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Full Length Article

XPS investigations of tribofilms formed on CrN coatings

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ABSTRACT

Action of lubrication additives in the case of uncoated steel surfaces, including the type and mechanism of tribofilm formation is well known and understood. However, contact type of tribofilms which might form under the tribological contact between CrN coated surfaces, remains more or less unexplored. The aim of this investigation was to study the type of tribofilms formed on the CrN coated steel samples subjected to lubricated reciprocating sliding contact under different contact conditions Contact surface and tribofilms formed were studied by X-ray Photoelectron Spectroscopy (XPS). Sample surfaces were first imaged by Scanning Electron Microscopy (SEM) to determine areas of tribofilm formation as well as areas not affected by tribological contact. In these areas survey and high resolution (HR) XPS measurements were performed to obtain information about surface chemistry and oxidation states of the constituent elements. It was found that differences between different samples, observed by the XPS measurements, may reflect differences in chemistry of tribofilms formed under different contact conditions.

1. Introduction

Majority of machine components, including gears, bearings, piston rings etc. are operating under very severe contact conditions, which require surface protection [1] and lubrication [2]. Recently, PVD and CVD coatings are very extensively used to increase components wear resistance. One of hard coatings, being popular in forming and automotive industry due to its low friction, high hardness, high thermal stability, galling resistance and excellent anti-corrosion properties is CrN coating [3]. However, although hard coatings show very high potential for reducing friction and wear, lubricants are still required in many applications due to different reasons [4]. Typical lubricants are composed of base oil and various additives which account for 4–10% [5] and play a crucial role under boundary lubrication characterized by high severity contacts and extensive interactions between the contact surfaces. The most important additives from the friction and wear protection point of view are friction modifiers, anti-wear and extreme-pressure additives [5]. These additives are chemical compounds, which react with metal surfaces at elevated temperatures and form protective tribofilms. Depending on the additive type and chemistry, surface composition and contact conditions different tribofilms are generated, ranging from different phosphates to sulphides [5,6]. Extreme pressure performance is enhanced by sulphur-based compounds through the formation of a chemisorbed load-carrying tribofilms of disulphide type (FeS_2, MoS_2, WS_2, ...) [7]. In the case of uncoated metallic surfaces [2,5–7], as well as DLC coatings [8–12], type of tribofilms generated and formation mechanisms are extensively studied and described in detail, as well positive action of S-based tribofilms well documented [13,14]. However, this is not the case for hard ceramic coatings like CrN. While hard coatings themselves can be considered thin films since they are of micron thickness, tribofilms that form at contact surfaces are much thinner (in 10–100 nm region). Surface sensitive analytical methods are thus advised for investigation of these tribofilms in order to minimize substrate influence. Surface sensitive analysis has already been used to study lubricant-coating interfaces [e.g. 15] while in some other cases, where average composition of thicker layer is of interest, analysis of penetration depth of the order of 1 μm is used [e.g. Energy Dispersive Spectroscopy (EDS) in 16]. This study presents use of XPS to obtain several information of interest from tribofilms formed on CrN hard coatings: confirm their formation, estimate thickness, chemistry and compounds formed, as well as show influence of tribofilms' formation conditions/parameters onto their properties.

2. Experimental

2.1. Samples preparation

Commercial, 2 μm thick PVD CrN coating with a hardness of 1750 HV was used in the present investigation. Coating was deposited on polished hardened ball-bearing steel discs (AISI 52100, 850 HV, R_a = 0.05 μm) using an industrial closed-field

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Table 1
Testing conditions and specimens' designation.

Specimen	Additive	Load [N]	Contact pressure [GPa]	Sliding speed [m/s]	Temperature [°C]
B0 (A2-s)	PAO	10	1.0	0.02	50
B1S (8)	PAO + 1%EP	10	1.0	0.02	50
B1P (A17-6)	PAO + 1%AW	10	1.0	0.02	50
B10S (2)	PAO + 10%EP	10	1.0	0.02	50
B1SL (A13-s)	PAO + 1%EP	250	3.0	0.02	50
B1SV (A11-12)	PAO + 1%EP	10	1.0	0.15	50
B1ST (A10-1)	PAO + 1%EP	10	1.0	0.02	150

unbalanced magnetron sputtering system. In order to ensure good coating adhesion a thin Cr interlayer of about 100 nm was applied. After coating process, specimens were ultrasonically cleaned in ethanol, dried in air and then subjected to tribological contact. Specimens' designations and corresponding contact conditions are listed in Table 1.

Tribological testing was done under lubricated reciprocating sliding conditions, with a standard 10 mm diameter steel ball bearing (750 HV, $R_a = 0.02\ \mu m$) used as the oscillating counter-body. Lubricants employed were based on poly-alpha-olefin oil (PAO 8, ν_{40} of 46.6 mm^2/s) and mixed with sulphur-based extreme-pressure additive or sulphur-phosphorous based anti-wear additive. Additives were added in concentrations of 1 and 10%. Sliding tests were performed at normal load of 10 and 250 N, corresponding to a maximum initial contact pressure of 1 and 3 GPa, relative sliding speed of 0.02 and 0.15 m/s and testing temperature of 50 and 150 °C. Each test was run for a total sliding distance of 150 m. Details about tribological testing, tribological properties as well as on the relationships between lubricant compositions, testing conditions and tribological properties of the CrN hard coatings can be found in [17].

2.2. Surface analysis

After tribological tests, coated CrN disc specimens were cut in $10 \times 10 \times 3\ mm^3$ platelets for further surface analyses of formed tribofilms and ultrasonically cleaned in ethanol. Test specimen platelets ($10 \times 10 \times 3\ mm^3$) were fixed onto sample holders for XPS investigations by means of UHV compatible double-sided adhesive silver sheets. Sample holders with samples were introduced into the UHV main vacuum chamber of the *VG-Scientific Microlab 310F* SEM/AES/XPS apparatus via fast entry air-lock. Sample surfaces were imaged by SEM. XPS measurements were performed as simplified depth profiling of the samples with only a few levels at increasing sputtering times, mainly to check the effects of surface cleaning. For sputtering, Ar^+ beam of 3 keV at 0.8 μA ion current over the $5 \times 4\ mm^2$ area was used. Estimate for sputtering rate at these parameters is approximately 0.2 nm/min, as measured on SiO_2 thin layers of known thickness (100 nm). For all XPS measurements Mg Kα radiation at 1253.6 eV from twin Mg/Al source with at anode voltage × emission current = 12.5 kV × 16 mA = 200 W power was used. C 1 s beneficial contamination peak at 284.7 eV was used for energy scale calibration. Pass energies of 20 and 100 eV were used for survey and high resolution measurements. Step size used in high resolution measurements was 200 meV with up to 20 scans averaged in measurement of one spectrum. Measurements and data acquisition were controlled by *Avantage 3.41v* data acquisition & data processing software supplied by the SEM/AES/XPS equipment manufacturer. Commercially available *Casa XPS* software for XPS and AES data processing [18] was also used, especially for further data processing, like e.g. fitting of high resolution peaks by components corresponding to different chemical states of elements.

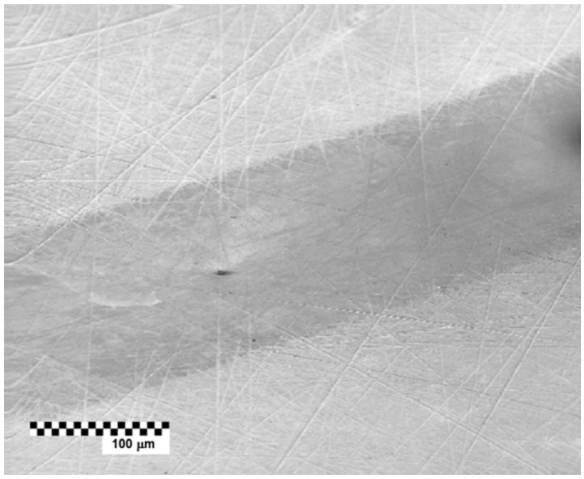

Fig. 1. Low magnification SEM image of CrN surface after 1200 s of sputtering; darker wear track from tribological testing is clearly visible.

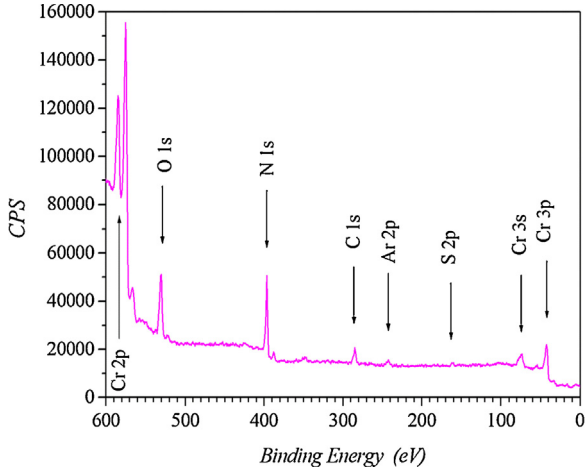

Fig. 2. 0–600 eV range of the XPS survey spectrum characteristic of the CrN wear track surface. All relevant peaks are identified. Ar 2p appears due to Ar implanted after 1200 s of Ar^+ sputtering.

3. Results and discussion

SEM image in Fig. 1 shows tribological testing wear track on the CrN surface after maximum sputtering time (1200 s). The track shows as darker band of approximately 120 μm width on lighter surface that was not subject to tribological contact. In Fig. 2 typical survey XPS spectrum of an investigated sample after maximum sputtering time is shown. All peaks relevant for this study are identified. These survey spectra were used to confirm expected compositions of the sample and, even more important, to obtain information about relative intensities of the peaks, thus assisting to determine HR XPS measurement parameters.

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