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Frictional properties of self-adaptive chromium doped tungsten–sulfur–carbon coatings at nanoscale

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ABSTRACT

Transition metal dichalcogenides (TMD) are excellent dry lubricants forming thin (~10 nm) tribolayer that simultaneously protects the coating from environmental attack and provides low friction. In this paper, we focus on nanoscale frictional properties of chromium doped tungsten–sulfur–carbon (WSC–Cr) coatings with various Cr content. Friction force microscopy was used to investigate friction force as a function of load. A non-linear contact area dependence on the normal force was observed. The calculated interfacial shear strength was relatively low in the region of 70–99 MPa. Friction coefficient decreased with increased applied load independently of chromium content in the coatings.

1. Introduction

Macroscopic tribology often focuses on determining the friction coefficient and wear rate for materials. Neither friction coefficient nor the wear rate are intrinsic physical property of the material in question, and both depend on the specific structure, chemistry, elastic/plastic properties of surfaces, as well as the environment in which measurements are performed, mechanics of instrument, etc. Nanometer-scale measurements of friction and intermolecular forces can disentangle the complex factors contributing to friction. Atomic force microscopy (AFM) can be used to measure normal and lateral forces at the nanometer scale and, thus, represents a powerful tool for probing the microscopic mechanisms of friction [1–3]. Studies of friction between probe tips and different surfaces have yielded a number of interesting observations, including atomic scale stick–slip motion [2,4], friction force dependence on contact area [3,5–12], or the dependence of functional groups such as COOH, CH_3 on friction [8,13].

Friction (also known as lateral) force microscopy (FFM, LFM) is often used to study nanoscale tribological properties of lamellar solid lubricants such as niobium diselenide ($NbSe_2$), molybdenum oxide (MoO_3), molybdenum disulphide (MoS_2), graphite and graphene, as well as non-layered carbon-based solids [9–11,14–18]. Most of those layered materials are used as solid lubricant films in engineering applications to reduce friction. Transition metal dichalcogenides (TMD), such as MoS_2 or WS_2, are excellent lubricants in vacuum and dry atmospheres. However, their tribological behaviour deteriorates in the presence of water vapour due to rapid oxidation. Moreover, TMD coatings deposited by sputtering, which is one of the most used and convenient methods, are soft and porous with limited load-bearing capacity. Among many attempts to improve TMD mechanical and tribological properties (e.g. co-sputtering with metals or compounds), the design of TMD coatings co-deposited with carbon (MoSeC [19,20], WSC [19,21,22]) emerges thanks to their unique self-adaptive structure. Such coatings produce during sliding a thin TMD tribolayer with basal planes parallel to the sliding direction; the tribolayer simultaneously protects the coating from environmental attack and provides low friction. Thickness of the tribolayer is typically lower than 10 nm, which makes its analysis very challenging.

In this paper we will focus on nanoscale frictional properties of as-deposited WSC–Cr coatings with different Cr content.

2. Experiment

2.1. Coating characterization

The W–S–C–Cr films were deposited using an r.f. magnetron sputtering chamber (Edwards, UK); the deposition conditions are in detail given in Ref. [22]. Prior to the coating deposition, the

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substrates were cleaned by establishing the plasma close to the substrates electrode for 20 min. Two targets were used: chromium (purity 99.9%) and carbon (graphite, purity 99.6%) with WS_2 pellets (purity 99%) placed on its erosion zone. The number of WS_2 pellets was determined empirically to obtain approximately 40 at.% of C in a deposition without Cr. The Cr content was controlled via the power applied to each target. A pure Cr interlayer was deposited on the substrates before every coating deposition, to improve adhesion.

The coatings were deposited on polished W.Nr. 1.2379 (X153CrMoV12; AISI D2) steel substrates (Ra < 30 nm, diameters of 50 and 22 mm, hardness 9 GPa) used for macroscopical tribological measurements and on Si wafer used in presented study.

The chemical composition of the coatings was evaluated by electron probe microanalysis (EPMA). Hardness (H) and reduced modulus (E_r) values were determined by depth-sensing indentation and adhesion was evaluated by progressive load scratch tests. The chemical bonding of the films was analyzed by Raman spectroscopy (DPSS laser, wavelength 532 nm), Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS; MgKα radiation). The structure was analyzed by X-ray diffraction (CuKα radiation) and by transmission electron microscopy (TEM); the morphology was observed by scanning electron microscopy (SEM).

2.2. Friction measurements using AFM

Measurements of surface topography and lateral force were performed in air at room temperature using atomic force microscope (MAC Mode III, 5500 Scanning Probe Microscopy, Agilent Technologies, US). PicoView 1.12 and PicoImage Basics 6.0 (Agilent Technologies, US) software were used for data acquisition and image analysis, respectively. Standard lateral force mode silicon probes (NanoWorld, distributed by Windsor Scientific, UK) with nominal spring constant of 0.2 N/m and tip radii of 8–10 nm were used. Actual spring constant values for every cantilever were obtained using built-in thermal noise method [23]. The measured constant varied in the range 0.2–0.45 N/m. Normal forces were calibrated by measuring the deflection sensitivity (nm/V) from the slope of the linear part of a force–displacement curve obtained on a flat silicon surface. The normal force, F_N, was set to be zero at the point where the cantilever left the surface. Calibration of lateral forces using commercially available gratings was achieved using the "wedge calibration method" according to Ogletree et al. [24]. The probe geometry was obtained from the reconstruction of the tip shape from imaging of a calibration sample consisting of sharp Si spikes, TGT1 (NT-MDT, cone angle 50°, Moscow, Russia) [25]. The spikes have very small radii and a cone half angle similar to an angle of AFM probe. Therefore, the image of the spike is virtually the image of the AFM tip representing more precise probe geometry. A reconstruction algorithm presented in Refs. [25,26] was built-in the PicoImage analytical software and was applied to recover the shape of the cantilever tip. The geometric mean radius of the tip was calculated by fit of a circle on the top of deconvoluted image profile. All calibration procedures were done before and after friction experiments. Tip radii were measured to be 8 ± 2 nm and 20 ± 3 nm before and after the experiments, respectively.

For the friction measurements the instrument was operating in contact mode with the long cantilever axis perpendicular to scanning direction. The lateral deflection was adjusted so that it was zero with the tip out of contact with the surface. The normal applied load varied from 0 to 80 nN. For each load, topography and friction maps over areas of 1 μm × 1 μm consisting of 512 lines were recorded at scanning speed of 3.99 lines/s. Friction forces were determined from trace–retrace loops acquired along single lines by subtracting and halving mean signals as described in Ref [1]. Surface area roughness of each sample was determined from topographical images of the size of 10 μm × 10 μm using PicoImage software. Mean surface roughness, S_a (arithmetic mean height deviation), related to the analysis of 3D areal surface texture, was calculated according to ISO 25178 standard using Gaussian filter 0.008 mm.

3. Results and discussion

3.1. Coating composition, structure and mechanical properties

Three series of coatings were deposited, two with different Cr content and WSC as a reference. The chemical composition measured by EPMA is shown in Table 1. To facilitate reading, we denominate coatings as WSC–Cr-X, where X is the chromium content. The WSC–Cr coatings thickness increased with chromium content from 1.7 to 2.4 μm including the 300 nm thick Cr interlayer improving adhesion. Coating structure and mechanical properties were described in detail in our previous paper [22] and, thus, we will just summarize the results here. XRD analysis of WSC coating showed very broad peak at $2\theta \approx 40°$ with an extended shoulder corresponding to a turbostrating stacking of (10L) planes (L = 0, 1, 2, 3), and peak at $2\theta \approx 70°$ indexed as (1 1 0) planes. Such spectrum is typical for structure with the lateral order of the basal planes not exceeding a couple of lattice parameters [21]. TEM observation supports XRD results showing randomly oriented separated WS_2 platelets embedded into a carbon matrix (Fig. 1). Co-sputtering of Cr with WSC led to completely amorphous structure, see Fig. 1. Surface topography of coatings measured with AFM is shown in Fig. 2 and corresponding areal surface roughness is given in Table 1. Addition of Cr resulted in the formation of larger columnar structures and correspondingly rougher surface.

XPS was carried out after sputter cleaning of approx. 5 nm of coating material. We identify W—S and W—C bonds together with small fraction of W—O bond. Chromium showed two peaks close to metallic Cr and Cr—O bond; however, binding energy of chromium carbide is very close to that of metal, so we cannot rule out the existence of Cr—C bond. Sharp WS_2 peaks observed on Raman spectrum of WSC–Cr-0 coating almost disappeared in spectra of chromium-containing coatings, which corroborates TEM observation.

Hardness and reduced elastic modulus of the coatings is given in Table 1. Doping of WSC with chromium led to higher hardness values, since easy shear of WS_2 platelets existing in W–S–C film was eliminated due to amorphous nature of WSC–Cr coatings.

3.2. Friction measurements

A large number of published works have indicated that AFM tip can form single asperity contact with the sample surface [2,3,6,7,9,10]. The measurements are usually performed in low load regime where tip–sample interaction during frictional sliding is believed to be completely elastic [2,4]. According to single-asperity theories based on continuum mechanics, friction force in solid–solid nanocontacts is proportional to the true contact area [2–4,6,7,27]. Therefore, the friction force, F_f, for single asperity contact is given by:

$$F_f = \tau A \tag{1}$$

where A is the contact area and τ is the interfacial shear strength, which represents the frictional force per interfacial atom. Typically, single-asperity contact area does not vary linearly with load. A model for non-adhesive contact developed by Hertz [28], showed that $A \propto F_N^{2/3}$. It is in a contrast to the dynamic contact of surfaces at macroscale, where friction force depends linearly on the normal load, F_N, $F_f = \mu F_N$, where μ is the friction coefficient. The contact