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Short Communication

Characterization of Molybdenum Based Coatings on 100Cr6 Bearing Steel Surfaces

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Abstract

Energy losses and friction locking are decisive factors in the conceptual design and sustainable realization of machine elements. Thus, the improvement of the tribological properties of rolling bearings by ceramic coatings on bearing surfaces represents a promising approach. These coatings are to be optimally adapted to the load case by minimizing the slip and resulting wear by rolling elements. For this purpose, molybdenum-based coatings were applied by means of magnetron sputtering in a vacuum atmosphere at controlled and adjusted oxygen partial pressure on 100Cr6 axial bearing washers. The effect of diffusing oxygen at near surface areas can be achieved during the physical vapor deposition (PVD) process itself as well as under adequate loading cases, so that a regenerative separation layer prevents high tribological wear at running surfaces. The generated layers were then characterized by high-resolution analysis with regard to morphology, attachment to the substrate and stoichiometry. The adjusted process parameters yielded pure molybdenum, as well as molybdenum oxide, dioxide and trioxide as a function of corresponding oxygen partial pressure. Scanning electron microscopy (SEM) was used for topographical evaluation, X-ray diffraction (XRD) for the characterization of stoichiometry and focussed ion beam cutting (FIB) for coating thickness determination. From selected surfaces, additional energy-dispersive X-ray spectroscopy (EDX) mappings were performed to quantify local oxygen contents at the border area of generated molybdenum layers. To record tribological characteristics, the layers were analyzed for their mechanical properties subsequently. Therefore, nanoindentational studies were carried out, which could provide information on the wear behavior in point contact in the form of nanoclay experiments. The results showed lower coefficients of friction for oxidized surfaces and thus a better resistance against sliding wear than uncoated specimen surfaces.

Keywords

magnetron sputtering, surface analysis, nano tribology

1 Introduction

In current research controlling wear and friction behaviour of machine elements in relative motion to each other is of utmost importance. In order to cope with the growing competition, today's industry places high demands on innovative materials. One of the main targets is to reduce friction and wear, as these annually cause enormous costs in the manufacturing industry. Currently, estimated direct losses due to friction and wear are up to 7% of the gross national product in industrialized countries [1-4]. The current study includes investigations of generated molybdenum based layer systems on ASSI 552100 (100Cr6) bearing washers through magnetron sputtering. To generate different stoichiometries, the oxygen partial pressure was varied corresponding to adequate process temperatures with respect to the annealing temperature of the substrate of 180°C. Generated layer systems were tested regarding their mechanical properties and wear behaviour [5-7].

2 Experimental methods

2.1 Material and preparation

The molybdenum based coatings were deposited on flat surfaces of axial bearing washers made of ASSI 552100. For surface analysis and scratch testing, cylindrical samples (diameter. 14 mm; height: 5 mm) were eroded by wire after the PVD procedure. The surfaces were polished to an average surface roughness of about *Sa* = 0,2 μm with diamond suspension. The roughness did not change significantly after the coating procedure.

2.2 Magnetron sputtering

The magnetron sputtering process was realized under argon/oxygen vacuum atmosphere with two molybdenum targets (target size: 210 mm x 90 mm) which guaranteed sufficient coatings on rotating flat surfaces of the bearing washers. By increasing the mass flow of oxygen at varied deposition power, different stoichiometries of molybdenum and oxygen were adjusted. The deposition time was 150 min for all procedures which were conducted under oxygen atmosphere, while pure molybdenum was sputtered for 90 min. The temperature of the substrate was 60°C at a constant target power of 1500 W. Prior to the sputtering process, a rf-cleaning plasma (power: 650 W at a frequency of 13.56 MHz) was used, to remove the surfaces from condensates and contaminations. The adjusted mass flows of oxygen was varied for every experiment corresponding to an adjusted range from 0 ml/min up to 300 ml/min. Various specimen conditions employed in the investigations are summarized in Table 1.

2.3 Nanotribological methods

To gain information about nano mechanical properties, nano indentational tests were conducted using a Hysitron TriboIndenter®TI950. The test setup was based on a 3D-transducer that allows vertical and horizontal displacement of the specimen. For measurements of young’s modulus and nano hardness, a triangular diamond tip (Berkovich; tip radius: 100 nm) was mounted on an elastically suspended pick-up electrode applying to the method of Oliver and Pharr. In addition to indention tests, the coated surfaces were evaluated by scratch tests to determine friction conditions. At an effective scratch length of 8 μm the load force was increased continuously reaching a final force of 1000 μN to record the coefficient of friction (CoF). For this purpose, a conical tip was used with a tip radius of 300 nm. An advantage of the conical tip is that there is no preferred direction of measurement.

2.4 Surface analysis

To quantify different stoichiometries of molybdenum and oxygen X-ray diffraction was conducted using a Bruker Discover D8® diffractometer. For high resolution analysis, a scanning electron microscope (Zeiss Supra 55 VP) equipped with different detectors (backscattered electron (BSE), secondary electron (SE) and Inlens detection) was used. Chemical composition of selected areas was probed using energy dispersive X-ray spectroscopy (EDX) with a Bruker Quantax XFlash ® SDDs 125 eV detector. The EDX data was collected at an acceleration voltage of 10 kV. Given the very thin molybdenum (oxide) layers, the SE, BSE and Inlens images were recorded at lower acceleration voltage (5 kV).

To obtain data on layer thickness, high resolution cross sections were prepared from the layers with a focused ion beam (Zeiss Auriga). This combined characterization approach was needed, assuming the sputtered layers being very thin.

Table 1 Experimental design of specimen conditions

specimen	Sputtering time [min]	Oxygen mass flow [ml/min]
R1 (virgin)	/	/
A	90	0
B	150	100
C	150	200
D	150	300

3 Results and discussion

XRD investigations on eroded specimen surfaces have been carried out for specimens B, C and D to determine the effect of different oxygen partial pressures during the PVD procedure. Assuming higher oxygen partial pressures for specimen D (Fig. 1 a)) and C (Fig. 1 b)) a formation of mixed oxide layers of MoO_3 and MoO_2 can be detected. Both spectra occur quite similar, while the substrate causes a peak at 52° assuming defects on the surfaces and very thin PVD coatings. Specimen B (Fig. 1 c)) features a peak at the same frequencies at a lesser extent with higher noise of measurement. Thus, it was not possible to produce selective molybdenum oxides because the process conditions simultaneously allowed the formation of different stoichiometries.

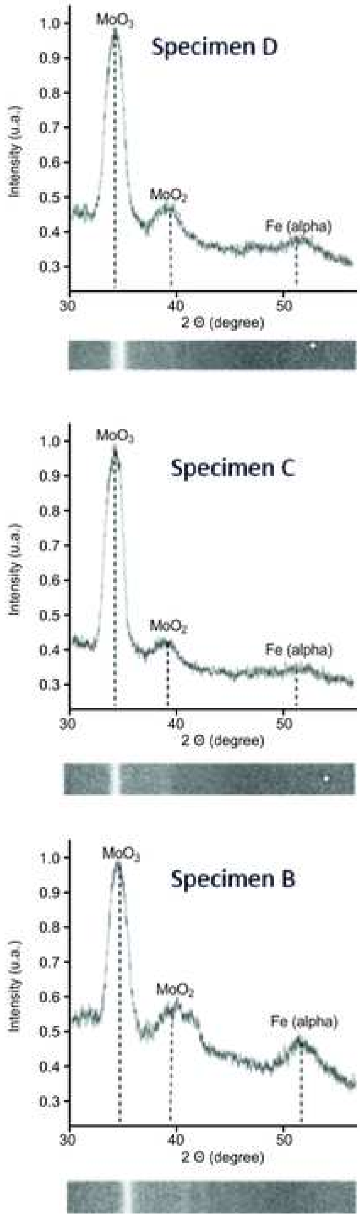

Fig. 1 Representative XRD spectra of specimen B, C and D

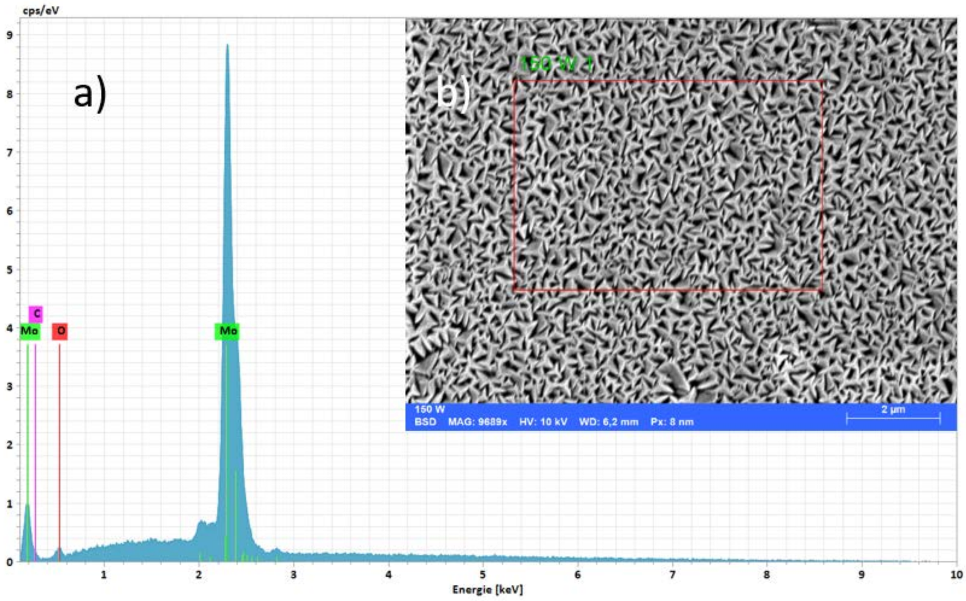

Fig. 2 a) EDX spectrum of red marked area, b) SE image of specimen A

Information about the morphology and the chemical composition of the surfaces were obtained by different surface sensitive analytical methods. Figure 2 b) shows a secondary electron image of specimen A that features a structure that is completely uniform with triangular particles of homogeneous size, which consists of molybdenum regarding the EDX analysis (Fig. 2 a)). Regarding the backscattered SE image which is shown in Fig. 3, a high resolution occurrence of the molybdenum coating occurs. The triangular particles feature sizes of 200 nm up to 300 nm (Fig. 3).

Specimen B was prepared using a focused ion beam to provide for high resolution information. Figure 4 shows a SE image of a cross section of the sputtered molybdenum layer, which has a thickness of about 1 µm. The black rectangle shows divided sections of the regarded system, including the protection (Pt) layer, the oxide system, the molybdenum layer and at last the substrate. The EDX mapping of oxygen (Fig. 4, top left) documents, that diffusing oxygen has formed an oxide layer in the near-surface area of the molybdenum layer. Below, there is a small reaction zone, which occurs lighter between the substrate and the molybdenum layer. However, the heat

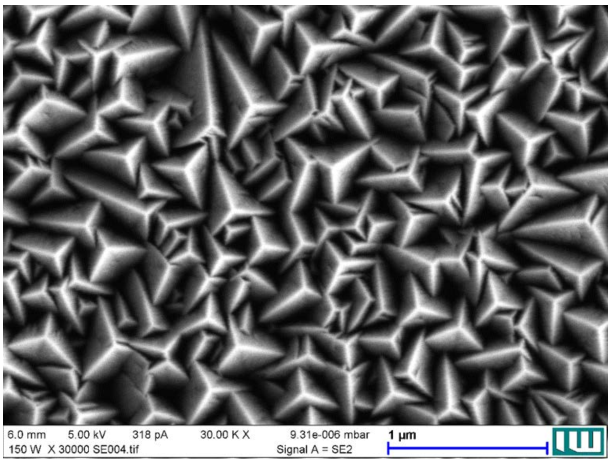

Fig. 3 Backscattered SE image of specimen A

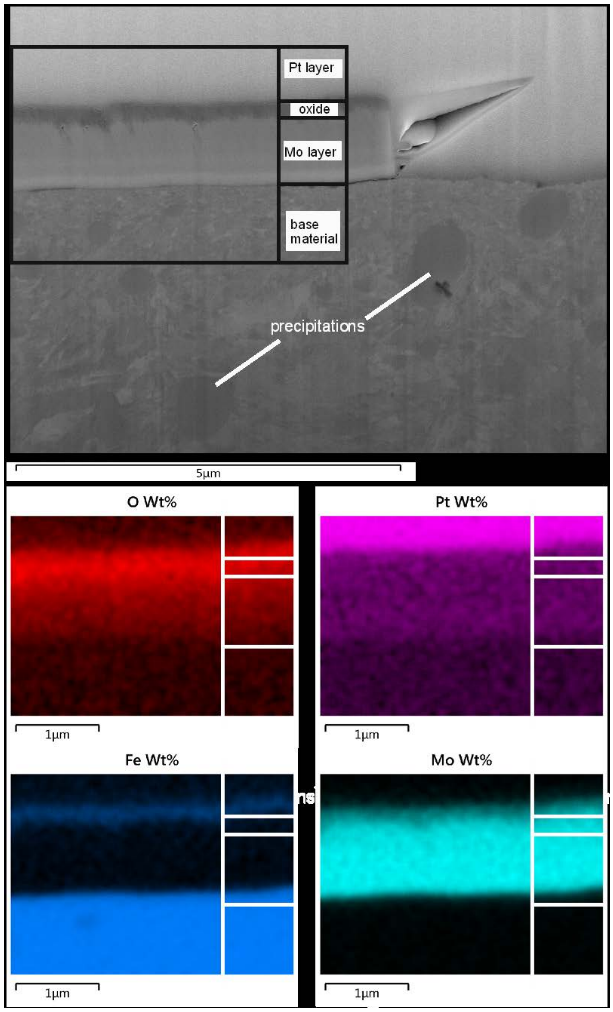

Fig. 4 SE image of a cross section prepared by focused-ion beam cutting of specimen B. The elemental mappings obtained from the region marked by the black rectangle were recorded at 15 keV.

treatment was noticeably below the annealing temperature of the bearing steel, the substrate features grain refinement at near-surface areas with larger chromium precipitations. Moreover, the oxide layer is rich in molybdenum, iron and oxygen. It has to be determined if the diffusion of iron through the molybdenum layer to the oxide system is kinetically and thermodynamically favourable.

The initial nano hardness as the young's modulus of the untreated bearing steel ASSI 552100 has been measured in former research activities and is described in detail in [2]. The median nano hardness amounts about 13.7 GPa at a young's modulus of 224 GPa. In comparison Figs. 5 and 6 show, that the located indents yielded results at a lesser extent. Specimen A had a median nano hardness of about 4 GPa, while the nano hardness of specimen C gained results of nearly 10 GPa. Thus, it can be assumed, that nano hardness results of molybdenum based layer systems were measured, without superpositional influencing nano hardness results of the substrate. In general, the hardness of the generated layer systems increases slightly with the oxygen partial pressure of the process, except for specimen D, which gained nano hardness results in the range of the pure molybdenum system of specimen A. The recorded young's modulus correlated well to the results of the nano hardness measurements, so that the experiments could gain reproducible results.

The measured coefficients of friction (COF) were recorded for an increasing normal load up to 1000 μN (Fig. 7). For all testet specimens, the scratch behaviour shows a transition from stiction to friction at the first μm which appears in shape of a drastically decreasing COF. The reference sample shows a slightly increasing trend and reaches a maximum of 0.4 at the end of scratch distance subsequently. Coated surfaces of specimens A and B showed almost constant COF after the transition zone, while specimen B features the lowest COF at 0.1. The recorded COF of specimen C and D showed oscillating results at a higher extend, while specimen D featured a discontinuous plot at the end of the scratch distance, probably caused by stick-slip effects.

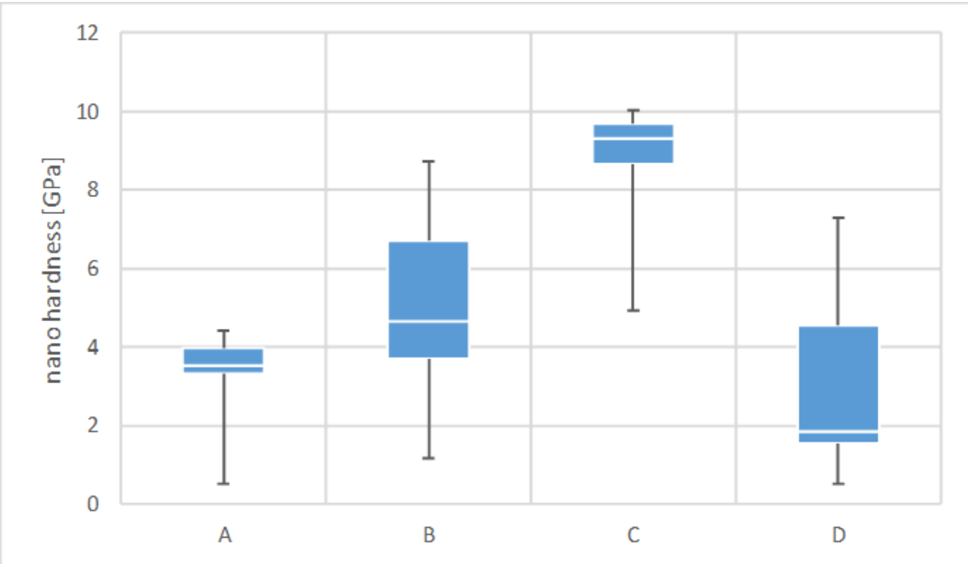

Fig. 5 Box-plots of measured nano hardness after magnetron sputtering

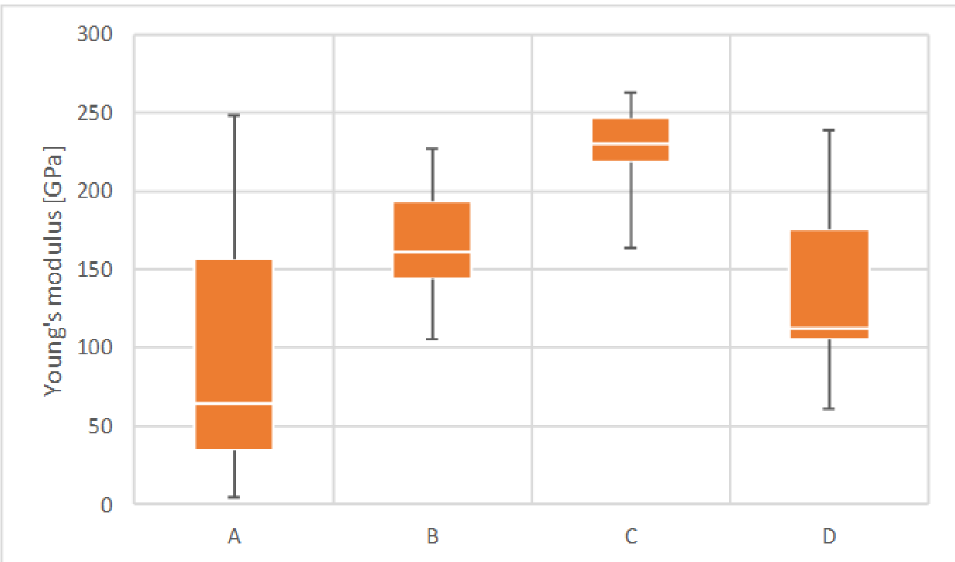

Fig. 6 Box-plots of measured young's modulus after magnetron sputtering

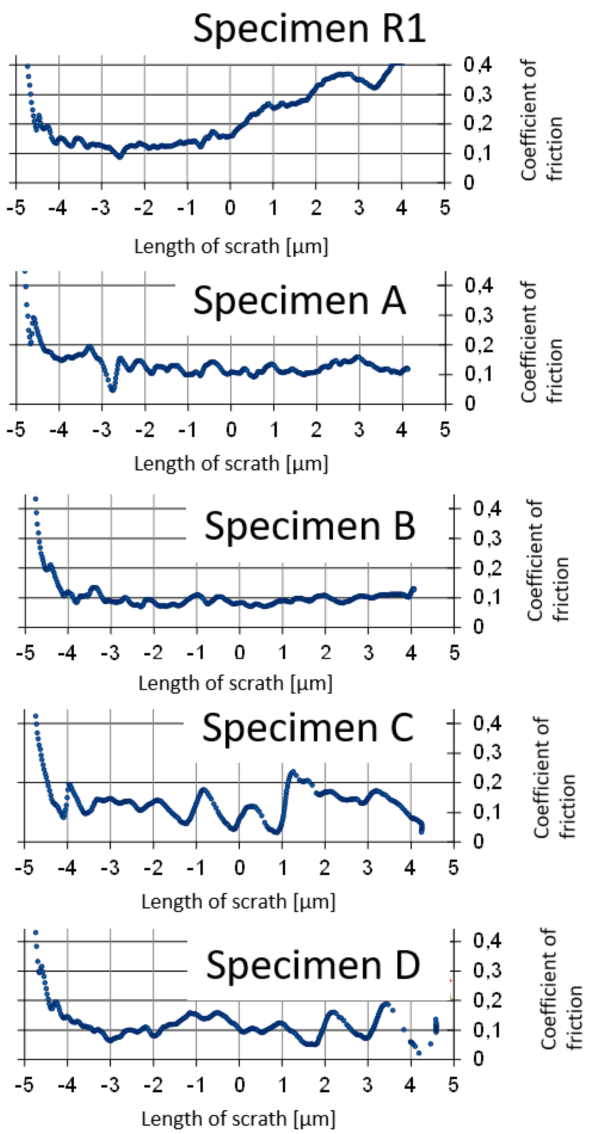

Fig. 7 Coefficient of friction as a function of scratch distance for increasing normal load up to 1000 µN

4 Conclusions

The results of the present study can be summarized as follows:

- The generation of molybdenum based layer systems on ASSI 552100 bearing washers could be realised sufficient through magnetron sputtering at adequate temperatures and oxygen partial pressure.
- By adjusting the oxygen content in the process, diffusing oxygen generated a very thin layer system of oxygen and molybdenum in the near surface areas.
- Measured coefficients of friction showed lower results for coated surfaces than for initial ones.

Acknowledgements

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