

## **SLIDING WEAR OF TiO<sub>2</sub> SOL-GEL COATING**

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### **ABSTRACT:**

*Nanostructured titanium dioxide (TiO<sub>2</sub>) coatings are interesting due to their good properties, such as high hardness, chemical stability, wear and oxidation resistance, high refractive index, high dielectric constant, good antibacterial and photoelectrochemical properties. In order to improve wear resistance of stainless steel AISI 304 (X5CrNi18-10), ceramics nanostructured TiO<sub>2</sub> thin films were deposited on the steel surface by the sol-gel process and dip coating technique. Stainless steel substrates were drawn from the sol at two different rates. After dip coating, the steel substrates were dried, first at room temperature and thereafter at 100 °C. In order to increase the coating thickness, the whole process was repeated three times. Subsequently, heat treatment at two different temperatures (401 °C and 500 °C) was conducted. Prior to sliding test, the thickness and composition of the deposited films were analyzed by Quantitative Depth Profile (QDP) analysis on the Glow Discharge Optical Emission Spectrometer (GDOES). Sliding tests were performed by modified "block on ring" method. Wear scars were analyzed by optical microscope and test results showed the influence of drawing rate during dip coating on the width of wear scars.*

**Key words:** titanium dioxide, sol-gel, stainless steel, sliding wear

### **1. INTRODUCTION**

The wear resistance of machine parts is an important characteristic, which impacts the quality of mechanical products, [1]. The improvement in manufacturing and extending the life expectancy of the design elements and tools, used in various domains, is taking place mostly because of the more and more common employment of the thin coatings deposition, made from hard, wear resistant ceramic materials, [2].

Titanium dioxide occurs in three different crystalline polymorphic forms: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic), [3].

Several methods can be used to obtain thin films of TiO<sub>2</sub>, including: DC-pulsed magnetron sputtering, rf sputtering, chemical vapour deposition (CVD), plasma enhanced chemical vapour deposition (PECVD), atomic layer deposition (ALD) and sol-gel method, [4].

The sol-gel method, also known as chemical solution deposition, is a wet-chemical technique, a process involving following steps: hydrolysis and polycondensation, gelation, aging, drying, densification and crystallization. The most important advantages of sol-gel process are: low equipment costs, low processing temperature, good homogeneity, use of compounds that do not introduce impurities into the end product as initial substances, thus making it "green", waste-free technology. These advantages make the sol-gel process one of the most appropriate technologies for preparation of thin, nanostructured films, [5].

### **2. SAMPLE PREPARATION AND SOL-GEL DEPOSITION METHOD**

In this investigation, four samples (dimensions: 17×17×80 mm) of stainless steel X5 CrNi 18-10 (AISI 304) were used as substrates for sol-gel deposition. Prior to the coating deposition, samples were ground with SiC abrasive discs of different granulation (180–1000 grit) and then polished with

diamond paste (3  $\mu\text{m}$  and 0.25  $\mu\text{m}$ ). Thereafter, substrates were ultrasonically cleaned in acetone and subsequently dried in an oven at 100  $^{\circ}\text{C}$  for an hour.

For the preparation of  $\text{TiO}_2$  sol, the following components were used:

- (i) 15 ml of titanium (IV) isopropoxide ( $\text{Ti}(\text{C}_3\text{H}_5\text{O}_2)_4$ ) – TIP, as a precursor,
- (ii) 132 ml of i-propanol ( $\text{C}_3\text{H}_7\text{OH}$ ) – POH, as a solvent,
- (iii) 6 ml of 0.5 M nitric acid ( $\text{HNO}_3$ ) as a catalyst,
- (iv) 3.3 ml of acetylacetonone ( $\text{CH}_3(\text{CO})\text{CH}_2(\text{CO})\text{CH}_3$ ) – AcAc, as a chelating agent.

Sol was prepared by dissolving the titanium (IV) isopropoxide in i-propanol. After that, acetylacetonone and nitric acid were added successively. A magnetic stirrer was used to continuously stir the liquid for 6 h at the room temperature. After 24 h of ageing, prepared sol was used for thin film deposition by the dip coating technique.

Coatings were deposited on 4 equal samples – 2 samples were dipped with rate of 0.17 mm/s, and 2 were dipped with rate of 1.7 mm/s. The substrates were held in solution for 3 minutes, in order to allow surface wetting. The samples were withdrawn from the sol with the same rate. After each dipping, the samples were air dried for an hour and subsequently dried in the oven at 100  $^{\circ}\text{C}$  for an hour as well. The whole deposition procedure (dipping, holding, withdrawing and drying, Figure 1) was repeated three times, in order to increase the coating thickness. After drying, 2 samples were calcined at 401  $^{\circ}\text{C}$  and 2 at 500  $^{\circ}\text{C}$  for 4 hours, with gradually heating and cooling.

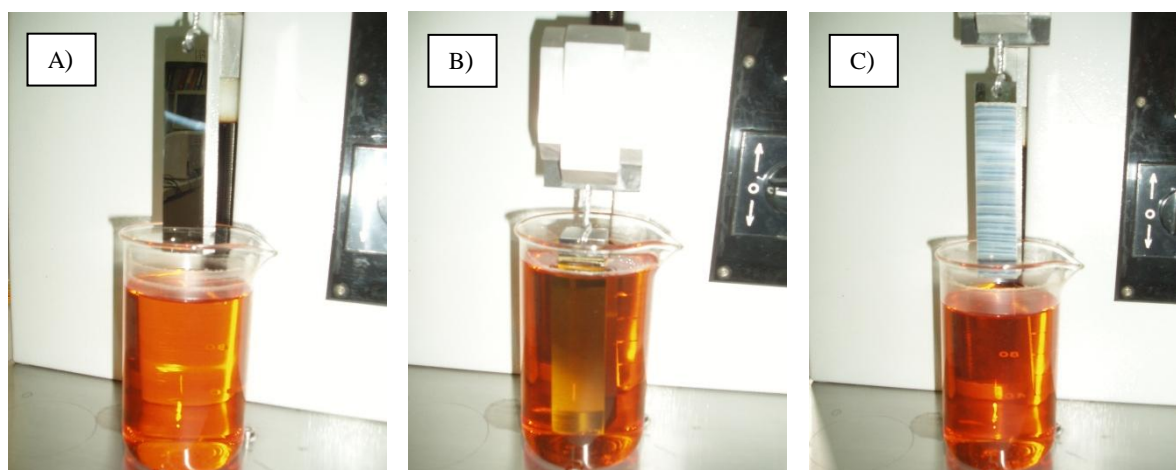


Figure 1 – Deposition procedure: dipping (A); holding (B), withdrawing (C).

Sample characteristics are shown in Table 1.

Table 1 – Dipping rates and calcination temperatures of investigated samples.

Sample	Dipping rate, mm/s	Calcination temperature, $^{\circ}\text{C}$
1	0.17	500
2	1.7	500
3	0.17	401
4	1.7	401

### 3. SURFACE ANALYSIS OF PREPARED SAMPLES

For surface analysis of deposited coatings, glow discharge optical emission spectrometer (GDS 850A, Leco) was used. This device can be used for elemental bulk analysis, but it can also be used for determination of coating thickness and quantitative depth profiling (QDP). In other words, it can show chemical composition of a coating, as well as distribution of chemical elements from the surface to the substrate.

Distribution of most important elements from surface to substrate for sample 4 is shown in Figure 2 ( $v=1.7$  mm/s;  $\vartheta=401^\circ\text{C}$ ;  $\text{Me}=\text{Ti, Ni, Cr, Fe}$ ). This diagram shows the element mass fraction  $w(\text{Me})$  in coating and in substrate. Titanium (Ti) is present in the coating (note: used device is not equipped with oxygen photomultiplier), while Ni, Cr and Fe are present in the substrate.

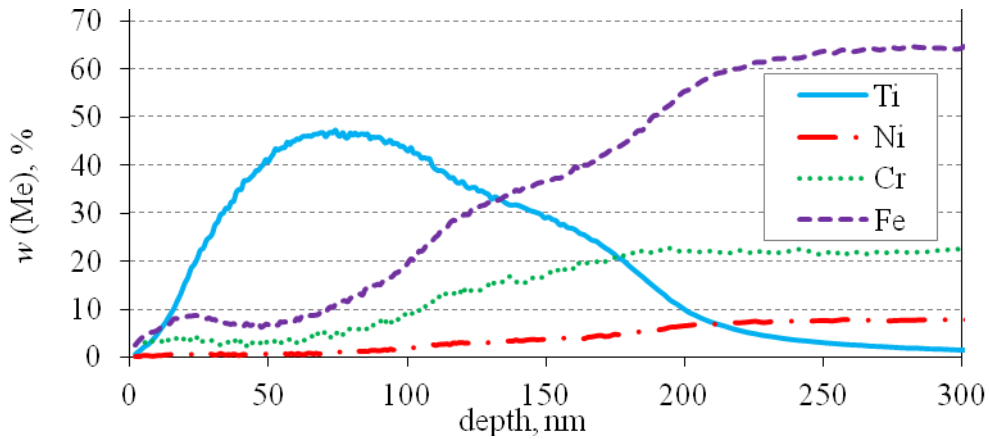


Figure 2 – Quantitative depth profiling of sample 4 ( $v=1.7$  mm/s;  $\vartheta=401^\circ\text{C}$ ;  $\text{Me}=\text{Ti, Ni, Cr, Fe}$ ).

All samples showed very thin (app. 10 nm) surface layer – adsorbed carbon layer, which indicates that samples should have been cleaned in an ultrasonic bath. Mass fraction of carbon isn't showed on Figure 2. Chemical analysis in inner surface layer showed uneven composition, showing the diffusion of elements from substrate (Fe, Cr, Ni) to coating and vice versa (Ti), resulting in inability to determine correct coating thickness. In order to compare coating thickness between samples, the depth on which mass fraction of titanium fell under 10 % has been taken as a referent value. Coating thickness of each layer determined that way is shown in Table 2.

Table 2 – Measured thickness of  $\text{TiO}_2$  coatings.

Sample	Coating thickness, nm
1 ( $v=0.17$ mm/s; $\vartheta=500^\circ\text{C}$ )	54
2 ( $v=1.7$ mm/s; $\vartheta=500^\circ\text{C}$ )	214
3 ( $v=0.17$ mm/s; $\vartheta=401^\circ\text{C}$ )	59
4 ( $v=1.7$ mm/s; $\vartheta=401^\circ\text{C}$ )	200

#### 4. SLIDING TEST

Sliding tests were performed by modified "block on ring" method (ASTM G 77).

Test parameters:

- Test ring material: steel
- Applied load: 10 N
- Ring diameter: 35 mm
- Rotational speed of the ring: 1.5 rpm
- Test duration: 60 s
- Sample dimensions: 17×8×5 mm

As it can be seen from Figure 3, wear scars on samples 2 and 4 ( $v=1.7$  mm/s) were significantly smaller than those on samples 1 and 3 ( $v=0.17$  mm/s), as well as on the untreated surface. The presence of "rainbow colours" on the surface after sol-gel deposition (sample 1 and 3) indicates uneven thickness of the coating, due to dipping device inability to withdraw the sample with constant rate at such low speed ( $v=0.17$  mm/s). Other two samples (2 and 4) didn't show such coloured lines. Coating with uneven thickness can be the cause of larger wear scars on samples 1 and 3.

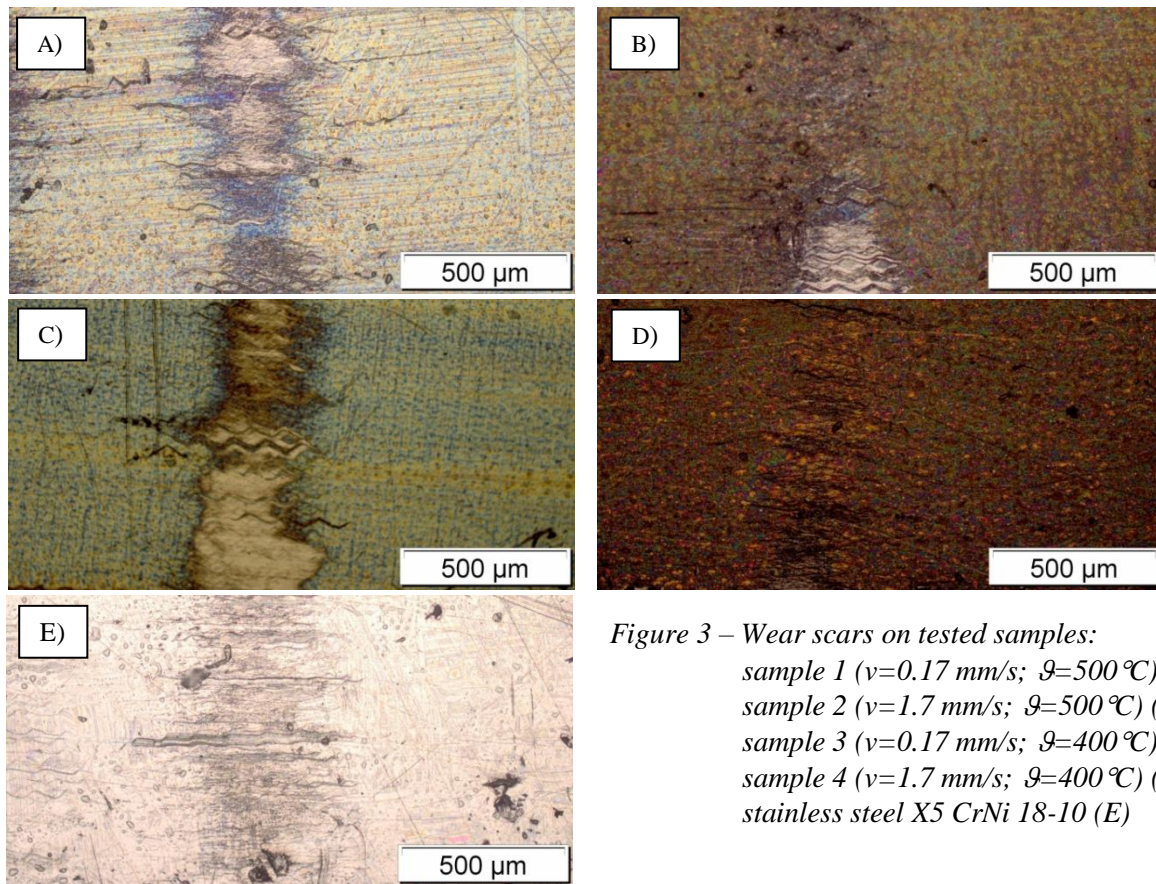


Figure 3 – Wear scars on tested samples:  
 sample 1 ( $v=0.17$  mm/s;  $\theta=500$  °C) (A);  
 sample 2 ( $v=1.7$  mm/s;  $\theta=500$  °C) (B);  
 sample 3 ( $v=0.17$  mm/s;  $\theta=400$  °C) (C);  
 sample 4 ( $v=1.7$  mm/s;  $\theta=400$  °C) (D);  
 stainless steel X5 CrNi 18-10 (E)

## 5. CONCLUSION

Sol-gel method and dip coating technique are convenient for deposition of  $\text{TiO}_2$  coating on the stainless steel substrate. If the process parameters are well chosen, deposited coating can achieve high quality without visible cracks. During the calcination, the diffusion of elements, from substrate to coating and vice versa, has been noticed. This investigation has shown that calcination temperature does not affect the coating thickness significantly.

The coating thickness increases with the increase in withdrawal rate, leading to reduced wear scars after tribological testing. Wear scars were larger on the untreated steel surface, indicating that sol-gel  $\text{TiO}_2$  coating improves tribological properties of stainless steel substrate.

## 6. REFERENCES:

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