Thin Solid Films 517 (2009) 5516–5522

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Nanostructural, electrical, and tribological properties of composite Au–MoS_2 coatings

Jeffrey R. Lince [a,*], Hyun I. Kim [a], Paul M. Adams [a], Daniel J. Dickrell [b], Michael T. Dugger [c]

[a] Space Materials Laboratory, The Aerospace Corporation, El Segundo, CA, USA
[b] Department of Mechanical Engineering, University of Florida, Gainesville, FL, USA
[c] Materials Science and Engineering Center, Sandia National Laboratories, Albuquerque, NM, USA

ARTICLE INFO

Article history:
Received 4 June 2008
Received in revised form 20 February 2009
Accepted 30 March 2009
Available online 6 April 2009

Keywords:
Nanocomposite films
Solid lubricant
Molybdenum disulfide
Sliding friction
Electrical contacts
Sputter deposition
X-ray diffraction
Auger electron spectroscopy

ABSTRACT

Considerable research has been done on the tribological properties of cosputtered metal/MoS_2 solid lubricant films with low metal content (<20 at.%) because of their usefulness in applications at high Hertzian contact stress (around 1 GPa). However, cosputtered Au–MoS_2 coatings with a much higher range of metal contents up to (95 at.%) have shown surprisingly good performance at low contact stresses (as low as 0.1 MPa). In the present study, transmission electron microscopy, X-ray diffraction and electrical resistance measurements of cosputtered Au–MoS_2 coatings reveal them to be composites of nanocrystalline Au particles within an amorphous MoS_2 matrix. Electrical conductivity images of the coatings displayed metallic (Au) and semi-conducting (MoS_2) domains of nanometer dimensions. Auger Nanoprobe analyses confirmed that sliding on the coatings causes the formation of a pure MoS_2 layer about a nanometer thick on top of the bulk of the coatings. Lattice resolution atomic force microscopy revealed that this nanometer-thick MoS_2 layer is crystalline, and oriented with the basal plane (0001) parallel to the coating surface. Electrical resistance obtained during sliding and pull-off force measurements was consistent with the structure of the coatings. Sliding friction data on the coatings support previous results showing that performance at different Hertzian contact stresses correlated strongly with Au content.

1. Introduction

Physical vapor deposited MoS_2-based coatings have been shown to exhibit superior tribological properties when mixed with small amounts of metals or inorganic compounds (generally <20%) using sputter-deposition [1–10] or other ion-based deposition techniques [11]. They are typically used in the high contact stress regime, i.e. 200 to 2000 MPa, for applications like ball bearings on spacecraft [6–8], and for terrestrial machining applications [9].

We published results on an earlier study of sputter-deposited Au–MoS_2 coatings including considerably higher metal additive contents than had been studied previously, over the entire range of Au contents from 0 to 100 at.% (i.e., pure MoS_2 and pure Au, respectively) [12]. Prior to this work, the highest metal content studied was 53 at.% [5]. In addition, we reported on the use of these coatings at much lower Hertzian contact stresses than previously studied (i.e., 0.1 MPa). Optimum performance (i.e., the lowest friction and highest endurance) at low contact stress was obtained for Au contents in the range of approximately 75 to 90 at.%. These results suggest that these coatings would be attractive for electrical contact applications such as slip rings on spacecraft [13,14], switches, and potentiometers, because their high metal contents yield low electrical resistance in sliding contact.

In the present study we investigated the electrical properties of the coatings during tribological action. Both sliding friction measurements and pull-off force measurements (i.e., motion parallel and perpendicular to the surface) were obtained. In addition, testing was done at contact stresses different than the previous study to further explore the relationship between optimum Au content and tribological performance. To investigate tribology on the nanoscale, atomic force microscopy (AFM) studies were conducted on the coatings.

The nanostructure of these coatings has not been adequately studied, especially for higher metal additive contents. In addition, their structures and crystallinity can vary with details of the deposition process. In the present study, we used transmission electron microscopy (TEM) and X-ray diffraction (XRD) to elucidate the nanostructure and crystallinity of Au–MoS_2 coatings. The nanostructure is correlated to both the tribological and electrical properties of the coatings.

2. Experimental method

Au–MoS_2 coatings were deposited onto hardened 440C steel disks for pin-on-disk tribometer testing at low and high contact stresses. They were deposited onto polished Si wafers for pin-on-disk testing at intermediate contact stresses, pull-off force testing, TEM, XRD analysis, and AFM. Silicon wafers were cleaned using isopropyl alcohol and dried with nitrogen prior to loading in the deposition chamber. Hardened 440C steel disks were polished to $R_a \approx 0.03$ μm roughness,

* Corresponding author.
E-mail address: jeffrey.r.lince@aero.org (J.R. Lince).

0040-6090/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2009.03.210

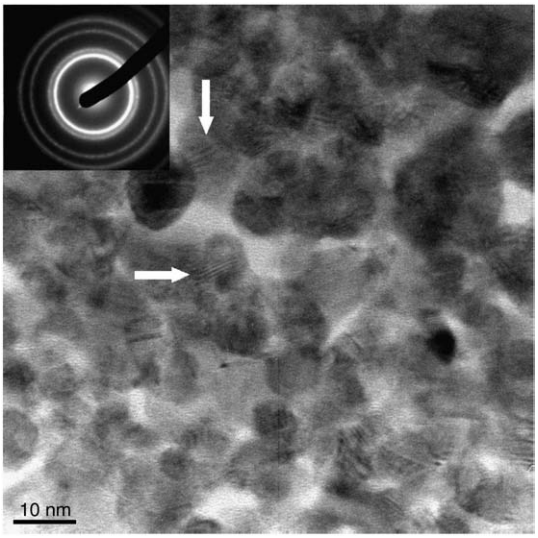

Fig. 1. A plan view transmission electron micrograph of a Au–MoS_2 coating with 59 at.% Au. The arrows indicate Moiré fringes that correspond to crystalline Au. No crystalline MoS_2 phases were seen.

degreased in heptane, and then cleaned in Brulin 815GD detergent (diluted in H_2O), followed by rinsing in distilled H_2O, and drying with nitrogen gas. After cleaning, the samples were then installed into a custom sputter-deposition system. Samples were introduced into a load lock chamber and turbomolecular pumped to a pressure below 1.33×10^{-5} Pa (1×10^{-7} Torr). They were then moved into the main deposition chamber, which is also turbomolecular pumped, and has a base pressure of 1.33×10^{-7} Pa (1×10^{-9} Torr). The system is fitted with three radio frequency sputtering sources, which can be swiveled, and for this study were pointed toward the center of the substrate table. A Au target and a pressed powder MoS_2 target were installed into two of the sources (10.2 cm in diameter). The sources were operated in an unbalanced mode to increase the ion flux on the substrate surface during deposition (the actual ion flux was not measured). Samples were mounted at the center of the table, which rotated during deposition to ensure film uniformity. Argon (99.999% nominal purity) was used as the sputtering gas, which was passed through an Aeronex Gatekeeper® getter (reduces O_2, H_2O, CO, CH_4, and other impurities to less than 1 ppb) before being introduced into each sputtering source. The gas flow rates were controlled using mass flow transducers. The Ar pressure in the chamber during deposition was generally 4 Pa (3×10^{-3} Torr). The Au and MoS_2 sputtering power densities were varied between 1 to 2.5 W/cm^2 to achieve films with varying Au:MoS_2 concentration ratios.

Composition analysis of the films was conducted semi-quantitatively via Auger sputter depth profiling using a PHI 680 Auger Nanoprobe. Ar gas was used as the sputtering gas, and approximate elemental compositions were determined by correcting the Auger electron intensity for each element using correction factors provided by PHI (incorporated into the analysis software). Because of preferential sputtering effects, there are significant systematic errors (as much as about 20 at.%) using this method, although it is useful for determining run-to-run composition variations. Improved compositions were determined subsequently using Rutherford backscattering spectrometry (RBS) at Evans Analytical Group. RBS uncertainties were 0.5 at.% for Mo and Au, and 1 at.% for S.

X-ray diffraction was conducted using a PANalytical X'Pert Pro diffractometer, with Cu-Kα radiation as the source. The angle between the surface and the incident X-rays (ω) was set to either 2° or 13° to achieve varying surface sensitivity. X-ray diffraction scans were obtained by scanning the detector in 2θ. Transmission electron microscopy results were obtained using a Hitachi H-9000 NAR transmission electron microscope operated at 300 keV electron energy. Plan views were prepared by standard dimpling and ion milling procedures.

Previous high and low contact stress friction/wear testing results were obtained from a CSEM pin-on-disk tribometer. The lower specimens (disk) were the Au–MoS_2-coated samples. The upper specimens for the high contact stress (ball-on-flat) tests were uncoated 6 mm diameter 440C steel balls (grade 3, $R_a = 0.01$ μm). The upper specimens for the low contact stress (flat-on-flat) tests were uncoated polished 6.4 mm diameter 440C steel flats. For all tests, a 5 N load was used, giving nominal mean Hertzian contact stresses of $S_m \approx 730$ MPa (106,000 psi) for the high contact stress tests, and $S_m \approx 0.1$ MPa (15 psi) for the low contact stress tests. The sliding speed was 8 cm/s and the tribometer enclosure was purged with nitrogen gas during the tests (relative humidity was reduced to below 1% RH). Further experimental details of this testing are presented elsewhere [12].

Additional sliding friction testing was conducted using a reciprocating linear wear test apparatus. The lower specimen was a Au–MoS_2 coating deposited on a polished Si(100) wafer, while the upper specimen was a Au-coated glass lens with a 184 mm diameter. The load was 5 mN, giving a nominal mean Hertzian contact stress of 8.5 MPa (1200 psi). The sliding speed was 1 cm/s. A sourced current of 1 mA was imposed between upper and lower specimens, and the voltage drop across the contact was read, allowing the resistance to be obtained. The open-circuit voltage was constrained to 1 V when the specimens were not in contact.

Electrical resistance and pull-off force measurements were obtained using a Nano UTM from MTS. The lower specimen was a Au–MoS_2 coating deposited on a polished Si(100) wafer, while the upper specimen was a Au-coated Si_3N_4 ball with a 1.6 mm diameter. The load was 100 μN, giving a nominal mean Hertzian contact stress of 30 MPa (4400 psi). Here also, a current source of 1 mA was imposed between upper and lower specimens with a 1 V open-circuit voltage constraint. The voltage drop across the contact was measured and allowed the contact resistance to be calculated. Multiple make-and-break contacts were made.

A Au–MoS_2 coating with 75 at.% Au was analyzed in an Omicron UHV VT AFM system under a 3×10^{-10} Torr (4×10^{-8} Pa) vacuum at room temperature. The sample was probed in contact mode while a bias voltage was applied to the conducting AFM probe, with the substrate grounded through the sample stage. Both Pt- and WC-coated Si tips were used for the conductive imaging studies. The normal and lateral deflections of the cantilever were monitored as well as the electrical current across the tip/sample interface in order

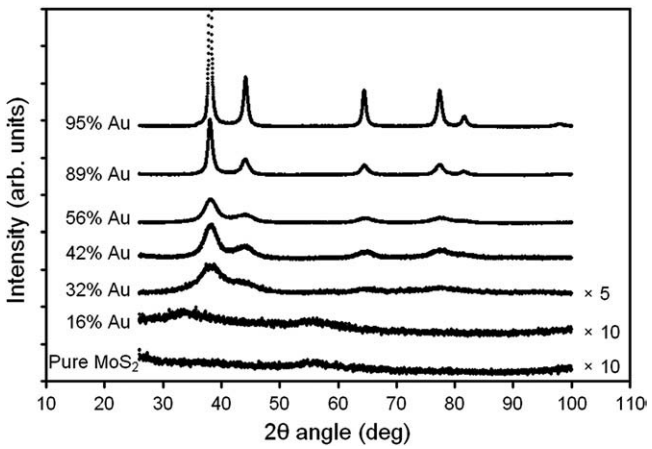

Fig. 2. X-ray diffraction scans for sputter-deposited MoS_2 and Au–MoS_2 samples with varying amounts of Au ($\omega = 13°$). The appearance of Au reflections indicates that Au is present as a crystalline phase. No reflections for MoS_2 are seen, indicating that MoS_2 is amorphous in the coatings.