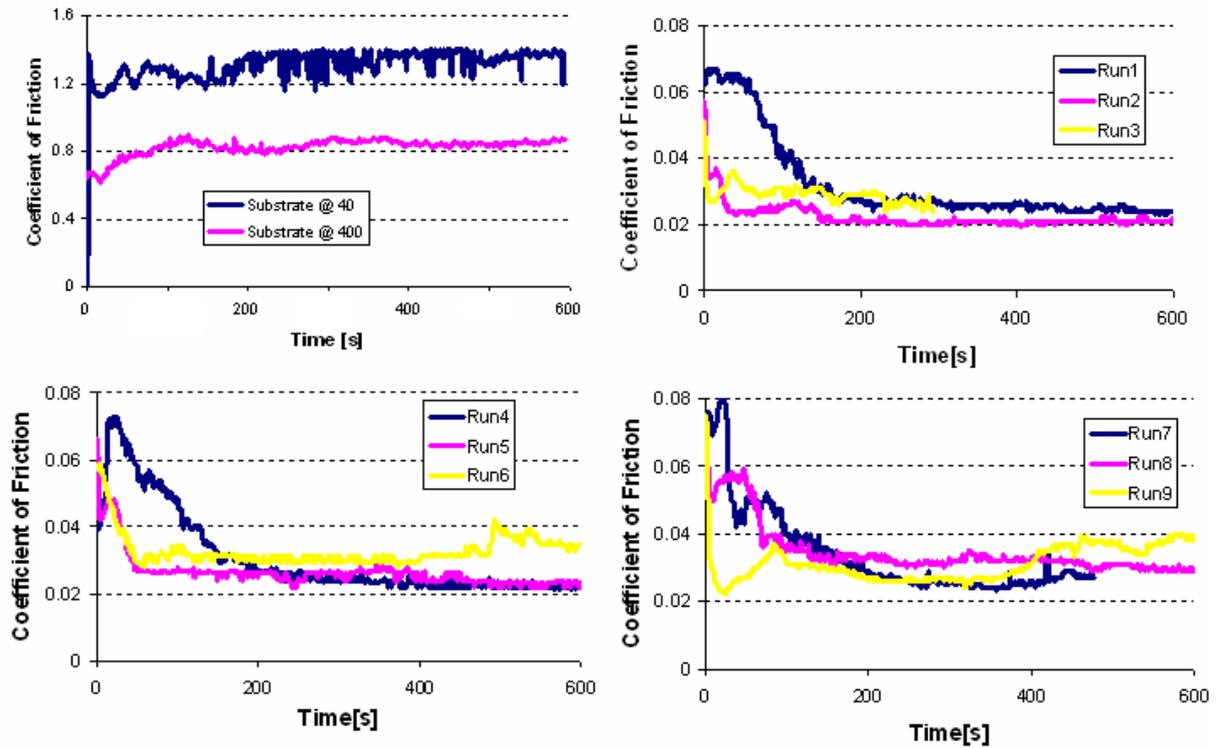Friction coefficient values between 0.02 and 0.034 were obtained. Figure 15 shows the friction coefficient values for all nine runs. The lowest coefficient of friction was obtained for Run 2 which shows the most pronounced peak for the MoS_2 (002) orientation in the XRD pattern. The coatings deposited at higher substrate bias shows higher friction coefficient. Considering the specimens prepared at the same nitrogen flow (for instance, Run1,2,3 or Run4,5 ,6 or Run7,8,9) the friction coefficient is 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 MoS_2-Ti layer, the dependence of the friction coefficient could be explained by noting the effect substrate bias on the S/Mo ratio. F. Bulbul et al. have shown that as the substrate bias increases the S/Mo ratio decreases. This was due to the fact that an increased ion bombardment from the plasma enhances the sputtering of sulfur by increasing atom mobility [27]. Furthermore, the morphology of a coating is known to be dependent on the temperature of substrate during deposition which is directly affected by a substrate bias. The increase in substrate bias increases the homologues temperature which is defined as a ratio of substrate temperature to the melting temperature of the coating (T/Tm)

andfavors formation of fully dense grain structures [23]. There is no obvious influence of the pulse on the friction coefficient of the coating.
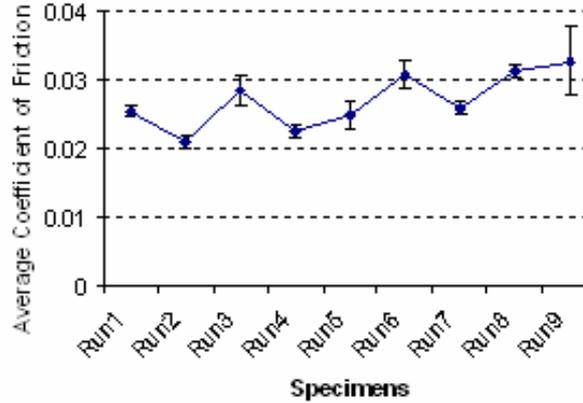
Figure 15. Average friction coefficient values for each of the coatings.

4.3 Load dependence of friction coefficient

The friction coefficient is found to decrease when the normal force increases and lowest friction coefficients were found at a load of 100N as it is clearly shown in Figure 16. For Run3 the coating fails at lower load levels. At lower loads the surface contact is not complete and slip does not takes place between fully conformal lamellae but as the load increases the surface contact increases slip takes place between fully conformal lamellae so that the friction coefficient decreases [24]. A minimum friction coefficient value of 0.019 was found except three of the coatings Run3, Run5 and Run7. The minimum friction coefficient values at 100N are found in Table 4.

Figure 16. Typical load dependent friction coefficient vs time graph

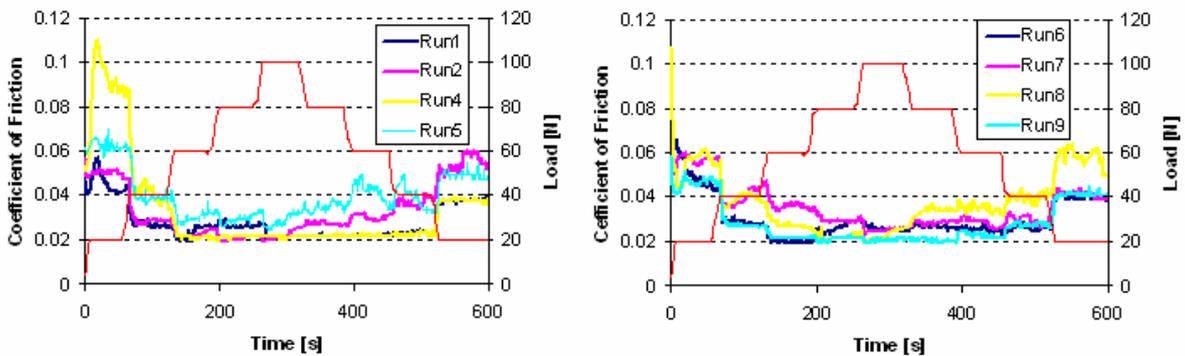*Table 4. Minimum coefficient of friction values for all specimens at 100 N*

Specimen	Run1	Run2	Run3*	Run4	Run5	Run6	Run7	Run8	Run9
Minimum Coefficient of friction (@100N)	0.019	0.019	0.022	0.019	0.024	0.019	0.023	0.019	0.019

* For Run3 the coating fails at the early stage of the test before it reaches to higher loads

4.4 Friction characteristics at high temperature

The friction property of the coating was found to be dependent on temperature as presented in Figure 17. One feature of the friction coefficient curve is that there is no steady range. Comparing with the friction and wear property of the coating at room temperature and at 400 ^{0}C two basic differences was observed. Firstly, the friction coefficient (from 0.07-0.08) increases significantly by three to four folds. Secondly, the life-time of the coating decreases significantly at 400 ^{0}C. These differences arise mainly from the structural changes brought 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 are abrasive in nature [24]. As a result, the proportion of the MoS_2 on the surface decreases which consequently increases the friction. The increases in friction and the presences of abrasive oxidation products at high temperature facilitate the wear process and result in shorter life time of the coating.
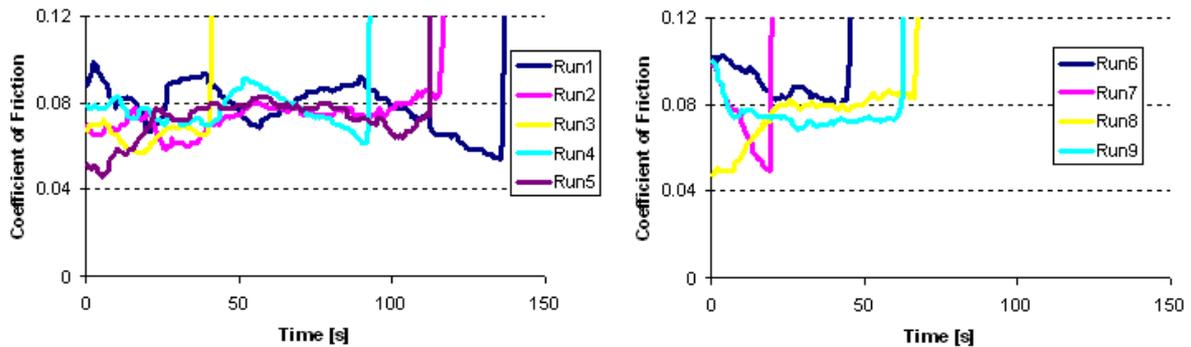

Figure 17. Coefficient of friction vs time at 400 °C

4.5 Durability

Many factors such as film thickness, adhesion of the coating and presence of defects on the film 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 research have shown

that even though high negative substrate bias increases the energy of the bombarding ions, it leads to defects in the film and increased film stress [23]. That could be the reason why Run 3 which was deposited at a substrate bias of -150 V failed at an early stage of the test. In contrast, Run1 and Run4, the multilayer coatings deposited at lower substrate bias (-50 V) shows longer durability. At room temperature the longest durability was recorded for Run 1 (1933 s) and the lowest durability was for Run3 (111 s). For the coatings deposited at 3 and 5% N_2 flow, the durability deteriorated as the bias voltage increased. But for the coatings deposited at a 7% N_2 flow the trend was reversed.

Figure 18 compares the durability of the multilayer coating at 40 °C and 400 °C. As it has been mentioned earlier, the durability of the coating at lower temperature is longer than at high temperature. The longest durability for the coatings at 400 °C was found to be 141 s which belongs for Run 1. The increase in temperature is accompanied by chemical and structural changes which in turn causes the friction and wear property to differ 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 lower layer is hard and brittle TiB_2. More importantly, the XRD pattern shows the presence of a (100) TiB_2 which posses a deteriorated tribological property than (001) TiB_2. Hence, once the top layers with lubricating property are removed, the lower layer is susceptible to complete wear in a very short period of time.
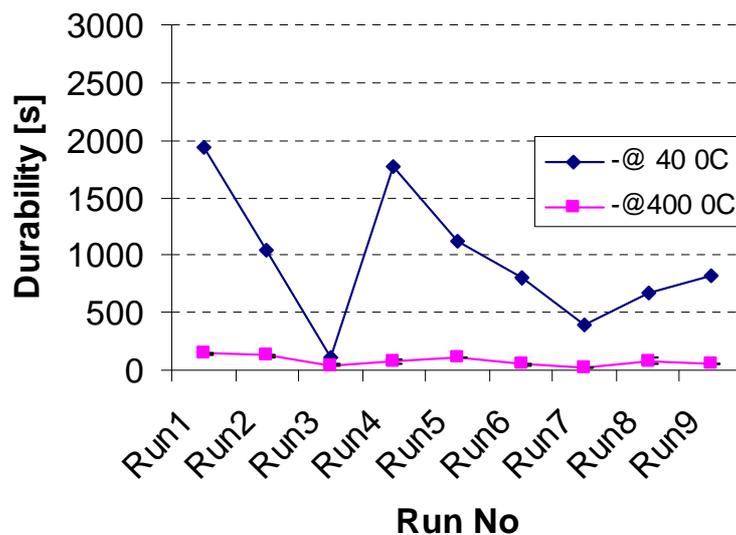

Figure 18. Durability of the multilayer coatings at 40 and 400 °C

4.6 Hardness of the coating

The hardness of the tool steel substrate was found to be improved by deposition of the multilayer coating. Run2 and Run 7 were found to exhibit hardness of 764 and 746 HV, respectively. The lowest hardness was found for Run 6 (578 HV). 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 determine the proportion of phases in the TiBN and the soft h-BN or the amount of Ti in the MoS_2Ti.

Similar to the friction and wear properties the hardness was also found to be dependent on temperature as shown in Figure 19. The hardness was measured for all specimens before and after exposure to the two temperatures. Specimens which were exposed to 400 ^{0}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 ^{0}C for 30 min [24]. More over, there is a possible diffusion process at higher temperature which may alter the hard TiB_2 phase into TiBN which is less hard than the TiB_2.
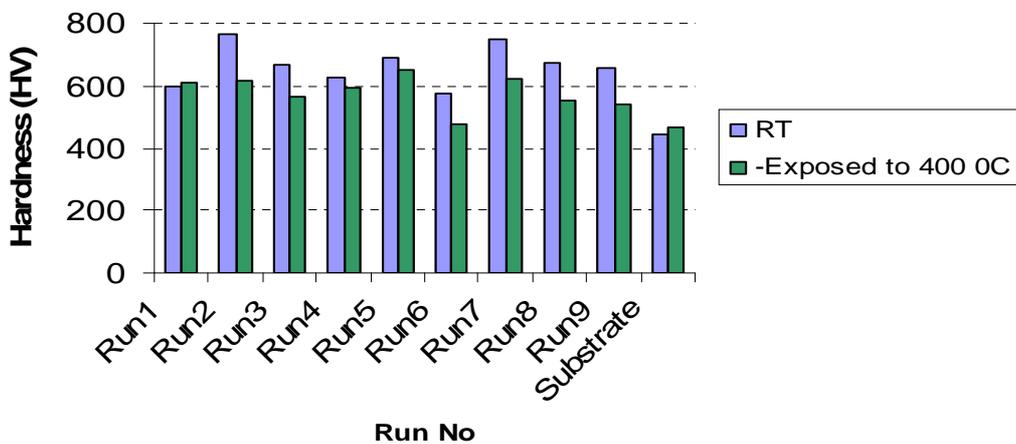

Figure 19. Hardness (HV)25g of the multilayer coating at RT and multilayer coatings exposed to 400 °C for 20 minutes.

4.7 Surface analysis of test specimens

Even though the life time of the coatings was quite different from each other the wear scars exhibit similar features. For instance, Run3 and Run 7 show a complete detachment of the multilayer coating after the test. But the other test specimens have not experienced a complete detachment of the coating.

With the help of SEM, the wear scars were examined to investigate the wear mechanism. Figure 20 shows the wear scar on the test specimens. The wear was clearly seen for Run 6 (b) where there is a complete detachment of the coating leaving the bare substrate and (c) shows the transfer of a coating material to the upper specimen (steel ball). This property is an important behaviour of the MoS_2 which is a prerequisite for its low friction coefficient. The transfer of the material is one step for an adhesive wear type. From the wear scars it can be said that the wear is an adhesive wear type.
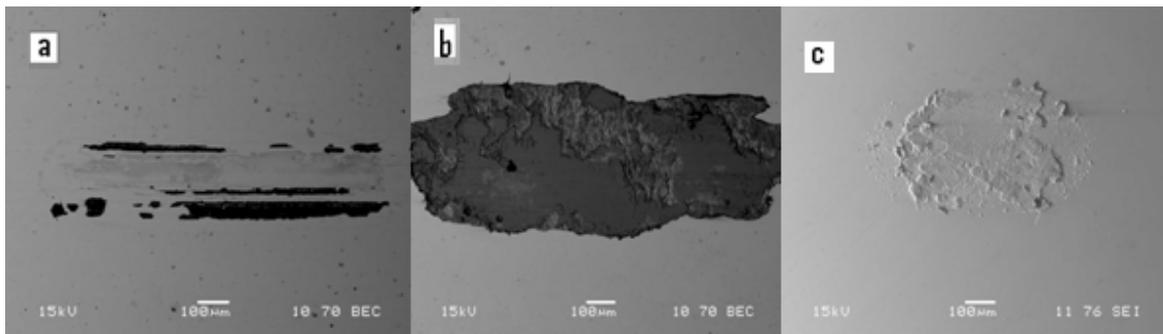

Figure 20. SEM images of wear scars of a) Run8, b) Run7 and c) upper specimen (Run4) at 40 °C

The EDS spectra in Figure 21 correspond to the elemental analysis of the black area on wear scar of Run 8. The black area in Figure 20 (a) show that there are only very small amount of nitrogen and sulphur and very large amount of Ti (63 at%). This confirms the detachment of the top layers except the Ti interlayer. Similar EDS spectra were found for all wear scars except those of the coatings which were completely detached.
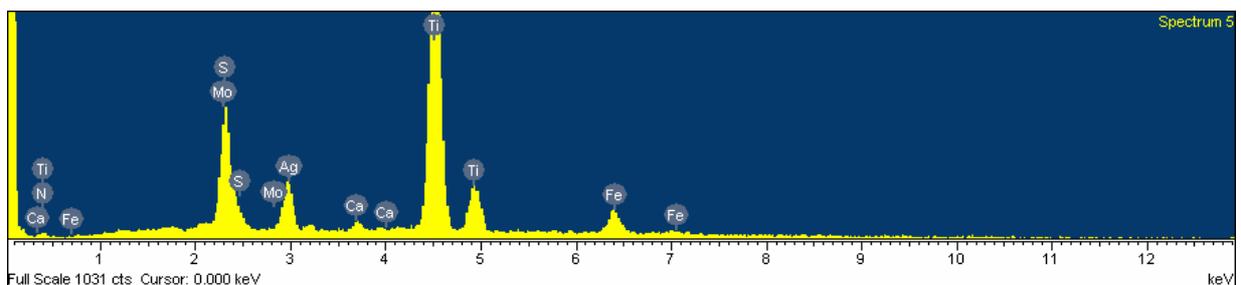

Figure 21. EDS spectra for the black areas in wear scars of Run 8

5. Conclusions

The CFUMS deposition technique is important in depositing the graded multilayer coating and the deposition parameters are found to affect the tribological performance of the coating. The friction coefficients of the coatings were very low at room temperatures for all of the coatings and in fact there is a wide difference in the friction coefficient value. For the coatings deposited at high substrate bias (-150 V) friction was found to be higher compared with the coatings deposited at lower substrate bias. Temperature is an important variable in determining the friction property of the coating. At high temperature the fiction coefficient values increased by three to four folds. The life time of the coating varies widely and the test specimen deposited at high substrate bias and low N_2 flow (Run 3) exhibited the lowest durability. At high temperature the wear behaviour deteriorated significantly. The hardness of the coating is higher at lower temperature than those exposed to high temperature. The SEM images and EDS elemental analysis of the wear scars confirmed that they are an adhesive wear type. This study confirms that the graded multilayer coatings deposited by the CFUMS perform well at room temperature.

6. References

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