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STUDY OF
CORROSION PROPERTIES OF TIN COATINGS IN A SULPHATE ENVIRONMENT

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The paper deals with the corrosion properties of TiN coatings in a 1 % Na_2SO_4 environment, which were determined by gravimetric analysis and corrosion potential measurement. The evaluation of the corrosion effect of the test electrolyte was completed by the samples surface observation by the LEICA macroscope before and after their exposure in a sulphate environment.

Key words: *corrosion properties, TiN, thin coating, corrosion potential*

Studija korozivnih svojstava zaštitnih TiN-prevlaka u sulfatnoj sredini. Rad se bavi korozivnim svojstvima prevlaka TiN uronjenih u 1 % Na_2SO_4 sredinu. Svojstva su utvrđena gravimetrijskom analizom i mjerenjem potencijalne korozije. Procjena korozivnog efekta na elektrolit testa upotpunjena je pregledom povšine uzoraka makroskopskom LEICA prije i nakon izlaganja u sulfatnoj sredini.

Ključne riječi: *korozijska svojstva, TiN, tanka zaštitna prevlaka, potencijal korozije*

INTRODUCTION

The Physical Vapour Deposition (PVD) technology of thin coatings belongs to technologies of coating formation deposited on cutting and forming tools and on mechanically loaded machine parts. Thin coatings give a new feature to the substrate surface and consequently change the properties of coated parts. Their main purpose is to increase the wear resistance. The environment in which metal parts work can react with the coating surface, which results in a decreased coating thickness, the formation of the corrosion products layer or the complete degradation of the coating. For this reason, the corrosion resistance of a coating is a primary importance in a range of applications.

EXPERIMENTAL MATERIALS AND METHODS

For experiments, the samples from carbon steel (ferrite-perlite structure), Figure 1. and high - speed steel (martensite - carbide structure) Figure 2., were used.

The shape and dimensions of samples are shown in Figure 3., their chemical composition is shown in Table 1. and 2., as compared with the composition according to STN 411 523 or STN 419 830 Standards.

Table 1. **Chemical composition of 11 523 steel**
Tablica 1. **Kemijski sastav čelika 11 523**

Steel	Actual chemical composition / %								
	C	Mn	Si	Cr	Mo	Al	Cu	P	S
11 523	0,18	1,0	0,42	0,034	0,005	0,046	0,079	0,02	0,014
Chemical composition according to STN 411 523 / %									
11 523	max 0,20	max 1,6	max 0,55					max 0,04	max 0,04

After polishing and degreasing in acetone, the substrate surface was cleaned, activated and heated to the required temperature by bombarding the ions of neutral gas Ar at 10^3 Pa directly in the coating device. The coating was deposited onto the surface of the basic material prepared in such

Table 2. **Chemical composition of 19 830 steel**
Tablica 2. **Kemijski sastav čelika 19 830**

Steel	Actual chemical composition / %								
	C	Mn	Si	Cr	Mo	V	W	P	S
11 830	0,86	0,24	0,14	3,96	5,15	1,88	0,003	0,02	0,011
Chemical composition according to STN 419 830 / %									
11 830	0,8- 0,9	max 0,45	max 0,45	3,8- 4,6	4,5- 5,5	1,5- 2,2	5,5- 7,0	max 0,035	max 0,035

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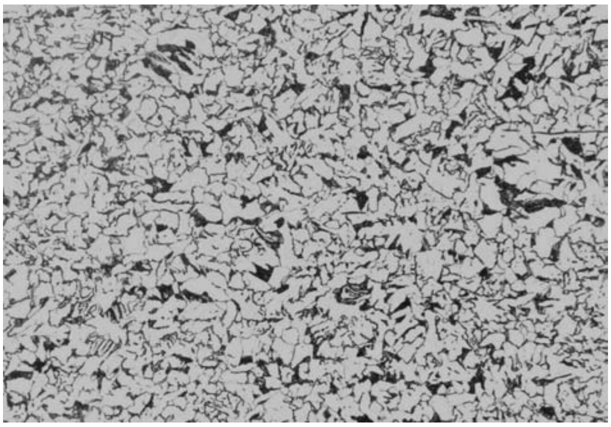

Figure 1. **Structure of 11 523 steel after controlled hot rolling, 500×, etched**
Slika 1. **Struktura čelika 11 523 nakon kontroliranog toplog valjanja, 500×, jetkan**

a way using the *reactive cathode vapour deposition* method. Particles released from the Ti cathode using an electric arc are accellerated with a bias voltage towards the substrate surface; during its movement and on the substrate surface, titanium reacts with the supplied nitrogen to form TiN [1].

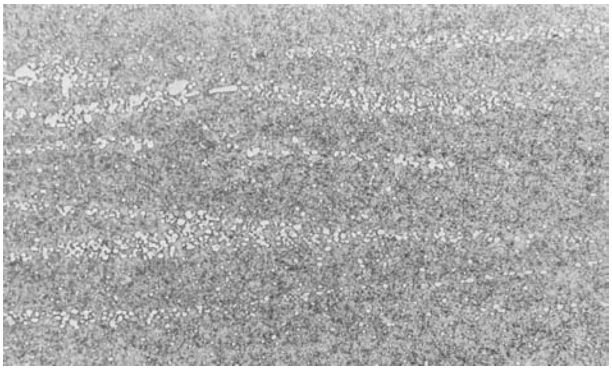

Figure 2. **Structure of 19 830 steel after heat treatment, 500×, etched**
Slika 2. **Struktura čelika 19 830 nakon toplinske obrade, 500×, jetkan**

The technological parameters of the coating deposition process were the same for both the materials; the substrate temperature of 450 °C, the nitrogen pressure of 2 Pa, the accelerating voltage of 300 V. The coating period changed depending on the required coating thickness; for the 2 μm coating it was 20 minutes, for the 4 μm coating 40 minutes. The result of the coating process was a TiN coating with the thickness of 2 μm and 4 μm depositted onto the 11 523 and 19 830 substrates.

The corrosion properties of the coated samples were evaluated using gravimetric analysis and by measuring the corrosion potentials in the 1% Na_2SO_4 water solution [2]. The evaluation of the corrosion effect of the electrolyte was supplemented by the observation of the coated sample surfaces using a macroscope. The weight changes of the tested samples were determined in selected time intervals: after 200 h, 800 h and at the end of the 1000 h of the corrosion test. Before weighing, corrosion products were mechanically removed from the surface of the exposed samples. After rinsing with methylalcohol and drying, the samples were weighed.

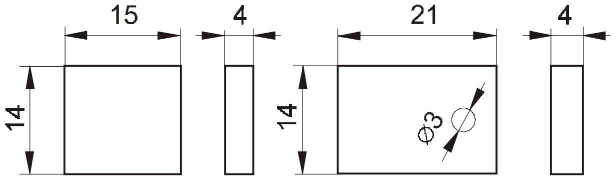

Figure 3. **Shape and dimensions of sample coated: a) horizontally, b) vertically**
Slika 3. **Oblik i dimenzije uzorka premazanog: a) vodoravno, b) okomito**

RESULTS OF EXPERIMENTS AND DISCUSSION

In Figures 4. and 5., weight changes of TiN coated samples after 200 h and 1000 h exposure in the test solution are documented graphically.

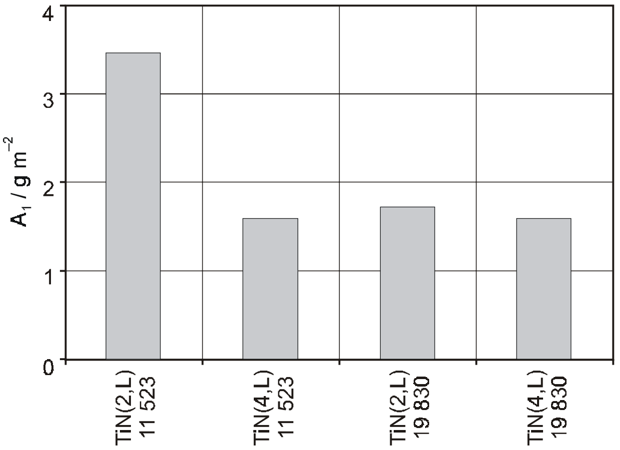

Figure 4. **Weight loss of TiN coated samples after 200 h in 1 % Na_2SO_4**
Slika 4. **Gubitak težine uzoraka zaštićenih TiN prevlakom nakon 200 sati izlaganja djelovanju u 1 % Na_2SO_4**

On the tested samples, the effect of the different coating thickness was shown; the corrosion loss of the 4 μm TiN coating, when compared with the 2 μm TiN coating, was lower after 200 h, as well after 1000 h of exposure to sulphate ions.

In all the samples, the corrosion loss grew with the exposure time: after the 200 h exposure, the highest corrosion loss was recorded for the sample with a 2 μm TiN coating on 11 523 steel, namely 3465 g·m^{-2}. On the sample with a 4 μm coating on 19 830 steel, the corrosion loss was the smallest, 1573 g·m^{-2}. At the end of the 1000 h corrosion test, the weight loss value increased to 72,97 g·m^{-2} for a 2 μm coating on 11 523 steel; for a 4 μm TiN coating on 19 830 steel, the weight loss increased to 46,86 g·m^{-2}.

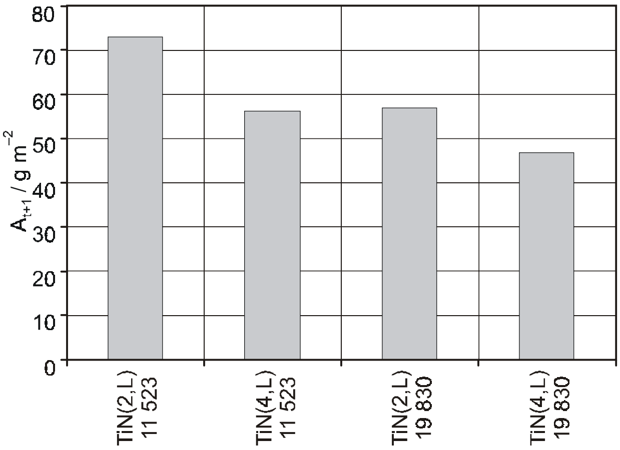

Figure 5. **Weight loss of TiN coated samples after 1000 h in 1% Na_2SO_4**

Slika 5. **Gubitak težine uzoraka zaštićenih TiN prevlakom nakon 1000 sati izlaganja djelovanju u 1 % Na_2SO_4**

The evaluation of the corrosion effect of 1 % Na_2SO_4 on the TiN –19 830 steel system was also supplemented by observations using a macroscope before exposure, after 200 h and at the end of the 1000 h test in the corrosion environment.

Figure 6. shows the TiN surface before exposure. Figure 7. documents the result of the test solution effect on the surface of the samples with the 4 μm TiN coating on the 11 523 steel substrate. Corrosion damage due to the effect of sulphate ions has a local nature; with an increasing exposure time, the steel substrate dissolves intensively into depth in points where the coating is damaged [2, 3].

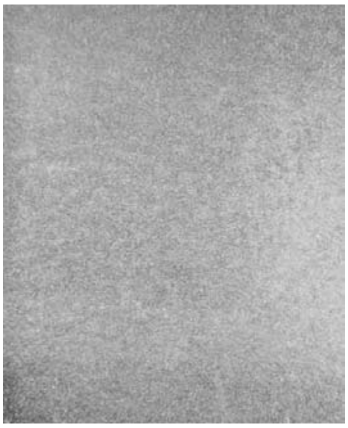

Figure 6. **Surface of samples with TiN coating before corrosion tests, 6,5×**

Slika 6. **Površina uzoraka zaštićenih prevlakom TiN prije ispitivanja na koroziju, 6,5×**

Figure 8. shows changes on the surface of the 4 μm TiN coating on 19 830 steel during exposure in 1 % Na_2SO_4. The extent of damage on these samples is less than on the coating deposited on 11 523 steel, Figure 7. However, in this case the corrosion attack takes place on both the coating and the steel substrate. Damaged areas are surrounded by highly adhesive corrosion products [2].

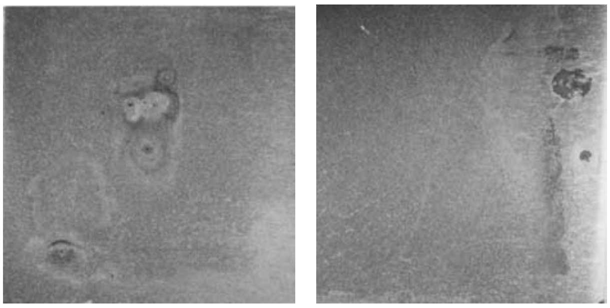

Figure 7. **Surface of samples with 4 μm TiN on 11 523 steel after: a) 200 h, b) 1000 h in 1 % Na_2SO_4, 6,5×**

Slika 7. **Površina uzoraka iz čelika 11 523 zaštićenih 4 μm TiN debelom prevlakom nakon: a) 200 sati, b) 1000 sati izlaganja djelovanju u 1 % Na_2SO_4, 6,5×**

The corrosion potential is a parameter that is very sensitive to the condition of the surface of the studied material. The relationship between the time and the corrosion potential, measured against the saturated calomel electrode, of the TiN coating on 11 523 steel in the sulphate medium is shown in Figure 9. During exposure, the corrosion po-

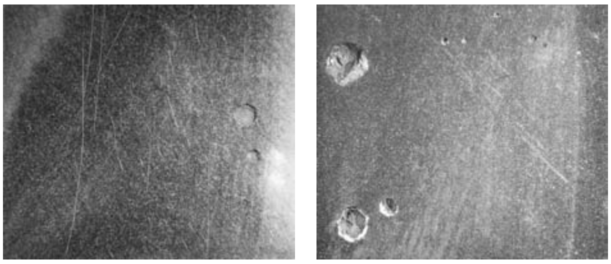

Figure 8. **Surface of samples with 4 μm TiN on 19 830 steel after: a) 200 h, b) 1000 h in 1% Na_2SO_4, 6,5×**

Slika 8. **Površina uzoraka iz čelika 19 830 zaštićenih 4 μm TiN debelom prevlakom nakon: a) 200 sati, b) 1000 sati izlaganja djelovanju u 1 % Na_2SO_4, 6,5×**

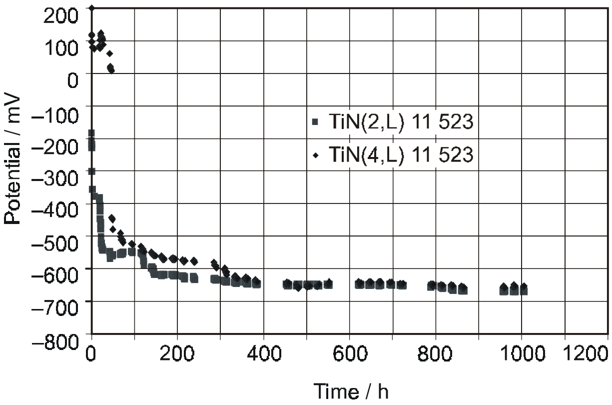

Figure 9. **Potential vs exposure time of TiN coating on 11 523 steel in 1 % Na_2SO_4**

Slika 9. **Potencijal ovisno o trajanju izlaganju zaštitne prevlake TiN na čeliku 11 523 u 1 % Na_2SO_4**

tential changed from +200 mV on the thicker coating or –198 mV on the thinner coating towards more negative values. The potentials were stabilized after ca 350 h at –670 mV measured at the end of the test on both the coatings, which is a value close to the potential of low carbon steel in 1 % Na_2SO_4, i.e. –700 mV [3].

Figure 10. documents the course of the corrosion potential E_{kor} on samples with TiN on 19 830 steel during the 1000 h corrosion test in 1 % Na_2SO_4. At the beginning of exposure, the measured corrosion potential was –20 mV on the sample with the thinner coating and +9 mV on the sample with the thicker coating.

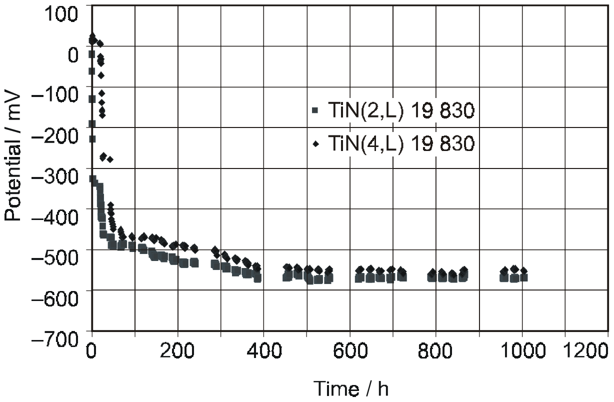

Figure 10. **Potential vs exposure time of TiN coating on 19 830 steel in 1 % Na_2SO_4**

Slika 10. **Potencijal ovisno o trajanju izlaganju zaštitne prevlake TiN na čeliku 19 830 u 1 % Na_2SO_4**

With the growing immersion time, the potential of the samples significantly decreased after ca 50 hours of the test. The E_{kor} values were stabilized after 400 h at –569 mV in case of the thinner coating and at –554 mV in case of the thicker coating, while the stabilized corrosion potential value of the 19 830 substrate in 1 % Na_2SO_4 is –530 mV.

Taking into account the above-mentioned course of potentials of the samples during the immersion tests, it is evident that the potentials measured at the beginning of exposure are, in fact, the corrosion potentials of the TiN coating, whose value is ca + 200 mV. However, on the samples of coatings deposited on 19 830 steel lower values were measured. It is necessary to assume that the difference could be caused by the contact of the substrate with the medium through the existing coating defects. As corrosion damage grows with the increasing share of the steel area that is in contact with the electrolyte, the measured potential value shifts towards values close to the potential of the substrate. The observed phenomenon is also supported by the formation of a cell between the nobler coating and the less noble substrate. Based on this, it should be stated that corrosion of the steel substrate also participates in the measured values of corrosion loss. This means that the corrosion losses of the coated samples represent the total sum of the loss of both the coating and the substrate.

This finding is also confirmed by the results of macroscopic analysis of the surface of the exposed samples in Figures 7. and 8., where corrosion damage of the coating is concentrated in circular grey areas, which represent the naked places of the steel substrate.

CONCLUSION

Based on the carried out set of experiments and achieved results it can be stated:

1. The weight losses determined using gravimetric analysis of the samples of the TiN coating deposited on the steel substrates 11 523 and 19 830 after exposure in 1 % Na_2SO_4 have shown that the coating thickness and the substrate type have dominant effects on the corrosion properties of the TiN coating.
2. A decrease of the corrosion potential measured against the saturated calomel electrode in the sulphate ion medium confirms that the coating is dissolved in the points of its defects, while the coating area on the sample surface gradually decreases and the naked steel substrate area increases, which was also confirmed by the results of macroscopic analysis of the surface of exposed samples.
3. Due to the different electrochemical nobility of the coating and the substrate, corrosion of the anodic steel substrate in the place of the TiN defect is stimulated by the formation of the coating-substrate corrosion cell.

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