Rev.Adv.Mater.Sci. 15(2007) 87-94

DEPOSITION AND CHARACTERIZTION OF A MULTILAYERED-COMPOSITE SOLID LUBRICANT COATING

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Received: January 22, 2007

Abstract. In the present investigation, TiN/TiAlN-MoS_2/MoS_2-Ti multilayer-composite solid lubricant coatings were deposited by magnetron sputtering from separate Ti, Al, and MoS_2 targets on D2 tool steel. EDS, X-ray diffraction, microhardness tester, scratch tester, and pin-on-disc tribo system were used to evaluate structural, mechanical and tribological properties of the coating. Pin-on-disc measurements at atmospheric condition against WC ball showed lower wear and friction coefficients. No evidence of interfacial failure(s) of the sub-layers was observed in the adhesion and tribo-wear tests.

1. INTRODUCTION

Last decade a number of multilayer coating systems have been investigated. The demand for high performance solid lubricant coatings low friction coefficient and high wear resistance severe environments is still increasing. Thin solid lubricant films can help to solve the tribological problem. When mechanical parts run under extreme conditions, one of the solution is to deposit low-friction wear resistant coatings. Vacuum technology and thin film technology commonly use carbon or molybdenum disulphide as lubricants. Because of the sensitivity of MoS_2 to humidity, the applications of this soft lubricant under certain conditions are limited. With specially developed PVD process, the tribological properties of the deposited coatings could be optimized. It has been recognized that friction and wear performances of sputtered MoS_2 and its composite form depend on the deposition conditions and the operation environment. Thanks to its good performance in space environment, MoS_2 films have been used for space applications. In addition, MoS_2 solid lubrication films have many non-space applications where dry lubrication is required, including X-ray rotation anodes, cryogenic coolers, air-bearing environments, cutting tools and as photoactive materials in solar energy conversion [1]. The most common dry solid lubricants are graphite, MoS_2, WS_2, TaS_2, and PTFE, among which, the most widely used lamellar compound solid lubricant is MoS_2 with hexagonal and anisotropic crystal layer structure. Having very low friction coefficient and high sensitivity to oxidation associated with easy-shear planes of the lamellar structure, MoS_2 suffers from rapid failure in air. It makes more suitable for use in vacuum environment [2-6].

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Development efforts have been concentrated on coatings in which alloyed MoS_2 is multilayered and/or composed in order to adapt significantly solid lubrication performance in existing problems of wear lifetime, adhesion and resistance to humidity [7-12]. It has been pointed out that its properties can be further improved by the co-deposition of small amounts of titanium with the MoS_2 [13-19]. In such systems, while MoS_2 provides the solid lubrication, existence of Ti is thought to improve the load capacity and the adhesion of the film to the substrate. More recently Ti addition to MoS_2 has been introduced to the market as MoST™ by Teer Coatings Ltd. One of the future directions for the development of low friction and high wear resistance coatings is a combination of a soft layer coated onto hard layer(s). Co-sputtering of C and TiB_2 has given the soft MoS_2 an improved tribological property at ambient conditions [20]. By alloying with selected metals and compounds, MoS_2 coatings become applicable to atmospheric conditions. In most cases, the machining is conducted under dry and fluid conditions. To reduce high friction coefficient, wear rate and to extend the tool life are commonly used. Manufacturers are continually searching for means to reduce production costs and to avoid environmental problems associated with the use of cutting fluids [21]. The current trend in modern tribology is to limit or reduce the use of liquid lubricants as much as possible, but increase the use of solid lubricant coatings with self-lubricating properties [22]. It has been widely known that a multilayer film can have many advantages. In this way, the load carrying capacity can be improved. Increased adhesion between the substrate and each individual layer can be obtained possible internal stresses in the nano-superlattice structure. Consequently, multilayered coatings have the potential to improve the tribological properties of tools.

Titanium nitride with NaCl-type structure, has many advantages such as excellent adhesion to substrates, high hardness and chemical stability which made TiN the one of the most popular film used on cutting, forming tools and for decorative applications. TiAlN is very popular coating for high speed cutting processes, due to its high hardness, excellent wear, oxidation and corrosion resistance. It is well known that when Ti atoms in the TiN lattice are substituted with Al atoms. Al containing cubic faced centered TiN structure shows high deformation resistant [23]. Incorporation of aluminum in TiN film improves the oxidation resistace and thermal stability of the coating. The metastable $(Ti_{1-x}Al_x)N$ coatings exhibit high microhardness and low coefficient of friction [24]. Rech *et. al.* [21] have shown that the MoS_2 coating improves the tribological behavior of the TiAlN coating due to important decrease in the heat transfer into the tool. Imbeni and co-workers have studied the effect of MoS_2 layers deposited on PVD nitride multi-layers. The results of tribological tests indicated an improvement of the wear resistance by the deposition of a MoS_2 film on the multilayer (TiCN and TiAlN based) [25]. The high hardness of TiAlN based coating combined with the good adhesion lead to very high load carrying capacity. In order to provide optimum wear protection for rubbing mechanism, it is necessary to use a true solid lubricant coating with low friction and transfer film on the opposing surface [26]. Recently, the interest has been growing in MoS_2 as a top layer on hard coatings for dry machining applications. In fact dry machining is becoming industrially feasible using the latest generation of TiAlN coatings [27] and its multilayers [28]. Haider and co-workers have studied deposition and characterization of hard-solid lubricant coatings by closed-field magnetron sputtering [29]. Their results have indicated that $TiN+MoS_x$ coatings show lower friction coefficient and hardness than pure TiN coating. Such mechanical behavior of coated materials can be explained by a combination of the residual stresses and the bending, hardness, critical load, erosion, abrasive wear [30].

The aim of this work is to study the properties of multilayered-composite coating systems for tribological applications. The effect of the deposition of a sputtered MoS_2-Ti on top of the multilayered-composite film is also evaluated. The high hardness of TiAlN based coating combined with the good adhesion lead to very high load carrying capacity.

TiN/TiAlN-MoS_2/MoS_2-Ti multilayered coatings in our study were deposited onto D2 tool steels using the closed field unbalanced magnetron sputter system (CFUBMS). The technique of unbalanced magnetron sputtering was first developed by Windows and Savvides [31]. In the closed-field system, first described by Teer [32], several magnetrons are used to surround a central substrate and adjacent magnetrons are manufactured with opposite polarities. Plasma is then confined within closed field, preventing loss of electrons to the chamber wall and creating intense ion bombardment of the substrate [33]. This was the technique used in the present work; it is described in the following section. Pin-on-disk sliding friction experi-

Table 1. Deposition parameters.

Substrate	Surface roughness R_a, µm	Microhardness GPa	Deposition parameters Working pressure (Pa)	Time (min)	Magnetron current (A)	Substrate dc bias	N_2 flow %
D2	0.12	9,22	0.4	60	1xTi: 6 2xMoS_2:0.6 1xAl: 3	50	60

ments were conducted with WC-%6Co balls in sliding contact with the multilayered-composite films at room temperature in humid air (%RH:45-50). The solid lubricating films and their wear surfaces were examined by SEM, EDS, and surface profilometry. SEM and EDS were used to determine the structural morphology and elemental composition of the worn surfaces and some wear debris. Surface profilometry was used to determine the surface roughness and wear-scar profile of the films. X-ray diffraction measurements were made using CuK_α radiation with a Rigaku Dmax diffractometer.

A qualitative evaluation of the adhesion between a coating and its substrate can be made using the scratch testing technique [34] which is the most frequently used method for testing of the adhesive-cohesive behavior of hard-soft coatings. Different failure modes (adhesive and cohesive) occur as a result of the compressive stress due to the nature of the magnetron sputtered process. Adhesion is measured by drawing a spherically tipped diamond indenter (Rockwell tip) over the coated surface under increasing normal load until a critical value is reached at which coating failure occurs [35-37]. The critical load (L_c) of the coating was determined using a CSM-Revetester equipment. Tests were carried out using loading rate (dL/dt) of 100 N/min and a table speed (scratching speed dx/dt) of 10 mm/min, with a total scratch length of 8 mm. Friction force monitoring was used to detect the point of coating failure, and the images of the scratches obtained using an optical microscope were digitalized by an image processing system. The adhesion strength represented by the critical load for coating removal L_c and the coefficient of friction at the critical load μ_{Lc} was determined. The formation of different crack orientations in the coatings during the sliding contact between scratch indenter and deformed coating structure is presented.

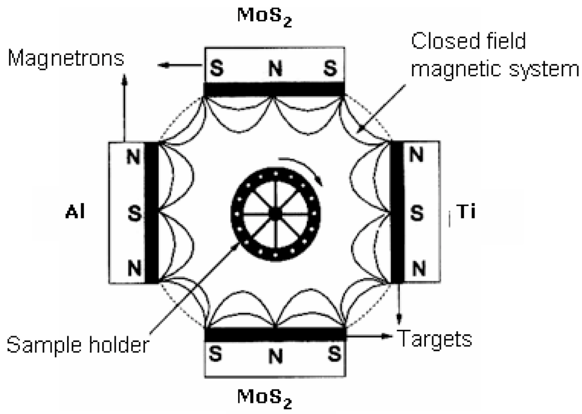

Fig. 1. Teer coating closed-field unbalanced magnetron coating system.

2. EXPERIMENTAL

Multilayered-composite films on the D2 tool steels were deposited by CFUBMS using biased-dc power which was applied to the substrates. The minimum number of magnetrons necessary to form a closed-field system is two. In the present work, four magnetron system illustrated in Fig. 1. was used, each of the magnetrons having a target area of 300x75 mm^2. The four-magnetron system allows great flexibility in the deposition of single and/or multilayer composite alloys and ceramic films and also allows uniform coatings to be deposited onto substrates of complex shape. Deposition parameters are given in Table 1*.* Prior to deposition of coatings, the substrate material was heat-treated (quenching and tempering) to a hardness of 9.22 GPa and polished (R_a≅0.12 µm). Before deposition, the samples were sputter ion cleaned for 20 min to remove possible contaminants. One pure

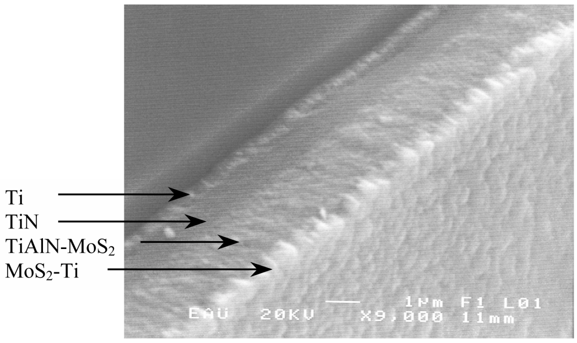

Fig. 2. SEM image showing the cross-section of the multilayer-composite thin film.

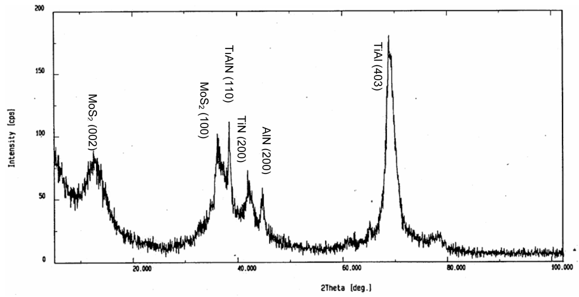

Fig. 3. XRD analysis from the coating.

Al target located in between two opposing pure MoS_2 targets. The fourth target, opposite to the Al, was pure Ti. The distance between the targets and the substrates was 95 mm. The depositions started with a titanium under layer (~0.2 μm), followed by TiN (~1 μm) and TiAlN-MoS_2 composite structures (~1.5 μm). Finally, MoS_2-Ti composite structure (~0.3 μm) was deposited as the top layer. The total thickness of the coating was 3 mm. The substrate temperature was 300 °C at the end of the run.

Film hardness was tested using a Buhler Microhardness Tester. At least five indentation measurements were averaged under 0.01N (10 gf) load for each sample. Microstructural characteristics of the multilayered-composite films were analysed by SEM (Jeol-6400). The composition of the films was determined by EDS.

Adhesion and failures mechanism of the coating were obtained from scratch test experiments using a CSM-Revetester equipped with 0.2mm radius Rockwell-C diamond tip. Scratch testing was carried out using a table speed of 10 mm min^{-1} under the stylus loading rate of 100 N min^{-1}. The coating adhesion failure could be monitored by optical microscopy, acoustic emission and friction force measurements. At least, three scratches were made for each coated specimen and an average value was taken.

XRD measurements of films deposited on reference silicon wafer substrates were performed using Rigaku 2200D/max diffractometer equipment with a Cu-Kα radiation source. Measurements were made in the 2θ: 5° - 90° scan range, at 2.5 deg/min scan speed. Interpretation of the X-ray results was undertaken using the JCPDS files.

It is often useful to evaluate the films first on a pin-on-disc tribometer to determine the best candidates for testing in the final end use application [35,38]. The pin-on-disc tribometer (Teer POD2) was used to investigate friction and wear properties of multilayered-composite films. These experiments were conducted at room temperature, in humid air (45-55% RH). The triotest wear tests were carried out with 5 mm-diameter WC-%6Co steel pin-balls at 10 N normal loads at the speed of 80 mm/s.

3. RESULTS AND DISCUSSION

Fig. 2 shows an SEM image of the cross-section of the coating, in which different structures can be seen. The morphology of the coating is very dense with little evidence of the columnar morphology of top layer as seen in Fig. 2. The total thickness of the coating was 3 μm (Ti~0.2 μm, TiN~1 μm, TiAlN-MoS_2~1.5 μm, MoS_2-Ti~0.3 μm). Microhardness measurement of the coating was carried out with a Vickers type indenter with a loading force of 0.01 N and the measured microhardness of 4.5 GPa.

XRD analyses

A typical plot of the X-ray diffraction measurement of the multiyear-composite coating is shown in Fig. 3. XRD analyses were performed on the coatings deposited onto Si-wafer substrates. MoS_2 phase is obviously nanocrystalline and in case of strong (002) texture, we should not see (100) peak. Chemically inert (002) planes parallel to the TiAlN-MoS_2 composite layer, preferred for a tribological application was observed. Fleischauer [39] indicated that this plane provides a low friction coefficient between sliding surfaces. XRD analyses show that all of the multilayered-composite films had

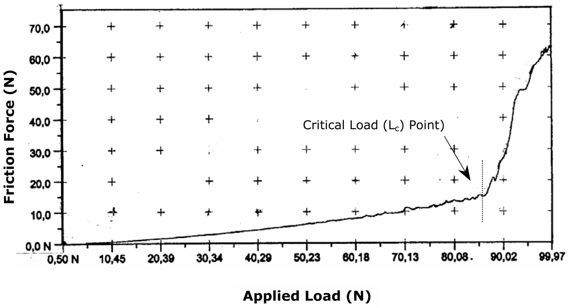

Fig. 4. Variations in the friction force and the applied load with scratch length.

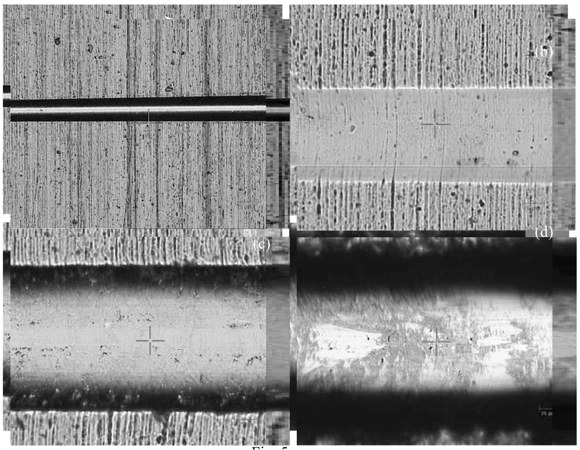

Fig. 5. SEM images of the scratch tracks in the tested film. The stylus sliding direction is indicated by the arrow.

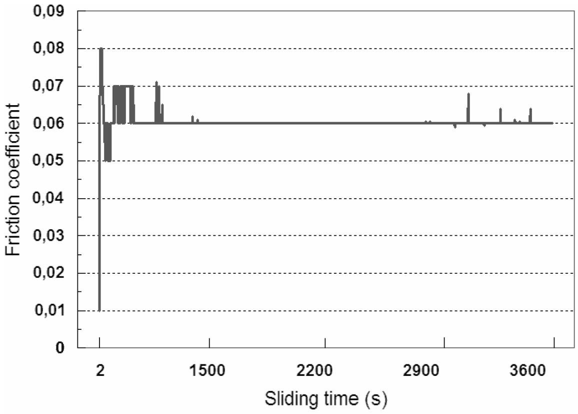

Fig. 6. Changes in friction coefficients for multilayered-composite film as function of the sliding time.

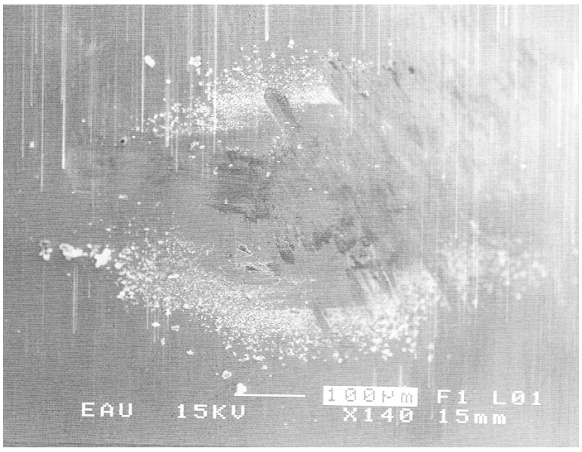

Fig. 7. SEM picture from the contacting area on the ball.

observable texture. Several peaks; MoS_2-(002)/(100), TiN-(200), AlN-(200), TiAlN-(110), and TiAl-(403) were identified indicating that this coating is crystalline where TiAl ($TiAl_3$), in particular, is referred to as a (403) oriented peak.

Scratch test results

Fig. 4 shows the result of a typical scratch test from the multilayered coating system. The critical load for the multilayer-composite system varied between 80-90 N. As Ma and co-workers [40] have indicated, the MoS_2-Ti lubricant layer effectively reduces the tensile stress and delays the development of the maximum shear stress at the interface, which favors a larger critical load. The test results confirmed the excellent adhesion of the multilayer-composite coating to the D2 tool steel substrate (Fig. 4). Many cohesive failures (sideward parallel flaking, sideward lateral flaking) occur at scratch sides [41]. As far as the coating failures are concerned, the coating showed no damage in the scratch sides and into the scratch path. Stresses in the coating at scratch sides are related to the compressive stress fields. As seen in Fig. 5, there are no adhesive and/or cohesive failures while the coating is thinning under indenter tip (Fig.5b). Figs. 5c and 5d also show a very clear progression of the thinning of the multilayer with no observable micro-cracks or deflects at the interface between MoS_2-Ti and TiAlN-MoS_2 layers. As the thinning process reaches to TiN and then to the substrate, micro-cracks (seen to be perpendicular to the scratch direction) appear. Panjan and co-workers [42] have studied with a new experimental method the cracking behavior of PVD multilayer coatings. Their results have indicated that the plastic deformation of the substrate has a strong influence on the cracking behavior of hard coatings. It must be noted here

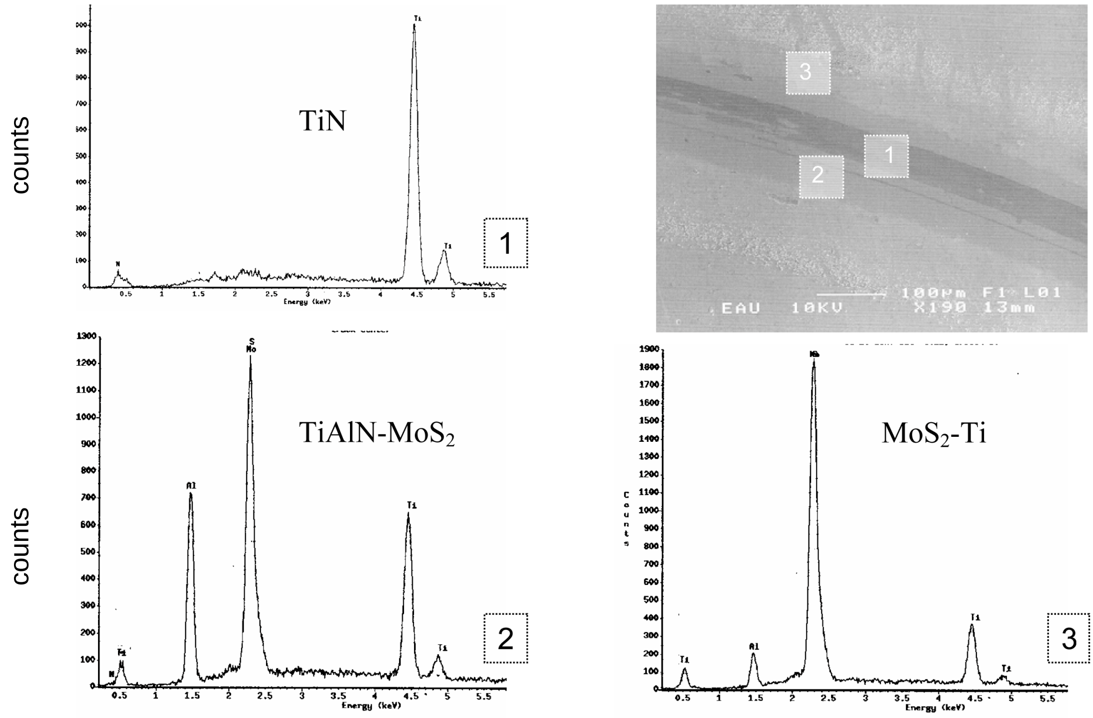

Fig. 8. EDS analysis from the wear scars.

Table 2. About quantitive values of TiN/TiAlN-MoS_2/-MoS_2-Ti film.

Elements	Mo	S	Ti	Al	N
at.%	25	32	22	10	11

that the multilayered structure dispersed the accumulated stress in its structure by plastic deformation and it is believed that the stress evolution was interrupted at the layer boundaries, which positively affected the adhesion property of the coating [43]. However, it is still not clear how a layer structure influences the cracking resistance [42].

Pin-on-disc test results

Fig. 6 illustrates the evolution of the friction coefficient of multilayered-composite coating under dry sliding for a duration of 1h. The friction coefficient changes as a function of the sliding time. The friction force was continuously monitored during the friction experiments. The sliding wear life for the coatings in this investigation was determined in terms of the number of passes at which the initial coefficient of friction was between 0.06-0.07 at the end of the 1100 s sliding time. As the sliding time increases to 3600 s, the friction coefficient has fallen to a low, constant value (μ:0.06) maintained until the end of the test (Fig. 6). A thin and uniform transfer film on the WC-6%Co ball is observed at the test conditions. Fig. 7 shows the contacting area on the ball. As seen Fig. 8, EDS data were taken from three positions in the wear track where the worn surface from the multilayered-composite indicates three worn zones. EDS analysis was performed to determine the surface composition in each of the three zones. A qualitative analysis by EDS confirmed the presence of Ti, Al, N, Mo, and S within the multilayered-composite coating (see Table 2). The worn area on the film counterbody is smooth without any debris. All worn debris piled up at the both side of the wear track with no abrasive wear effect. This is the reason why the friction coefficient remained very stable during the 1 h sliding test. The overall aspects of this worn surface image are typical of all the multilayer systems that we have studied. It is well known that the main reason for low COF seems to be presence composite structure of TiAlN-MoS_2 and MoS_2-Ti top layer. Otherwise, it has been noted that one of the reasons for the low coefficient of friction obtained by pin-on-disc tribotest system is the oxidation resistance of the TiAl based phases in the coating structure. This was pointed out on the wear scar by EDS examination (see Fig. 8). This observation is also known in the Ti-Al system [44,45], $TiAl_3$ is known as an alumina former with reasonably good oxidation resistance. $TiAl_3$ is generally considered as a coating material for oxidation protection of the Ti_3Al and TiAl based materials. The coating produced as multilayered-composite film showed quite high wear resistance owing to the middle composite layer (TiAlN-MoS_2) and adhesion strength. The calculated wear rate (0.35 $\times 10^{-6}$ mm^3/Nm) was taken after 9000 revolutions of the tribotest. This value is lower then our previous works [46,47]. This is expected that the multilayered-composite TiN/TiAlN-MoS_2 should be harder then the top layer.

4. CONCLUSIONS

1. XRD analyses indicated that the multilayered-composite film had observable texture. Several peaks; MoS_2-(002), TiN-(200), AlN-(200), TiAlN-(110), and TiAl-(403) were observed for the multilayered-composite coating indicating that this coating is crystalline where TiAl is one of the referred to as (403) oriented peak.
2. No adhesive and/or cohesive failure was observed as the coating thins under the indenter tip. The results showed very clear multilayer thinning progress with no micro-cracks or deflects at the interface between MoS_2-Ti and TiAlN-MoS_2 layers.
3. The multilayered structure dispersed the accumulated stress in its structure by plastic deformation and it is believed that the stress evolution was interrupted at the layer boundaries, which positively affected the adhesion property of the coating.
4. The initial coefficient of friction was between 0.06-0.07 at the end of the 1100 s sliding time. As the sliding time increases to 3600 s, the friction coefficient falls to a low, constant value (μ:0.06) maintained until the end of the test.
5. The main reason for low COF seems to be presence composite structure of TiAlN-MoS_2 and MoS_2-Ti top layer. Otherwise, it has been noted that the other reason for the low coefficient of friction obtained by pin-on-disc tribotest system is the oxidation resistance of the TiAl based phases in the coating structure.
6. No evidence of interfacial failure(s) of the sublayers was observed in the adhesion and tribowear tests.

ACKNOWLEDGEMENTS

This research was conducted as part of a TUBITAK (The Scientific and Technical Research Council of Turkey) project, supported by grant no: MISAG-219. The author thanks the TUBITAK for funding the project.

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