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# PROPERTIES OF $TiO_2$ COATINGS APPLIED BY ATOMIC LAYER DEPOSITION (ALD) ON 100Cr6 STEEL

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The paper presents the method of forming $TiO_2$ coatings on 100Cr6 steel using the ALD method and assessing the properties of the obtained coatings. The coatings were assessed in terms of surface morphology, chemical composition, contact angle and tribological properties. The performed tribological tests show that $TiO_2$ coatings are characterized by lower resistance to motion. During measuring the geometric structure of surfaces on samples with $TiO_2$ coating, smaller wear traces were recorded than for 100Cr6 steel. The obtained values of the contact angles prove that the 100Cr6 steel coated with $TiO_2$ is more hydrophobic than the uncoated 100Cr6 steel. $TiO_2$ coatings can be used in low-loaded tribological systems and as barrier coatings.

*Keywords:* 100Cr6, coatings $TiO_2$, surface, friction, X-ray research

## INTRODUCTION

Surface engineering plays an important role in current science. It involves modifying the surface layer of materials to increase the service life of machine parts. As a result, many researches have been carried out to produce coatings that increase the hardness and wear resistance of the surface. One of the methods of surface layer modification is the production of coatings that improve the chemical, mechanical and physical properties of materials. The most important methods of advanced surface engineering are: thermal methods [1], electrochemical and chemical methods [2], physical methods [3]. In recent years, the popularity of thin, hard and low-friction diamond-like coatings (DLC) has been growing. Thin coatings include, inter alia, DLC diamond-like carbon coatings (DLC) [4, 5]. DLC coatings are most often obtained in chemical vapour deposition processes. A promising example of chemical vapour deposition is atomic layers deposition (ALD). It involves the sequential application of a chemical process in the gas phase. Two chemical substances, so-called precursors, react in most ALD reactions [6, 7]. The coatings are used in the power industry in the form of functional thin-film coatings that protect against corrosive and tribological wear, as well as bactericidal coatings, protective layers (mainly silver), but also wear-resistant coatings and nanolaminates (the most popular are $Al_2O_3$ + $TiO_2$, mirrors or dielectrics) and multilayer coatings, e.g. electroluminescent [8, 9]. $TiO_2$ coating significantly improves the surface properties, such as strength, reflectivity and hardness. The use of this coating greatly improves the protective properties of the substrates on which they are applied. It protects them, inter alia, against dangerous ultraviolet radiation [10]. The ALD atomic layer deposition technology enables the production of new and improved materials with excellent mechanical, tribological, corrosive and optical properties. Thanks to the ALD method, it is possible to obtain new materials with properties impossible to obtain using any other technique. In the case of such thin coatings, the roughness of the surface plays a very important role [11].

## MATERIALS AND EXPERIMENTAL METHODS

The test specimens used were discs with a diameter of 42 mm and a height of 5 mm made of 100Cr6 steel coated with $TiO_2$. The thickness of the coating is 100 nm. As a reference material, measurements were also made for bare 100Cr6 specimens (Table 1). The coating was applied using the Atomic Layer Deposition method at a temperature of 140 $^{o}$C, using two precursors: water and $TiCl_4$.

Surface morphology was observed on a scanning electron microscope (SEM), and the chemical composi-

Table 1 **Chemical composition of 100Cr6 steel /wt. % [12]**

| | |
|---|---|
| C | 0,93 – 1,05 |
| Mn | 0,25 – 0,45 |
| Si | 0,15 – 0,35 |
| P | max. 0,025 |
| S | max. 0,030 |
| Cr | 1,35 – 1,6 |
| Mo | max. 0,1 |
| Al | max. 0,05 |
| Cu | max. 0,30 |
| O | max. 0,0015 |

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tion of the specimens was checked by an energy dispersive spectroscopy (EDS) analyser. The observations were made at three magnifications: 1 000, 3 000, 5 000. The wettability of the $TiO_2$ coating surface was determined utilizing an optical tensiometer. The geometrical structure of the surface before and after the tribological tests was analysed using a confocal microscope with an interferometric mode, using a 20-fold magnification lens in a confocal mode. The tribological tests were performed on the nano tribometer ($NTR^3$) in a reciprocating motion (Table 2).

Table 2 **Parameters of the tribological test**

| | |
|---|---|
| Normal load | 2 mN |
| Speed | 0,2 m/s |
| Full amplitude | 5 mm |
| Frequency | 1 Hz |
| Distance | 1000 m |
| Temperature | 25 ± 2°C |
| Shear pair | Counter-specimen: 100Cr6 steel ball with a diameter of 2 mm Specimen: 100Cr6 steel disc without coating |
| | Counter-specimen: 100Cr6 steel ball with a diameter of 2 mm Specimen: 100Cr6 steel disc with $TiO_2$ coating |
| Lubrication | no lubrication |
| | synthetic oil PAO 8 |

## RESULTS AND DISCUSSION

Figure 1 shows the surface morphology of the $TiO_2$ coating on SEM, and Figure 2 shows the characteristic X-ray spectrum for this coating.

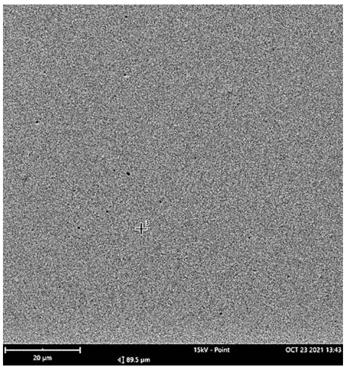

**Figure 1** Surface morphology of the $TiO_2$ coating

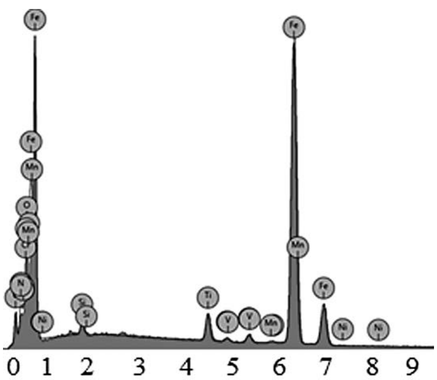


**Figure 2** The characteristic X-ray spectrum for $TiO_2$ coating

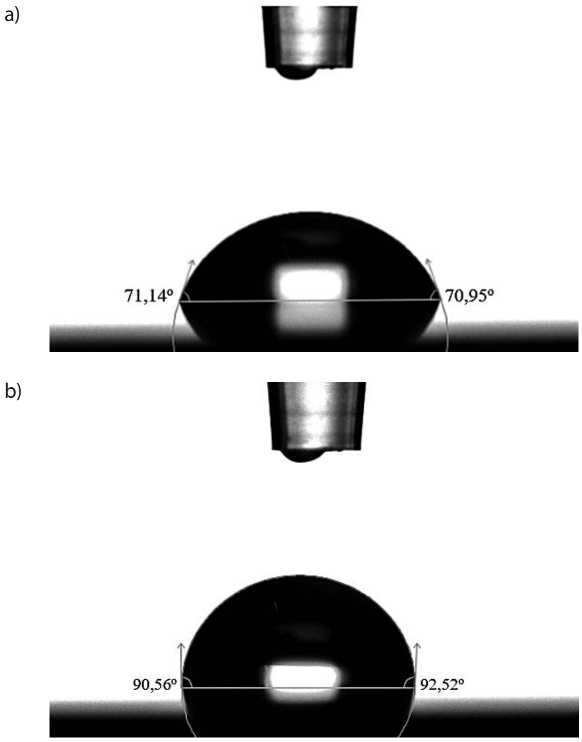


**Figure 3** A view of a drop of distilled water on the surface of a) 100Cr6 steel b) $TiO_2$ coating

Figures 3a and 3b show a view of a drop of distilled water on the surface of 100Cr6 steel without coating and with the $TiO_2$ coating.

Figure 4 show the average wetting angles for 100Cr6 steel, and Figure 5 show the average wetting angles for the $TiO_2$ coating. Surface wetting was assessed using distilled water, diiodomethane and PAO 8.

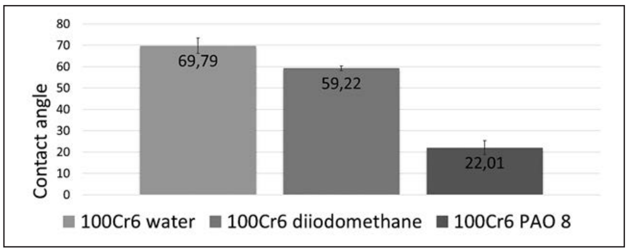


**Figure 4** The average wetting angles for 100Cr6 steel

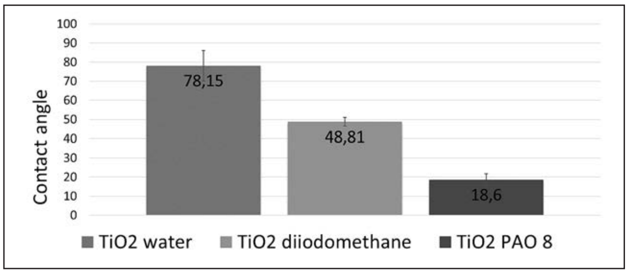


**Figure 5** The average wetting angles for the $TiO_2$ coating

The $TiO_2$ coating is more hydrophobic than 100Cr6 steel.

Figure 6 shows the average friction coefficients for 100Cr6 steel and the $TiO_2$ coating.

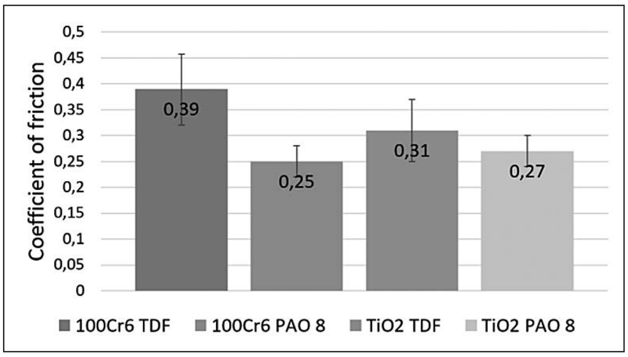


**Figure 6** The average friction coefficients

Figures 7a and 7b show the surface morphology of the $TiO_2$ coating after the technically dry friction test and after the test with the use of the PAO 8 oil lubrication.

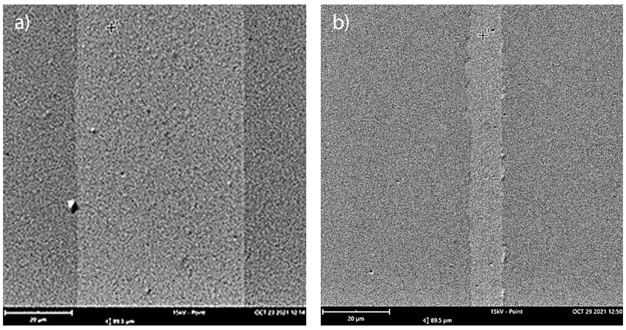


**Figure 7** The surface morphology of the $TiO_2$ coating after a) the technically dry friction test b) the test with the use of the PAO 8 oil lubrication

The wear mark after the technically dry friction test is much wider than the wear mark after the friction test with the use of the PAO 8 synthetic oil.

Isometric images of the $TiO_2$ coating surface after tribological tests obtained using a confocal microscope with Leica interferometric mode. Figures 8 and 9 show the surface profiles for the $TiO_2$ coating after the friction test.

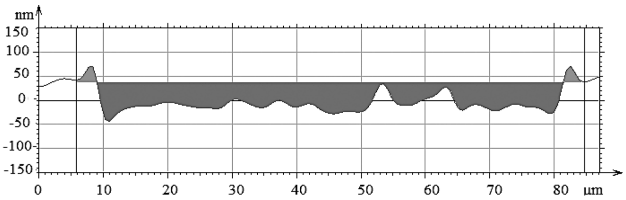


**Figure 8** The surface profiles for the $TiO_2$ coating after the technically dry friction test

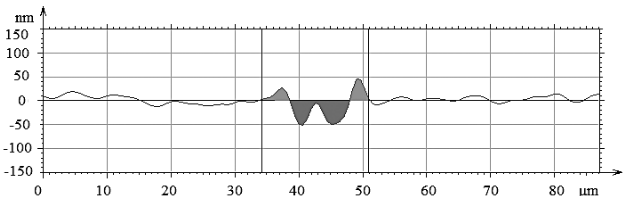


**Figure 9** The surface profiles for the $TiO_2$ coating after the test with the use of the PAO 8 oil lubrication

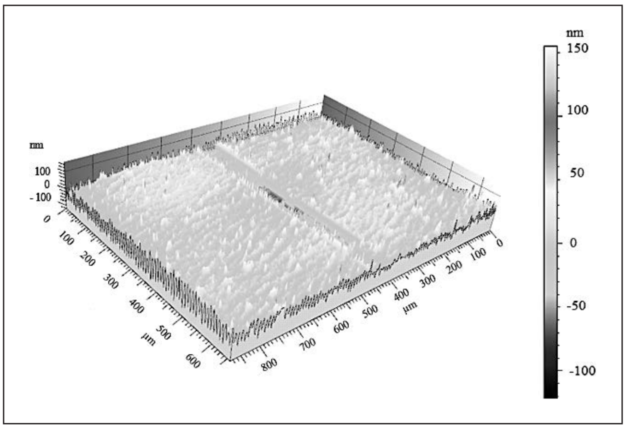


**Figure 10** Isometric images of the $TiO_2$ coating surface after the technically dry friction test

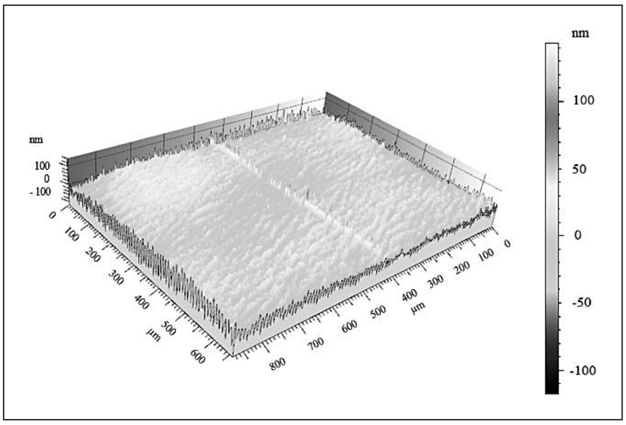


**Figure 11** Isometric images of the $TiO_2$ coating surface after test with the use of the PAO 8 oil lubrication

Isometric views of the $TiO_2$ surface coating specimen on 100Cr6 steel after tribological tests is shown in Figures 10 and 11.

The highest wear was observed on 100Cr6 steel with $TiO_2$ coating after the technically dry friction test. The polyalphaolefin resulted in a significant reduction in coating wear. The maximum depth of abrasion measured on the $TiO_2$ coating after the technically dry friction test was 84 nm, whereas the depth of abrasion measured after the test with the use of the PAO 8 polyalphaolefin was 54 nm. The area of the wear mark on the $TiO_2$ coating after the technically dry friction - 3,608,010 $nm^2$ and the area after the test with the use of the PAO 8 polyalphaolefin - 320,743 $nm^2$.

Further tribological tests of the $TiO_2$ coating will be carried out with the use of other lubricants.

## CONCLUSIONS

Based on the research, the following conclusions have been drawn:

The SEM (scanning electron microscope) images show the homogeneity of the $TiO_2$ coating obtained.

The analysis of the elemental chemical composition confirms the composition assumed in the technological process.

The obtained values of the angles have confirmed the greater hydrophobicity of 100Cr6 steel with the $TiO_2$ coating than observed on bare 100Cr6 steel. The values of the diiodomethane and PAO 8 polyalphaolefin wetting angles were lower for the $TiO_2$ coating.

During the technically dry friction tests, the mean coefficient of friction was 21 % lower for the $TiO_2$ coating than for bare 100Cr6 steel. Measurements of the surface geometrical structure on the specimens with the $TiO_2$ coating proved that the wear marks are smaller than the wear marks on bare 100Cr6 steel. The use of PAO 8 polyalphaolefin additionally intensified the anti-wear effect of the $TiO_2$ coating. The wear areas of the $TiO_2$ coating is measured after the tests with the PAO 8 lubrication was lower by about 90 % than in the case of technically dry friction.

The $TiO_2$ coatings obtained with the use of the ALD technique can be used in tribological systems and as barrier coatings.

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**Note:** The responsible for English language is Małgorzata Dembińska Lingua Lab