Wear 278–279 (2012) 62–70

Contents lists available at SciVerse ScienceDirect

Wear

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

Residual stresses, interfacial adhesion and tribological properties of MoN/Cu composite coatings

K.E. Pappacena[a,*], D. Singh[b], O.O. Ajayi[a], J.L. Routbort[a], O.L. Erilymaz[a], N.G. Demas[a], G. Chen[c]

[a] Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439, USA
[b] Nuclear Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA
[c] Department of Physics and Astronomy, Ohio University, Athens, OH 45701, USA

ARTICLE INFO

Article history:
Received 13 May 2011
Received in revised form
29 December 2011
Accepted 3 January 2012
Available online 12 January 2012

Keywords:
Tribology
Molybdenum nitride
Adhesion energy
Residual stress
Wear

ABSTRACT

Ceramic thin film coatings, such as MoN/Cu, are attractive for engine applications due to their low friction, high hardness and high wear resistance. However, there is a need to establish a reliable connection between the deposition parameters of the thin film and its tribological performance. In this study, two coating compositions, MoN and MoN with Cu were deposited on H-13 tool steel substrates in order to correlate compositional variables that result from processing to their respective tribological properties. The efficacy of the coating in protecting surfaces is highly dependent on its adhesion to the substrate and its tribological properties. Residual stresses resulting from the coating deposition were evaluated using an X-ray microprobe. Scratch testing was performed to measure the coating adhesion energy, and the wear rate was determined using a ball-on-flat contact configuration on a high frequency reciprocating test rig. It was observed that coatings with lower copper content performed better in the wear test and exhibited higher coating adhesion energy. A primary wear damage mechanism was coating removal by delamination and spallation, which is related to the adhesion energy. Since coating processing variables determine the structure and properties, and hence affect the tribological properties of these MoN based coatings, these parameters can be used to optimize coating composition for enhanced tribological performance.

1. Introduction

Thin film coatings are useful for protecting materials from corrosion and abrasion in cutting tools, medical implants, microelectromechanical devices, spacecrafts, and engines. Particularly in vehicle system engines, hard thin film coatings can be used to reduce friction and wear, which can increase fuel efficiency. In other machine element components where sliding and rolling contacts are prevalent, these coatings can also protect the surfaces from various tribological damage because of their high wear resistance. The performance and durability of these coatings, particularly for engine and machine component related applications, are strongly dependent on their adhesion and tribological behaviors.

Ceramics, particularly nitrides and carbides, are popular materials for these tribological coatings due to their typically high hardness and modulus values, which are generally indicative of high wear resistance. Often, the coatings are deposited onto the substrate surface via a high temperature deposition process, which can result in thermal residual stresses upon cooling. Residual stresses can be intrinsic or extrinsic in nature [1]. Intrinsic residual stresses in the coating arise from the deposition process and depend on processing variables such as deposition temperature, gas pressure, deposition power, and bias conditions [2]. Extrinsic residual stresses, however, are generated from thermal expansion mismatch between the coating and the substrate. Residual stresses may also be present due to the intrinsic interfacial relationship between the coating and the substrate. The presence of such residual stresses can have a significant impact on the tribological properties of the system, including the adhesion of the coating to the substrate and the wear resistance.

Molybdenum nitride ceramic coatings in particular, with and without copper additions, have been investigated previously for such applications [3–11]. These coatings have been shown to have superior wear resistance compared to TiN type coatings [10]. Copper has been used as an addition because it is expected to segregate to the grain boundaries, forming a nanoscale, compliant phase [5]. This helps to achieve a material with a high hardness to modulus ratio, reducing the mismatch and enhancing wear and abrasion resistance [12].

This work focuses on correlating the compositional processing variables to the measured residual stress values of two compositions of MoN/Cu coatings deposited on H-13 tool steel substrates.

* Corresponding author. Fax: +1 630 252 5568.
E-mail address: dsingh@anl.gov (D. Singh).

0043-1648/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.wear.2012.01.007

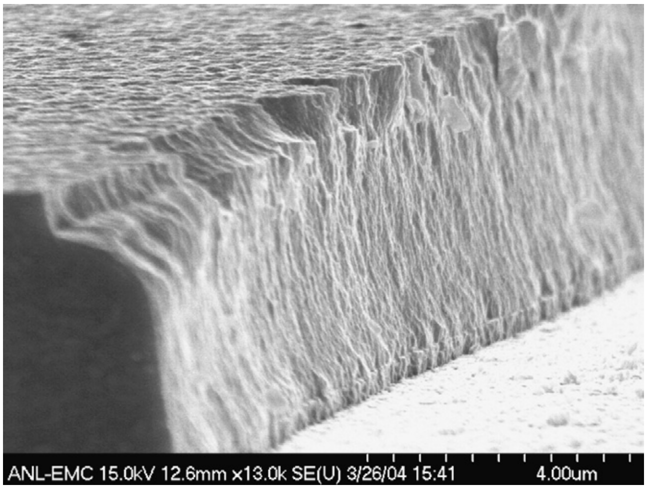

Fig. 1. Scanning electron micrograph of MoN coating deposited on a steel substrate.

Subsequently, the resulting adhesion energy and wear resistance for each of the samples were evaluated. Correlations are made between the residual stresses generated as a result of processing conditions and their effect on coating performance. It is important to monitor not only how these coatings withstand tribological situations, but also how the variations during processing affect the resulting properties.

2. Experimental

2.1. Coating processing

Coatings of MoN with different Cu compositions were deposited onto steel substrates with physical vapor deposition (PVD) using magnetron sputtering (CemeCon CC800-9, Würeslen, Germany). The Mo coating deposition power was 8 kW for each of the coatings. The two Cu deposition powers (and deposition times) were 0 kW (7200 s), and 0.8 kW (7200 s). These samples will be referred to as 0Cu and 8Cu, respectively. A scanning electron micrograph (SEM) of a MoN coating deposited on a steel substrate is shown in Fig. 1. The surface roughnesses (R_a values) of the coatings are 18.4 ± 4.7, and 16.4 ± 7.8 nm for 0Cu and 8Cu samples, respectively.

2.2. Mechanical properties

Hardness and reduced modulus values were determined for both coatings using a nanoindenter (Hysitron TI-950, Minneapolis, MN). Tests were performed at loads of up to 10 mN to a displacement of up to 120 nm. Coating thickness (t) was determined using a Calotest® (CSM Instruments, Needham, MA) for up to 600 s with an 18.8 mm diameter steel ball (d). An example Calotest® performed on the 0Cu sample is shown in Fig. 2 with geometrical parameters x and y labeled. Image J software [13] was used to measure x and y and the coating thickness was calculated using the simple geometrical equation (1):

$$t = \frac{xy}{d} \quad (1)$$

2.3. Residual stress measurements

X-ray microdiffraction, in conjunction with an edge scan approach, was performed on beamlines 2-ID-D and 34-ID-E at the Advanced Photon Source (Argonne National Laboratory) to determine the residual stresses. The X-ray beam was focused by Kirkpatrick–Baez mirrors down to 0.2 (horizontal) μm × 0.3

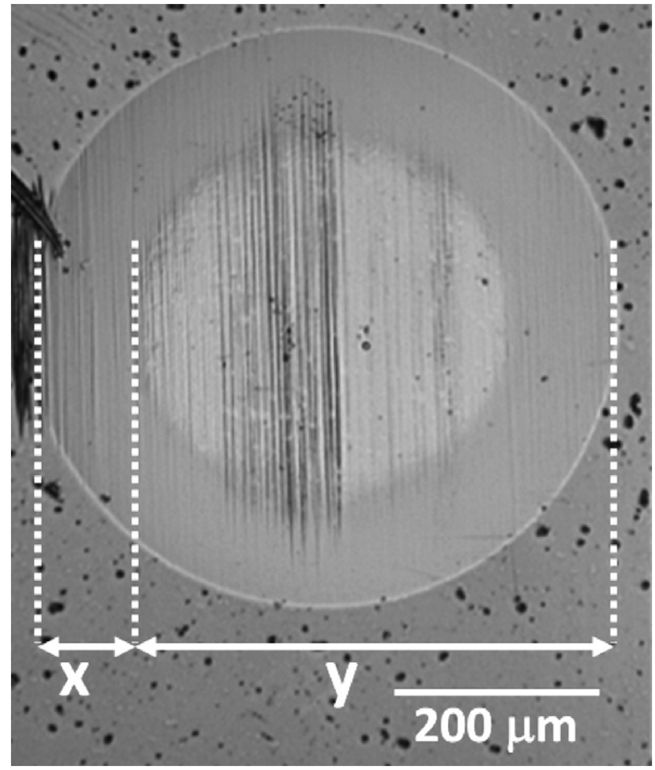

Fig. 2. Typical Calotest® on 0Cu sample with x and y parameters indicated.

(vertical) μm. A high-resolution charged coupled device (CCD) X-ray detector was used to collect X-ray diffraction (XRD) patterns from the X-ray micro-beam with energy of 10.0 keV (1.24125 Å). Strains and stresses were evaluated from the change in the lattice spacing determined from diffraction pattern of MoN (2 2 2) planes from coatings and its stress free state.

A schematic of the edge scan technique is shown in Fig. 3. One of the sample edges was aligned perpendicular to the X-ray beam by an X-ray fluorescence method so that the film surface was parallel to the X-ray beam. After alignment, the sample was scanned with respect to the X-ray beam with a step size of 0.20 μm. In-plane strains were determined by placing the detector such that

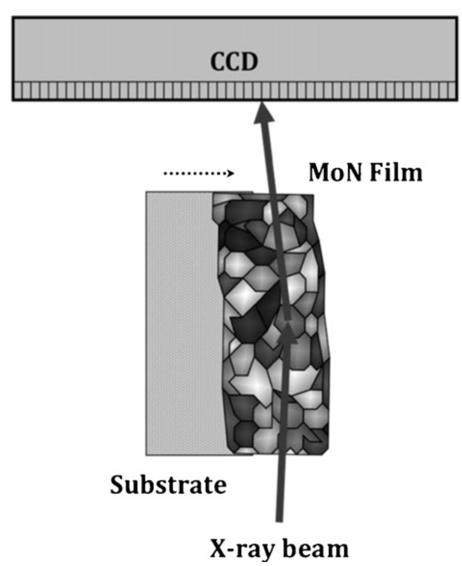

Fig. 3. Schematic of the edge scan technique used to measure residual stresses in the coatings using high energy X-rays.