Morphology, composition and tribological properties of tantalum coatings deposited onto a rubber substrate

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Abstract. The paper analyzes the features of morphology and composition impact on tribological characteristics of tantalum coatings sputtered on to a rubber substrate. It is shown the influence of sputtering time on the structural changes in the form of clusters and grains that made up the coating. The morphology and composition features correlation with the coatings’ wear–resistance characteristics was investigated.

1. Introduction
One of the promising ways of products’ creation with high performance characteristics is the direction based on the raw materials modification. There are various approaches and methods of materials’ surface modification. One widely used approach is the modification of bulk materials. This method is extensively used for modification of elastomers. The volumetric modification is made by inserting the fillers and modifiers in the matrix. With all the benefits of this method it has disadvantages such as mostly low economy and efficiency. Surface modification is an alternative approach that has become widespread in recent years and consists in modifier’s deposition onto the surface of substrate [1]. This method allows obtaining elastomers with improved physical, mechanical and performance properties. It is equally important to solve the same problems at the area of nanostructured coatings deposited onto the surface of rubber. Despite of the small coating thickness it significantly improves the mechanical properties of the products [2] and increases its tribological characteristics.

Processing of the products including the rubber parts without production technology changing should be attributed to advantages of surface modification methods [3]. One of the promising method at this direction is the magnetron sputtering of the nano–dispersed refractory metals onto a rubber substrate. Magnetron sputtering has lots of advantages such as 1) application convenience, 2) high coatings’ continuity and 3) possibility of modifiers’ deposition at low temperatures. The last of mentioned advantages is particularly important in the case of rubber [4]. As the literature review shown [1, 4] at the present time there are enough investigations devoted to coatings’ deposition in application to metal and composite materials modification. With regard to coatings applied to elastomers and particular to rubber products this direction are currently paid insufficient attention. In order to increase the rubber products’ efficiency it is important to establish a correlation between morphology and composition of the surface layers with performance characteristics of the products. At
the same time it is necessary to establish the effect of sputtering conditions (in particular time and thickness) on the morphology features of the coatings and on the properties of a bulk rubber. The purpose of this paper is devoted to the morphology and composition investigation of the coatings deposited on a rubber substrate by usage tantalum as one of refractory metals in dependence on the sputtering time. The influence of a rubber morphology and composition with tantalum coatings on its abrasive wear and friction coefficient was also developed.

2. Materials and methods
In this study rubber samples were modified by tantalum magnetron sputtering with ADVAVAC VSM–200 setup usage. Samples’ preparation, composition and experimental methods are presenter in reference [5, 6]. Investigation of the coatings’ morphology was carried out on JEOL JCM–5700 scanning electron microscope equipped with JED–2300 spectrometer. Rubber surface modification was made at the same conditions except the sputtering time (thickness). The rubber samples were preliminarily grinded and polished and then subjected to examination. Tribological properties of rubber were studied on the MI–2 setup (GOST 426–77). The tests were performed with the metallic surface disk used as a counter face under the normal force equal to 26 N (2.6 kgf). The turnovers number of the 11KP structural steel disk during the test for all samples was 5.000.

3. Results and discussion
SEM surface images of the initial rubber and of a rubber modified by tantalum magnetron sputtering are shown on figure 1a and 1b. For comparison on figure 1c is represented a SEM image of the coating after molybdenum sputtering [6]. The figures 1b and 1c show that the morphology of the modified samples substantially different from the initial one (figure 1a). Image analysis suggests a cluster structure of the coatings while maintaining various forms: tantalum clusters unlike the molybdenum clusters have a more elongated shape in one direction. The clusters in both cases have a grain structure. Studying the effect of sputtering time (while maintaining the other parameters) on the morphology, composition and properties of coatings based on refractory metals and possessed the effective protection features for rubber has a great applied interest. Detailed analysis of the time influence on the coatings’ morphology showed that during tantalum sputtering on the rubber substrate two stage of grain growth occurs. At the first stage grains with an average grain size of about 3 microns arise after which begins the formation and growth of new smaller grains.

After continuous sputtering of more than 170 minutes cracks were appeared on the sample surface and «scaly–form» morphology was formed. Dependence of the average grain size at clusters from the thickness measured by deposition controller is shown on figure 2. The solid line shows the dependence for molybdenum coating, dashed line – for tantalum coating relative to the surface without coating.
Figure 2. Dependence of the average grain size from coating thickness for tantalum and molybdenum coatings.

As can be seen from the figure 2 the average grain size ranges in a complicated way from about 3 µm (34 minutes sputtering time) to about 0.5 µm (233 minutes sputtering time) with increasing sputtering time. An important role in the coatings’ properties formation plays the chemical composition. The chemical composition of the initial rubber and the rubber coated by tantalum for different sputtering times before and after wear resistance test is presented in table 1 and table 2.

### Table 1. Chemical composition of the samples before wear resistance test.

| Chemical elements and oxides | Mass (%)  |
|------------------------------|-----------|
|                              | ST³0 34 100 168 233 |
| C                            | 84.3 13.81 16.52 10.05 5.18 |
| Cl                           | 11.8 2.75 0.00 0.00 0.00 |
| Ta₂O₅                         | 0.00 83.02 83.48 89.95 94.82 |
| SO₃                          | 2.27 0.42 0.00 0.00 0.00 |
| MgO, ZnO                     | 1.60 0.00 0.00 0.00 0.00 |

³ST – sputtering time (minutes).

The results of tribological tests for tantalum coatings deposited onto a rubber substrate for different sputtering time are presented in table 3. From the experimental results we can conclude that the tantalum–based coatings has morphology characteristics defined apparently by peculiarities of plasma forming in the vacuum chamber and by reacting the metal ions with the rubber substrate. Significant influence on the surface morphology formation confirmed by a noticeable difference between the sensor’s thickness (tens of nanometers) and the average grain size on the surface of the rubber substrate. Rubber substrate influence on the thickness of coating based on refractory metals shows a rubber cross–section SEM image of the sample with a molybdenum coating presented on figure 3. As can be seen from the figure 3 the coatings’ thickness amounts to a few microns.

### Table 2. Chemical composition of the samples after wear resistance test.

| Chemical elements and oxides | Mass (%)  |
|------------------------------|-----------|
| C                            |           |
| Cl                           |           |
| Ta₂O₅                         |           |
| SO₃                          |           |
| MgO, ZnO                     |           |
elements and oxides & ST\textsuperscript{a} & 0 & 34 & 100 & 168 & 233 \\ 
\hline 
C & 84.30 & 37.94 & 36.04 & 28.57 & 19.83 \\
Cl & 11.80 & 9.46 & 22.71 & 14.08 & 4.78 \\
Ta\textsubscript{2}O\textsubscript{5} & 0.00 & 47.99 & 31.79 & 51.54 & 71.91 \\
SO\textsubscript{3} & 2.27 & 0.85 & 3.75 & 2.38 & 3.48 \\
MgO, ZnO & 1.60 & 3.76 & 5.73 & 3.43 & 0.00 \\
\hline 
\textsuperscript{a}ST – sputtering time (minutes).

Sputtering time has a significant impact on the coatings’ morphology. Two trends should be allocated in the coatings’ structure formation: the first is the grain refinement in clusters formation with increased sputtering time and the second is «scaly–form» structure appearance with infringement of the coatings’ integrity for a sufficiently large sputtering time which is more than 170 minutes. Similar trends are not observed in the molybdenum coating’s morphology (figure 1c).

Table 3. Abrasive wear and friction coefficient for initial samples and samples modified by tantalum.

| Tests’ parameters | Sputtering time (minutes) |
|-------------------|--------------------------|
|                   | 0 | 34 | 100 | 168 | 233 |
| abrasive wear, cm\textsuperscript{3}/kW-h | 2.390 | 0.274 | 1.124 | 1.440 | 2.060 |
| friction coefficient | 0.870 | 0.472 | 0.517 | 0.527 | 0.469 |

A great impact on rubber performance characteristics including tribological properties must have a chemical composition of the coating in common with the morphology. Analysis of the sample’s composition shows that the main component of the coating is apparently tantalum pentoxide (Ta\textsubscript{2}O\textsubscript{5}) formed by tantalum oxidation by oxygen remaining in the chamber after evacuating.

The coating also contains carbon inclusions which is confirmed by point analysis. Chemical elements and oxides (C, Cl, SO\textsubscript{3}) most likely belong to the near–surface layers of the rubber substrate as
indicated by the appearance of these elements and oxides in the samples with a relatively large sputtering time after wear resistance testing. EDS analysis also captures the presence of these elements at low coatings’ thicknesses.

Data from the table 3 show that tantalum–based coatings demonstrate a significant improvement of rubber’s tribological characteristics. An average friction coefficient is reduced from 1.7 times to 1.8 times at sputtering time of 168 minutes. Tribological characteristics depend on a number of factors. The most important factors are the state of the rubbing surfaces defined by its morphology and composition, surface roughness and adhesion, mechanical properties. The many factors of tribological characteristics make them difficult to analyze. The results obtained in this study allow us to make only a few conclusions about correlation between morphology and abrasion wear of tantalum–based coatings. There is no appreciable necessity for coatings formation with great thickness. Sputtering time can be limited from 30 to 60 minutes. Coatings’ continuity is retained at such sputtering time and the grain size is likely to be optimal in terms of surface roughness. Increasing of coating thickness leads to continuity disruption and «scaly–form» structure formation which in turn increases the coatings’ wear.

4. Conclusion

As a result it is possible to make a conclusion that the morphology features of tantalum–based coatings on the rubber substrate depend on the sputtering time.

The special features of the tantalum–based coatings’ morphology should be attributed the grain’s grinding with increasing of sputtering time and the «scaly–form» structure formation with infringement of the coating continuity at a sufficiently high sputtering time (more than 170 minutes).

A coatings formed during tantalum magnetron sputtering consist presumably of tantalum pentoxide with carbon inclusions. The chemical composition of the coatings before and after abrasive wear tests remains invariant. Formation of tantalum–based coatings leads to significant improvements of rubber’s tribological characteristics. The friction coefficient is reduced on average in 1.7 times while abrasive wear decreased in 1.8 times (for 168 minutes of sputtering time). The growth of abrasive wear with increasing of sputtering time is explained by morphology features of the coatings. As shown by the abrasive wear test results the optimal sputtering time ranges from 30 to 60 minutes.

For a more detailed research of morphology and composition influence of tantalum–based coatings on tribological properties of rubber products additional studies are needed with attraction of other characteristics such as deformation–strength properties, adhesion and roughness.

Acknowledgments

The work was carried out under the research project № 17053В in Omsk State Technical University (OmSTU).

References

[1] Vityaz P A and Solntsev A K 2011 Construction technology of nanostructured materials and coatings (Minsk: Navuka) p 283
[2] Grinberg P B, Poleshchenko K N, Surikov V I and Tarasov E E 2012 Herald of the Omsk University 2(64) 249–252
[3] Makhkamov K K 2016 J. Fric. Wear 37(5) 500–506
[4] Berlin E V and Seidman L A 2010 Ion–plasma processes in thin–film technology (Moscow: Technosphere) p 457
[5] Tselykh E P, Polonyankin D A, Rogachev E A and Surikov V I 2015 Omsk scientific Herald 1(137) 97–100
[6] Surikov V I, Tselykh E P, Polonyankin D A and Rogachev E A 2014 Dynamics of systems, mechanisms and machines (Dynamics 2014) 1–6