



Regular Article

Stages in the tribologically-induced oxidation of high-purity copper

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ARTICLE INFO

Article history:

Received 30 January 2018

Received in revised form 30 April 2018

Accepted 5 May 2018

Available online xxxx

Keywords:

Tribology

Copper

Oxidation

Transmission electron microscopy (TEM)

Energy dispersive X-ray spectroscopy (EDXS)

ABSTRACT

Surface modification through tribological loading is understood as a mechanically driven process. Yet, potentially complex chemical reactions can be critical since their products influence contact mechanics and affect friction and wear. Here we investigate the tribologically driven surface oxidation of pure copper in contact with a sapphire sphere. Different electron microscopy techniques reveal the formation of (amorphous) patches of copper oxide after very few loading cycles and their growth to semicircular amorphous/nanocrystalline cuprous oxide clusters under tribological loading. Understanding this elementary mechanism is of the utmost importance for a strategic tailoring of materials' microstructures for superior tribological performance.

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Tribology has a long history as a transdisciplinary field, attracting researchers from materials science, contact mechanics, surface chemistry, and fluid dynamics [1]. This is particularly true for metallic materials as they are ubiquitously used in engineering components [2,3] or artificial limbs and joints [4]. Since Bowden and Tabor's seminal contribution that the coefficient of friction (COF) is a function of the strength of the metals constituting the contact [5], tribological studies focused on the microstructure of the material underneath the contacting surfaces, uncovering that these microstructures are highly dynamic [6–9]. The elementary mechanisms behind several tribologically induced microstructural changes have been revealed [10–15] and computational materials science helped to understand the sliding contact at the atomic scale [16–18].

Tribologically modified microstructures are commonly observed as different layers in the subsurface area, often referred to as “tribolayers” [6,9,11,14,15,19–24]. These layers are critical because their microstructure determines the tribological performance of the material [22,23], as recently described in a feedback loop between friction force, contact stress and microstructure [19]. Among these tribolayers, the most important one is the top layer, because it is in direct contact with the counter body and the environment; it is where friction is mainly determined and wear is generated [25]. Tribological performance can be

significantly improved by controlling the chemical and mechanical properties of this top layer [26–28].

The potentially complex chemical composition of a tribological contact (two contacting bodies and optional lubricants), significant local stresses, uncertain local temperature, and mechanically driven chemical reactions may govern the contact [29]. The contact area therefore may be made up of materials with significantly different mechanical properties as well as chemical compositions, compared to the initial contacting bodies [24]. In case the surface layers are much harder than the bulk material, cracks are more likely to be initiated at the interface between these layers, leading to a higher wear rate [30] and potentially high friction forces, e.g., the high friction regime between pure aluminum and stainless steel [31]. In mechanically softer surface layers, some of the sliding energy is dissipated to grow and plastically deform the tribolayers [16]. This is in competition to the generation of wear particles and cracks are less likely generated in the top layers [32]. This is why aluminum silicon alloys build up a silicon-rich top layer and show improved friction and wear performance [33]. However, the pathway for the development of such a chemically different layer still is elusive. Here, we embarked on investigating the microstructural and chemical changes inside the top layer for mild sliding conditions. Using pure copper in contact with a sapphire sphere as a model tribological system and surface oxidation as the subject of our investigation, our aim is to shed light on the mechanisms for the formation of tribologically induced surface oxides.

Annealed oxygen-free high conductivity (OFHC) copper samples (Goodfellow, Friedberg, Germany) were electro-polished right before

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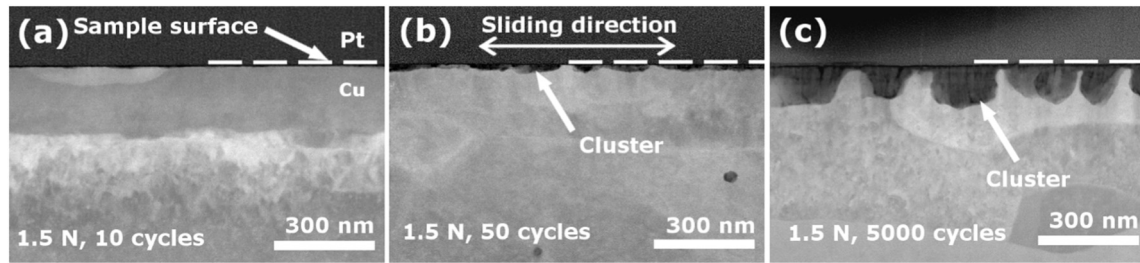


Fig. 1. STEM images of nanocrystalline/amorphous copper oxide clusters at OFHC copper surfaces after different numbers of reciprocating cycles (HAADF mode). (a) 10 cycles; (b) 50 cycles; (c) 5000 cycles. The TEM foils were prepared in the middle of the wear tracks, along the sliding direction perpendicular to the sliding surface. The contrast above the samples' surfaces stems from the protective platinum layer.

the tribological tests to produce a surface with minimal pre-test oxidation from the environment and no plastic deformation (demonstrated by the STEM image in Fig. S1a in the Supplementary Material). Sapphire spheres with a diameter of 10 mm (SWIP, Bruegg, Switzerland) were used as counter bodies. More details of our sample preparation are given in [15].

Tribological tests were performed on a reciprocating linear tribometer [34] (Fig. S1b). The normal load was 1.5 N with a corresponding Hertzian pressure of around 480 MPa (with a Young's modulus/Poisson ratio of copper 117 GPa/0.34 and sapphire 345 GPa/0.30). The sliding speed was kept at 0.5 mm/s. The experiments were performed without any lubricant in air at a relative humidity of 50% at room temperature. The coefficient of friction is plotted against the sliding cycle number (Fig. S2). Surfaces were investigated after 10, 50 and 5000 reciprocating sliding cycles to systematically investigate the early and late stages of surface oxidation.

Cross-section transmission electron microscopy (TEM) specimens were extracted using a focused ion beam/scanning electron microscope (FIB/SEM, FEI Helios 650, Hillsboro, Oregon USA) [35]. The preparation was performed immediately after the tribological tests, to avoid possible oxidation during sample storage. The TEM-specimens were prepared in the center of the wear tracks, along the sliding direction, perpendicular to the sliding surface (cross-sectional view, Fig. S1c).

The subsurface microstructure was investigated with an FEI Titan³ G2 80-300 TEM at an acceleration voltage of 300 kV. For details on the applied characterization techniques, including TEM imaging, energy dispersive X-ray spectroscopy (EDXS) and nano-beam diffraction (NBD) please see the Supplementary Materials.

Fig. 1 presents STEM images in HAADF mode for samples after 10, 50 and 5000 sliding cycles. Compared to BF and DF, HAADF yields the most contrast induced by an atom mass difference between the different elements constituting a material (Z-contrast), and is ideal for observing differences in chemical composition. After ten sliding cycles (Fig. 1a), there

is no drastic HAADF contrast change, indicating that no chemical modification can be observed (see Fig. S3). After 50 sliding cycles (Fig. 1b), a wavy and discontinuous layer appears at the sample surface with a thickness of around 30 nm. The wavy shape stems from semicircular features (henceforth referred to as “clusters”) which make up this layer. The darker contrast inside this layer strongly suggests a different chemical composition compared to the bulk material underneath and an average atom mass smaller compared to pure copper. After 5000 cycles (Fig. 1c), the semicircular clusters are clearly observed in form of the darker contrast appearing at and below the sample surface.

To reveal the microstructure of the clusters in more detail, (HR)TEM was applied to a sample after 50 cycles (Fig. 2). Fig. 2a presents one of the clusters in BF contrast. Fig. 2b is a DF image of the same area. To illuminate the crystals in the materials, a DF image was taken by shifting the aperture away from the central beam. Areas with bright contrast can be observed inside the cluster suggesting the same crystallographic orientation of these parts of the cluster. This strongly hints to the existence of crystalline structures inside the clusters. The HRTEM image (Fig. 2c) taken inside the cluster (area marked by a red rectangle in Fig. 2b), shows evidence of a nanocrystalline structure in a possibly amorphous matrix.

The distribution of copper and oxygen after 50 cycles of sliding is shown in a subsurface area including two clusters (Fig. 3). The mapped area as well as the two windows in which the EDXS spectra were taken are shown in the STEM image (Fig. 3a). The contrasts observed in these EDXS maps give a quasi-quantitative distribution of these elements in the area of Fig. 3a. The clusters appear to be oxygen-rich and copper-poor. The EDXS spectra for different ranges in X-Ray energy in Fig. 3d + e demonstrate that there is no significant amount of any other element inside the clusters, indicating the formation of copper oxides. This, and especially the lack of aluminum, strongly suggests that there was no mechanical mixing between copper and sapphire (Al_2O_3). The absence of copper on the sapphire sphere (Fig. S4) agrees very well

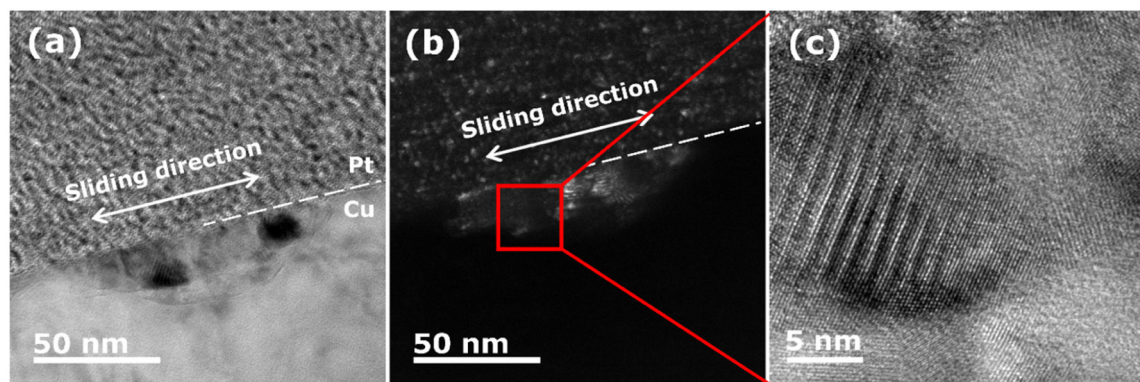


Fig. 2. (HR)TEM images of a nanocrystalline/amorphous oxide cluster at an OFHC copper surface after 50 cycles. (a) Bright field image; (b) dark field image using one of the diffraction beams; (c) HRTEM image from the area in the red rectangle in (b). The results are taken from the same foil as the one presented in Fig. 1b. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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