MICRO- AND NANOTRIBOLOGICAL CHARACTERIZATION OF MOLYBDENUM OXIDE BASED COATINGS ON 100CR6 BEARING STEEL SURFACES

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Abstract: Dry lubricated bearings are used in applications that are exposed to high temperatures or other ambient conditions that prohibit the use of lubricants. Examples can be found in the chemical or food industries. To handle such conditions, a molybdenum based layer system was developed for the dry lubrication of rolling contacts. The molybdenum oxide layers are generated by Physical Vapor Deposition (PVD). By using a magnetron sputter cathode, it is possible to produce a PVD molybdenum oxide multiple layer system. In the pre-investigation phase, various parameters (power, sputtering time, oxygen mass flow, etc.) were used for the preparation in order to achieve optimum adhesion and material strength. In the current project phase, the coatings were qualified by applying microtribological methods. In a first step of qualification, the nano hardness and Young’s modulus were investigated via nanoindentation. Additional nano scratch tests allow conclusions regarding the friction and elastic properties of the coatings. In the second step of qualification, the coatings were applied by micro wear and scratch tests by applying a milli-tribometer. The setup allows the measurement of the frictional properties of a 100Cr6 (AISI 52100) ball against a coated counterpart under oscillating motion. Scratch tests were performed by applying a Rockwell diamond tip with a radius of 5 µm with forces of up to 1 N and scratch lengths of up to 20 mm. The properties of the coatings regarding the transition from nano to micro scale are observed and taken into account for the layer development. With these results it is possible to characterize the generated layers and to define the wear and the optimal parameters for the PVD process. After qualification the coatings will be applied to radial bearing surfaces. The intended use of dry lubricant coating systems on rolling bearings will be presented.

Keywords: Molybdenum, Molybdenum oxide, Dry lubrication, Microtribology, Scratch test, Friction, Wear

1. INTRODUCTION

Because rolling bearings as tribological machine elements have an increased economic influence on the society (for example, a study shows that 25 % of energy consumption in the USA is attributed to tribological systems [1]), many different areas of industry and engineering science are endeavouring to gain greater knowledge of tribological phenomena. Especially in the science of friction, wear and corrosion, one aims to reduce the losses of natural resources and energy [2]. Dry lubricated systems are a special discipline within tribology. They are used, for example, in the chemical and food industries, which have higher hygiene requirements and may also be subject to legal conditions. For example, molybdenum sulphide, graphite or silver are used for solid lubricant systems [3].

For the processing of the Priority Program 2074 (“Fluidless lubrication systems with high mechanical load”) project, the subproject “Dry lubrication of rolling contacts by self-regenerating molybdenum-oxide coatings” in particular is attempting to coat a metallic surface with multiple molybdenum oxide
layers. The project aims to use a molybdenum oxide coat as a solid lubricant with regenerative properties. As a dry lubricant, the coating systems could offer a hard, wear-resistant surface and elastic properties in the matrix. In [4] appropriate preliminary investigations with molybdenum-based coatings have been carried out. These showed that a low coefficient of friction is achieved and that the coating is useful. In the case of material removal, the underlying layers react with the oxygen so that a suitable surface is created again. The application limits of this innovative solid lubricant system are to be investigated. In the beginning of the investigations, the focus and the analysis will be on the bonding of the substrate with the layer system. The so-called bonding layer is produced with a pure molybdenum.

Figure 1. Schematic illustration of the used sample (left) and the planned multi-layer coating (right).

The molybdenum coatings are produced by PVD [5]. Various process parameters are used in the production of the coatings, which should help in the determination of a suitable bonding layer. For example, the analysis is supported by using a milli tribometer and 3D laser scanner. In addition, the adhesion strength, friction and wear mechanisms of the produced bonding layers are to be investigated as well. For the bonding layer, nanoscale investigations has already been carried out in [6]. This paper focuses on the micro tribology scales.

2. EXPERIMENTAL

For the characterization of the corresponding coating, the specimens used are described in the following. In addition to this, the test methods and analytical equipment used will be described.

2.1 Preparation of Samples

The samples to be characterized in this paper are coated with molybdenum. A rolling bearing steel 100Cr6 was chosen as a substrate. The coating is produced via the PVD process. For this purpose, molybdenum is applied to the surface of the substrate by magnetic cathode sputtering. Before this, the surface to be coated was grinded and polished as well as cleaned by plasma sterilization. For the preparation of the samples, a fine vacuum with a pressure of $2 \times 10^{-2}$ mbar and a temperature of 180°C was selected for the sputtering process. The atmosphere was pressurized with argon gas. A list of the samples manufactured via different process is listed in Table 1 below.

Table 1. Overview of sputtered samples as well as additionally used reference Sample G (only substrate material) and Sample R (axial washer).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Sputtering duration, h</th>
<th>Sputtering power, W</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.5</td>
<td>150</td>
</tr>
<tr>
<td>B</td>
<td>2.5</td>
<td>150</td>
</tr>
<tr>
<td>C</td>
<td>4.5</td>
<td>150</td>
</tr>
<tr>
<td>D</td>
<td>4.5</td>
<td>200</td>
</tr>
<tr>
<td>G (substrate)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R (axial washer)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The samples were manufactured as circular plates with a diameter of 10 mm and a thickness of 4 mm. The specific layer thickness in particular could vary with various sputtering times and powers [3]. In addition, reference samples are used for the analysis. The first reference Sample G consists of the base material used for the coated samples (100Cr6). These have also been taken into account for evaluating the roughness of the coating. The reference Sample R is a bearing washer from a commercial axial
bearing 81212 (Schaeffler INA, Germany). This material is S235 steel. The characterization is considered here because conventional bearings are to be coated later.

### 2.2 Characterization of the Friction Coefficient

In order to characterize the samples, the coatings were investigated using various methods. On the one hand, the coefficients of friction (CoF) were determined under defined conditions. In particular, the correlation to the various manufacturing parameters had to be investigated. On the other hand, the plastic and elastic material properties and the adhesive strength between the substrate and the sputtered molybdenum layer are to be analyzed by using a scratch test [7]. In addition to the comparison between the different coated samples, the behavior of the reference samples under identical test conditions is also investigated. The tests were executed with a Milli-Tribometer (TriboTechnic, France). To determine the CoF, a ball was stressed with a defined normal force on the flat surface of the test sample. The ball has a diameter of 6 mm and consists of a hardened rolling bearing steel (100Cr6). The sample was moved relative to the ball with a constant velocity and an oscillating stroke. The roll-over frequency is defined by the test distance. The Milli-Tribometer was also used for the scratch test (Fig. 2). In this case, the ball used is exchanged for a diamond tip (Rockwell C geometry) with a tip radius of 5 µm.

![Figure 2. Principle execution of the scratch test with the corresponding sample geometry. A Rockwell C tip with radius 5 µm was used.](image)

The tip is carefully placed on the coated surface and the sample is moved linearly, while the force on the tip is linearly increased. This motion causes the diamond tip to penetrate the surface; this process is called scratching. This test method allows on the one hand to characterize the plastic deformation on the surface and on the other hand to determine the possible penetration of the coating as a function of the normal force. The focus here is on the amount of force needed to penetrate the coating. In addition to the expected penetration, corresponding crack networks or other conspicuous features are also investigated. In the later analysis of the scratch, the adhesive strength can be calculated by means of the critical force [8, 9].

### 2.3 Analysis of Surfaces

The surfaces of the coatings were be analyzed before application. In order to obtain the important information of this investigation, the samples are analyzed on the microscopic range by using a 3D laser scanning microscope VK-X250K (Keyence Deutschland GmbH, Germany). For the evaluation of the tests, various 3D images are created along the scratches or movement paths. In addition, the surface profile was measured tactilely by using a perthometer (Mahr GmbH, Germany) with a diamond tip with a radius of 2 µm to gain information about the roughness. In the end, the layer thickness is measured. This may be possible by scanning a layer step between the coated and uncoated surfaces (area of material spalling). The roughness properties can change depending on the layer thickness. However, it is assumed that the sputtered surface structures are adopted by the substrate [3].
3. RESULTS & DISCUSSION

For this purpose, the results are split into two subchapters with regard to the different questions. The first subchapter describes the tribological investigations. In the following subchapter, the adhesive strength is explained by means of the generated results from the scratch test. In general, the investigations were conducted at an ambient temperature of about 25 °C. The tribological tests were carried out under dry-lubricating conditions.

3.1. Coefficient of Friction

In this test, explained in Chapter 2.2, the coefficient of friction of each sample (in combination with the ball) was determined. The contact partner is sliding in an oscillating motion on the surface with a velocity \(v\) of 5 mm/s and a normal force \(F_N\) of 500 mN. The raceway had a stroke \(s\) of 5 mm. The running time and thus the total distance (cumulated value of oscillating cycles) is defined by the length \(l\) of 1 000 mm. The general sample conditions were constant within the test matrix. Prior to the experiment, the samples were placed in washing benzine for 15 min using an ultrasonic bath and subsequently cleaned with isopropanol. Dry-lubricated friction could be achieved under comparable conditions by means of an appropriate drying time. It should be mentioned that the tests were performed under sliding conditions and no rolling was considered. In Figure 3a), the CoF mentioned have been determined as a function of the total distance.

![Graph](image)

**Figure 3.** a) Overview of the used samples in the analysis of the coefficient of friction. b) Repeated test with Sample C (150 W & 4.5 h) with a longer test length.

It is noticeable that Sample R reaches the highest CoF in relation to the other specimens. In comparison to D and G, however, the CoF of Specimen R can be observed to have a flat linear increase between 0 mm and 600 mm. The CoF of curve D rises from 0.3 to a maximum of 0.6. Especially the approximation of the CoF curves of Specimens D and G is worth mentioning here, since the coating is worn through at a distance of about 600 mm (pos. 1) and the contact partner continues to rub on the substrate surface. This can be concluded from the tendency to observe identical curves at distances of 600 mm or more. When considering the coefficient of friction of C, a constant curve over the whole test length is detected. In the initial phase up to approximately 100 mm, a typical run-in phase can be detected [1]. Furthermore, the coefficient of friction is not significantly high even after passing through this phase and reaches a maximum coefficient of friction of 0.3. Because the coefficient of friction does not approximate the reference value of G, it can be assumed that the coating did not have to endure any significant wear and that no penetration into the substrate is to be expected. However, the focus is on the moment when the coating fails, so the experiment was repeated with a longer distance. Figure 3b) shows the already presented curve of Specimen C (with...
l=1 000 mm) again for comparison and additionally a further experiment with the identical sample at extended distance (l = 2 500 mm). When considering the development of the coefficient of friction, an increase starting at 1 m can be seen. This stabilizes after a distance of 1 750 mm and reaches a CoF max. value of 0.65 (pos. 2). This is the value for the reference Sample G (see Figure 3a), so it can therefore be assumed that, starting from a distance of 1 750 mm the coating is worn and the coefficient of friction of the substrate is measured.

Figure 4. a-d) Damage patterns of the worn sample surfaces. e-f) Sample C (4c) and Sample D (4d) mixed areas can be seen where coating is still partially present.

In the following surface analysis, the samples used in the experiment (see Figure 3a) are compared once again. In Figure 4, the comparison of the two coatings is particularly interesting. Figure 4c) shows a relatively wide track width and the shimmer of the substrate material is visible on the raceway. It seems, although smaller mixing areas (Figure 4e) are still visible, that the coating material is worn away. A comparison of Sample C (Fig. 4d) shows a significantly thinner track. Furthermore, although a track indentation can be seen, it can be noted that there was no penetration on the coating.

Table 2. Tabular summary of the investigations of the friction coefficients.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Ra, µm</th>
<th>Rz, µm</th>
<th>CoF&lt;sub&gt;max&lt;/sub&gt; - (until 1 m)</th>
<th>Track width, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (150 W &amp; 4.5 h)</td>
<td>0.006</td>
<td>0.041</td>
<td>0.27</td>
<td>59.10</td>
</tr>
<tr>
<td>D (200 W &amp; 4.5 h)</td>
<td>0.007</td>
<td>0.055</td>
<td>0.60</td>
<td>161.91</td>
</tr>
<tr>
<td>G (substrate)</td>
<td>0.004</td>
<td>0.030</td>
<td>0.60</td>
<td>133.87</td>
</tr>
<tr>
<td>R (axial washer)</td>
<td>0.052</td>
<td>0.325</td>
<td>0.78</td>
<td>97.92</td>
</tr>
</tbody>
</table>

Table 2 gives a final overview of the samples. In addition to the aforementioned track width, the roughness (Ra, Rz) was also measured. The coating material in the sputtering process assumes the surface structure of the substrate and becomes a bit roughened, depending on the layer thickness. In direct comparison to the axial disc, the coated samples have significantly smoother surfaces.

3.2 Scratch tests

In the next step, the adhesive strength was analyzed by means of the scratch test. For this purpose, the diamond tip is carefully placed on the surface. For the test, a maximum normal force of 500 mN and a stroke of 5 mm are chosen. In addition to the linearly increasing force, the velocity is configured to be constant at 5 mm/s. Adhesion is one of the most important properties for improving the load carrying capacity and scratch resistance of a coating system. If a coating does not bond to the substrate, it may crack, peel or flake. The scratch test induces elastic and plastic deformation until surface damage occurs. By determining the critical force, the mechanical adhesion of the coating can be defined and characterized [10].
Figure 5. Presentation of the sputtered samples (A-D) in the scratch test.

Figure 5 shows the sample surfaces after the scratch tests. The scratch extends from left to right and is performed under ramped load (linear increased force). First noticeable features are light spalling or crack networks. In Figure 5c), large areas are chipped off. The reason for this could be that the layer thickness has generated increased residual stresses and the delamination has already occurred before the start of the experiment or has caused direct delamination when force is applied. Figure 5d) shows a delamination that has not yet formed any cracks or spallings. The layer delamination is difficult to see in top view, therefore a height profile was created by means of 3D laser scanning (Figure 6).

Figure 6. Height profile images of Sample C (6a) and Sample D (6b). These show delamination and spalling (only in 6a).

In Figure 6a, the scratch test of Specimen C (Figure 5c) is shown as a 3D height profile. The picture was taken directly after the experiment. It can be clearly seen that the delamination led to increased tensile/residual stress in the coating and that macroscopic spalling of the coating occurred. The cracked fragments of the surrounding particles of the coating are clearly visible. In comparison to Figure 5c, the sample was not cleaned after the experiment. The cleaning (ultrasonic bath) after the test caused further (already detached) particles or coating components to be removed. The resulting delamination in Figure 6 has caused a height change of up to 60 µm (Figure 6a) and ca. 30 µm (Figure 6b).

Table 3. Summary of the determined layer thicknesses and critical load.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>h_{Coating} µm</th>
<th>F_{max} mN</th>
<th>R_{Hf} N/mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (150 W &amp; 1.5 h)</td>
<td>≈ 1.4</td>
<td>75.71</td>
<td>964</td>
</tr>
<tr>
<td>B (150 W &amp; 2.5 h)</td>
<td>≈ 2.6</td>
<td>183.86</td>
<td>2341</td>
</tr>
<tr>
<td>C (150 W &amp; 4.5 h)</td>
<td>≈ 7.2</td>
<td>142.56</td>
<td>1815</td>
</tr>
<tr>
<td>D (200 W &amp; 4.5 h)</td>
<td>≈ 8.9</td>
<td>263.43</td>
<td>3354</td>
</tr>
</tbody>
</table>
Table 3 lists the examinations of the samples. The critical force was determined according to the definition of [8]. This means that the distance from the beginning of the scratch to the first noticeable was determined and the force was calculated. It becomes particularly clear that Sample A has a low adhesive strength compared to the other samples. The highest adhesive strength is occurring for Sample D. In addition to the calculated critical forces, the layer height is also determined in the tests. Particularly large spalling areas made it possible to determine the exact height by means of difference formation between the coating and substrate surface. The height profiles could be validated in terms of micrographs.

Figure 7 shows an example of how to determine the layer height. Three different micrographs have been created on the left in the picture. The marking corresponds to the samples from Table 1. On the right in the picture the optical determination is executed by laser scanning microscopy. Sample C with a layer height of approximately 7 µm is shown here as an example. The difference between the layer heights shown in Figure 7 and in Table 3 could have various reasons. Here, for example, are two different samples. These have been produced with identical process parameters. An inhomogeneity of the coatings within a single sample or a charge has not been determined in the tests, but has not yet been implicitly tested. The delaminations detected in the scratch tests are an indicator of increased residual stresses. Since these are initiated accordingly at thicker layers, a process time in the magnetron sputter process of 4.5 h could possibly be too long.

4. CONCLUSION

The molybdenum coating represents the interlayer between the substrate and the self-regeneration molybdenum-oxide coating. In the present study, this interlayer was investigated in terms of microtribological method as applying wear and scratch tests. The coefficient of friction for the coating was recorded. Additionally, the fracture toughness and the surface adhesion was determined. This approach allows improving the PVD coating process and assisting the coating development. Further studies will be conducted regarding carried surface processing steps like milling and plasma etching the respective influence on the adhesion strength. After validating a benefited interlayer, the self-regenerative molybdenum oxide coating will be developed applying the same kind of process qualification which was proven within this work. It could be shown that a sputter duration of 2.5–4.5 h combined with a sputter power of 150 W results in advantage coatings for adequate load conditions.

In later project steps these coatings have to resist the tribological load in bearing components; the investigated contact conditions were adjusted to ensure a safe operation.
5. ACKNOWLEDGEMENTS

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