Tribological Behaviour of Ti:Ta-DLC Films Under Different Tribo-Test Conditions

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Abstract

Diamond-like carbon (DLC) films are suitable applicants for cutting tools due to their high hardness, low friction coefficient and wear rate. Doping metals in DLC films have been improved its tribological properties. In this study, titanium and tantalum doped hydrogenated DLC films were deposited by closed-field unbalanced magnetron sputtering system onto M2 high speed steels in Ar/N2/C2H2 atmosphere. The friction and wear properties of Ti:Ta-DLC film were investigated under different tribo-test conditions including in atmospheric pressure, distilled water, commercial oil and Ar atmosphere. The coated specimens were characterized by SEM and X-ray diffraction techniques. The bonding state of C-C (sp 3) and C=C (sp 2) were obtained with XPS. The tribological properties of Ti:Ta-DLC were investigated with pin-on-disc wear test. Hardness measurements performed by micro-indentation. Our results suggest that Ti:Ta-doped DLC film shows very dense columnar microstructure, high hardness (38.2 GPa) with low CoF (μ≈0.02) and high wear resistance (0.5E-6 mm3/Nm).

Keywords: Magnetron sputtering, Ti:Ta-DLC, friction, wear

1. Introduction

Lubrication of machine elements provides low coefficient of friction and wear rate so that energy losses are avoided and operating life is increased. But under some of the condition of operating (high and cryogenic temperatures, vacuum, etc.). Liquid lubrication is not convenient. In similar conditions, liquid lubricants are replaced by solid lubricants [1]. The most commonly used solid lubricants are Diamond Like Carbon (DLC), transition metal dichalcogenides (TMDC) and polymeric composite coatings [2]. DLC coatings provide low friction and high wear resistance in oil-lubricated conditions. DLC is a metastable form of amorphous carbon consists of sp² and sp³ bonds. Having high hardness, chemically inert and semiconductor DLC coatings can be used some many applications including machine parts, cutting tools, parts of automotive [3], Li-ion baterry[4]. But the low adhesion properties are the major disadvantage of the DLC films [5]. For this reason elements or compounds doped the DLC films to improve some properties such as adhesion between the substrate, wear resistance, etc. According to the literature, there are some study about the doped DLC films. For example; Ag doped in DLC films by unbalanced magnetron sputtering reduce coefficient of friction (CoF.) [6], Mo doped DLC coatings by CFUBMS (Closed Field Unbalanced Magnetron Sputtering) have good adhesion and
low CoF. [7], Zr doped DLC coatings decreased too small values coefficient of friction [8]. Ti doped DLC coatings by using CFUBMS is decreased CoF. [9] and also the reduced CoF was affected TiC interlayer on a DLC coatings by using CFUBMS [10]. Deposition method, substrate material, chemical and structural nature, working temperature, contact pressure and test environment are the significant on the friction and wear properties of DLC coating films [11]. For example, DLC films that contain hydrogen have ultra-low friction in inert or vacuum environments but DLC films that not contain hydrogen have ultra-low friction and wear in the presence of oxygen, hydrogen or water molecules [12-13]. Searching literature, it was shown that tribological properties of Ta doped DLC coatings have not been investigated upto now. Ta has attractive properties like corrosion resistance, thermal stability, high resistivity, fracture toughness. Ta affects material’s performance through microstructural modifications. Through carbide formation, Ta provides strength, malleable and thermal stability [14].

In the present research; Ti and Ta doped hydrogenated DLC films were deposited by closed field unbalanced magnetron sputtering (CFUBMS) system onto M2 high speed steels in Ar/N2/C2H2 atmosphere. The friction and wear properties of Ti:Ta-DLC film were investigated under different tribo-test conditions including in atmospheric pressure, distilled water, commercial oil and the Ar atmosphere. The results showed that Ti:Ta-doped DLC film shows very dense microstructure, high hardness with low CoF and high wear resistance.

2. Experimental Methods

Ti and Ta doped DLC was coated on M2 high speed steel, in size 25x25x2 mm³, as a substrate metal and glass wafer by CFUBMS. The chemical composition of steel is 0.3 wt% Si, 4.2 wt% Cr, 0.3 wt% Mn, 5.1 wt% Mo, 6.3 wt% W, 2 wt% S and C balance. The substrates were polished to a roughness value of R ≤ 0.1 μm, ultrasonically cleaned with ethyl alcohol and then etched in the 2% Nital solution and dried. The Ti:Ta doped DLC was performed by CFUBMS system by produced Teer Coating Ltd [15]. Schematic picture of magnetron configuration system is shown Figure 1.

![Figure 1. Schematic picture of magnetron configuration CFUBMS system](image)

Depositing the Ti:Ta DLC films; 2 Ta and 2 Ti targets and N2, C2H2 reactive gases were used and for ionization Ar gas was used. Before deposition process to eliminate contamination and improve adhesion on the substrate metals, ion cleaning was realized for 20 minutes. The parameters of coating process were given in Table 1. The Ti targets were kept constant at 5 A in 3 runs during process and the current values of Ta targets were 5A, 4A and 3A, respectively. The pulsed DC bias was applied to the substrates rotated in the system. For deposition Ti-Ta DLC were bias voltage -60 V, working pressure 0.33 Pa. The deposition time was 75 min and to improve adhesion between substrate
and DLC coating. Ti/TiN/TiTaN/TiTaCN graded layer was coated on substrate. The schematic picture of coating was shown Figure 2.

![Graded layers](image)

**Figure 2.** The schematic picture of DLC coating

The thickness of coating, the microstructure, the stoichiometry and the wear tracks were analyzed with JEOL-6400-SEM and energy dispersive spectrometry (EDS). The microhardness of the coatings was measured by Buehler Micromet 2001 microhardness tester (using Knoop indenter, 10gf load). The crystallographic orientation was characterized using Rigaku DMax-2000 XRD with a Cu-Kα radiation source (at 5º to 100º scan range). The bonding state of C-C and C=C were obtained by PHI 5000 VersaProbe XPS. The wear tests under different conditions were carried out CSM high temperatuere tribo-tester (3N load, 25 ºC, %45-55RH, 10cm/s velocity, Si3N4 counterpart), respectively.

| Table 1. The Deposition Parameters |
|-----------------------------------|
| Coating Film Parameters           |
| Number of Coating | Target Currents (A) |
| R1 | Ta | Ti |
|    | 5  | 5  |
| R2 | 4  |    |
| R3 | 3  |    |
| Constant Parameters               |
| Substrate Bias Voltage (-V) | 60 |
| Working Pressure (Pa)             | 0.33 |
| Coating Time                      | 75 |

3. Results And Discussion

3.1. Microstructure of Coating

Cross-section and surface SEM images of the Ti:Ta-DLC film coatings are given in Figure 3.
The cross-section and the surface SEM images showed that all Ti:Ta-DLC films grown as dense columnar structures. It seems that the density of the columns decreased with decreasing target current values of Ta. The interfaces between the substrate and the Ti:Ta-DLC films were well defined. Run 3 (R3) films showed brittle type fracture and the other Run 1 (R1) and Run 2 (R2) films showed ductile fractures. According to these results, it can be said that when the Ta target current value increase, it caused the change of fracture type of the film from brittle to ductile.

The total coating thickness for the Ti:Ta-DLC films were 3.0 μm, 2.9 μm, 2.8 μm for R1, R2 and R3 respectively. It was observed that thickness of the films was affected directly from the Ta target current value increasing in a linear manner.

Chemical compositions of the films determined by EDS. The results of the films are given in Table 2.

Table 2: Chemical composition of the Ti:Ta-DLC films

| Elements | R1 (at.%) | R2 (at.%) | R3 (at.%) |
|----------|-----------|-----------|-----------|
| C        | 44,5      | 48,2      | 64,8      |
| N        | 19,1      | 18,3      | 10,7      |
| O        | 4,8       | 4,2       | 3,4       |
| Ta       | 14,7      | 16,5      | 17,2      |
| Ti       | 16,9      | 12,8      | 3,9       |

According to EDS analyzes, when the Ta target current increased chemical composition ratio (at.%) of Ta in films increased and Ti ratio decreased as expected. When looking at the carbon content in the
films, the highest carbon ratio (R3) obtained from the highest Ta target current (5A) and the lowest (R1) obtained the lowest Ta current (3A). It is clearly seen that carbon content directly affected the Ta target current with parallel behavior. The chemical ratio of nitrogen showed an inverse status with carbon. Reducing the carbon content of the film was increased the nitrogen content. It appeared that oxygen ration in the films showed the same behavior with the nitrogen.

XRD analysis was performed to investigate the crystal structure of the Ti:Ta-DLC films. XRD patterns of the films were given in Figure 4 comparatively.

![Figure 4](image)

**Figure 4.** XRD patterns of Ti:Ta-DLC deposited films.

The XRD patterns showed that lots of different crystal structure such as TiC, TaC, CN, TaC, TiN formed by used elements (Ti, Ta, C, N). It was observed that TiC (111) and TaC (111) phases predominantly placed in the films. The TiC (111) peak reached the highest value at the R3 film with increasing the Ti ratio (at. %) and decreasing the Ta ratio (at.%) in film. It was found that crystallographic orientation depends on the Ta target current. TiC (200) phase is second dominant phase in the films although some reduction at R2. TiC (220), TaC (222), TiN (222), CN (110), CN (220) and TaN (110) peaks do not show significant change at the films. On the other hand, although the TiCN (111) peak clearly appears at R1, but it disappears at R2 and R3 films with the decreasing of carbon content ratio from %64 to approximate %44,5.

The XPS patterns of bonding state of C-C (C-sp^3) and C=C (C-sp^2) were shown Figure 5. Some researchers reported that the peaks at around 284.3 ±0.1 eV and 285.3±0.1 eV were attributed to C-sp^2 and C-sp^3 bondings [17, 18]. The figure 5 showed that C-1s, C-sp^2 and C-sp^3 bondings were measured...
282.6 eV, 284.4 eV and 285.2 eV, respectively. The ratio of \( \text{sp}^3/(\text{sp}^3+\text{sp}^2) \) was found 0.45 for R1, 0.48 for R2 and 0.52 for R3. It is evident that Ta facilitates the growth of C=C (sp\(^2\)) bonding in DLC coating.

![XPS spectra of Carbon Element of The Coatings](image)

Figure 5. The XPS spectra of Carbon Element of The Coatings

3.2. Microhardness of films

The microhardness of Ti-Ta DLC films at a 10 gf load was R1, R2 and R3, from low to high, respectively. The value of hardness with ascending order was 13.9 GPa, 17.8 GPa and 38.2 GPa. It was observed that decreasing the Ta current values, the microhardness and the carbon content increased. According to EDS analyze, R3 has the highest value of the carbon content. It seems that large crystallite disperses in high C-C (C-sp\(^3\)) content amorphous carbon shows the highest hardness among the films [19]. The hardness of the DLC films depends on the C=C (C-sp\(^3\))/C-C (C-sp\(^3\)) ratio of the films [20]. Results show that the hardness of the DLC films increase with decreasing C=C (C-sp\(^3\))/C-C (C-sp\(^3\)) ratio of the DLC films.

3.3. Coefficient of Friction (CoF) and Wear Rate of films

Four different environments were used to investigation for tribological properties of the Ti-Ta-DLC films. The coefficient of friction of films under atmosphere, argon, commercial oil and distilled water conditions were given in Figure 6. It is shown that the friction coefficient at the begin of the test (approximate 0-500 s) exhibited a high value (for atmosphere condition: R1≈0.35µ, R2≈0.30µ, R3≈0.32µ, for Argon atmosphere condition: R1≈0.34µ, R2≈0.32µ, R3≈0.25µ, for Distilled water condition: R1≈0.25µ, R2≈0.15µ, R3≈0.12µ, for Commercial Oil condition: R1≈0.12µ, R2≈0.04µ, R3≈0.03µ). After then the friction returned again a stable value by showing a decreasing tendency. This case was related to a transfer film formation on the counterpart and dense film structure result.

It was shown that the hardest R3 was the lowest coefficient of friction and wear rate in all conditions. It is realized that the R1 has the highest CoF and wear rate in all conditions and also it has the lowest
hardness value. Compared with different conditions, it is reported that the CoF was changed in commercial oil condition, distilled water condition, argon condition and atmosphere condition, from low to high, respectively. It was obtained that the friction coefficient of R3 films were 0.03 - 0.1 - 0.16 and 0.25 and the wear rate were 0.45x10⁻⁶ mm³/Nm, 11.5x10⁻⁶ mm³/Nm, 15.7x10⁻⁶ mm³/Nm ve 18.3x10⁻⁶ mm³/Nm commercial oil condition, distilled water condition, argon condition and atmosphere condition, from low to high, respectively. According to classical theories of wear, hardness affects the wear resistance of a film and higher hardness led to lower wear rate [19, 21]. According to the results, the R3 that was deposited at low Ta currents shows the highest hardness among DLC films. The friction of coefficient of R3 has stable all of the conditions. This cause of ability of R3 has ability to soften small debris of wear from the counterpart. It is very important for stable coefficient of friction [22].
Figure 6. Coefficient of Films a) Atmosphere condition b) Argon Atmosphere condition c) Distilled water condition d) Commercial Oil condition

SEM images of wear tracks of the film and Optical images of abrasive balls at four different environments are given in Figure 7.
Figure 7. SEM images of wear tracks of the films and Optical images of abrasive balls

It was seen that the wear track obtained for the all wear conditions, the R3 film is very smooth and steady, but it did not have deep abrasive scratches on track as that of the films obtained under the same wear conditions. While plenty of small particles dragged on the sides of wear track obtained from the film grown by R1 and R2 were observed, less particles and some flakes on track existed also in that of grown by R3 at the same condition. The wear track obtained from the R3 includes plenty of wear debris as a result of abrasion due to the high Ta content (Table 3). But wear debris amount is more than that of the film obtained by R1 and R2 under the same wear conditions. It can be said that the wear mechanism of the Ti:Ta-DLC films produced by lower Ta content is more abrasive according to that of R3 because of higher Ta content.

When evaluated in terms of EDS analyzes after wear test (Table 3), R3 has the highest value of the carbon and Ta content. The wear track and the counterpart ball images show that the highest value of the carbon and Ta content in R3 films caused not showing an abrasive behavior.
Table 3. Chemical composition of wear tracks

| % Atomic | Elements | R1 | R2 | R3 |
|----------|----------|----|----|----|
| Atmosphere | C | 49 | 57,8 | 62,4 |
| | N | 20,9 | 12,8 | 10,2 |
| | O | 12,3 | 18,6 | 15,7 |
| | Fe | 0,1 | 0,1 | 0,5 |
| | Ta | 4,4 | 3,4 | 6,1 |
| | Ti | 13,3 | 7,3 | 5,1 |
| Argon | C | 52,4 | 56,1 | 69,1 |
| | N | 20,7 | 12,9 | 10,5 |
| | O | 11,8 | 18,5 | 10,3 |
| | Fe | 0,1 | 0,2 | 0,4 |
| | Ta | 4,6 | 3,6 | 5,8 |
| | Ti | 10,4 | 8,7 | 3,9 |
| Distilled Water | C | 46,5 | 50,5 | 63,6 |
| | N | 23,6 | 20,6 | 17,16 |
| | O | 10,8 | 12,8 | 9,15 |
| | Fe | 0 | 0,4 | 0,2 |
| | Ta | 4,6 | 5,4 | 5,5 |
| | Ti | 14,5 | 10,3 | 4,3 |
| Oil | C | 56,5 | 56,7 | 62,9 |
| | N | 16,4 | 15,1 | 12,5 |
| | O | 11,2 | 19,1 | 14,1 |
| | Fe | 0,1 | 0,1 | 0,1 |
| | Ta | 4,5 | 3,2 | 6,3 |
| | Ti | 11,3 | 5,8 | 4,1 |
4. Conclusions

The following conclusions can be derived from the above results and discussion:

- All three films grown as dense columnar structures. It was seen that the density of the columns decreased with decreasing target current values of Ta.
- With decreasing Ta current, carbon content was increased and therefore the hardness of film was increased. The hardness value of the hardest coated sample was 38.2 MPa.
- The reason of low friction coefficient was Ta current. With decreasing current of Ta, hardness value was increased and this reason CoF (μ≈0.02) and wear rate (0.5E-6 mm³/Nm) were decreased.

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