STUDY OF CORROSION PROPERTIES OF TIN COATINGS IN A SULPHATE ENVIRONMENT

The paper deals with the corrosion properties of TiN coatings in a 1% Na$_2$SO$_4$ 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

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>
<thead>
<tr>
<th>Steel</th>
<th>Actual chemical composition / %</th>
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<tr>
<td></td>
<td>C</td>
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<tr>
<td>11 523</td>
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<tr>
<td>Chemical composition according to STN 411 523 / %</td>
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<tr>
<td>11 523</td>
<td>max</td>
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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$^7$ Pa directly in the coating device. The coating was deposited onto the surface of the basic material prepared in such

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<td></td>
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<tr>
<td>11 830</td>
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<td>Chemical composition according to STN 419 830 / %</td>
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Table 1. Chemical composition of 11 523 steel
Table 2. Chemical composition of 11 830 steel

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a way using the reactive cathode vapour deposition method. Particles released from the Ti cathode using an electric arc are accelerated 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].

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 deposited 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$_2$SO$_4$ 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 1. Structure of 11 523 steel after controlled hot rolling, 500×, etched](image1)

![Figure 2. Structure of 19 830 steel after heat treatment, 500×, etched](image2)

![Figure 3. Shape and dimensions of sample coated: a) horizontally, b) vertically](image3)

### 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$_2$SO$_4$](image4)

![Figure 5. Weight loss of TiN coated samples after 1000 h in 1% Na$_2$SO$_4$](image5)

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 as 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 small-
est, 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.

The evaluation of the corrosion effect of 1 % Na₂SO₄ on the TiN – 19 830 steel system was also supplemented by observations using a microscope 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 8. shows changes on the surface of the 4 μm TiN coating on 19 830 steel during exposure in 1 % Na₂SO₄. 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]. 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-

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**Figure 7.** Surface of samples with 4 μm TiN on 11 523 steel after:
- a) 200 h, b) 1000 h in 1 % Na₂SO₄, 6.5×

**Slika 7.** Površina uzoraka težinskih TiN prevlakom nakon 1000 sati izlaganja u 1 % Na₂SO₄, 6.5×

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**Figure 8.** Surface of samples with 4 μm TiN on 19 830 steel after:
- a) 200 h, b) 1000 h in 1 % Na₂SO₄, 6.5×

**Slika 8.** Površina uzoraka težinskih TiN prevlakom nakon 1000 sati u 1 % Na₂SO₄, 6.5×

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**Figure 9.** Potential vs exposure time of TiN coating on 11 523 steel in 1 % Na₂SO₄.

**Slika 9.** Potencijal protiv vremena izlaganja začnite prevlake TiN na čeliku 11 523 u 1 % Na₂SO₄.
potential changed from +200 mV on the thicker coating or –
198 mV on the thinner coating towards more negative val-
ues. 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 % Na₂SO₄, i.e. –700 mV [3].

Figure 10. documents the course of the corrosion po-
tential \( E_{\text{corr}} \) on samples with TiN on 19 830 steel during the
1000 h corrosion test in 1 % Na₂SO₄. 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.

![Graph showing corrosion potential vs. exposure time](image)

With the growing immersion time, the potential of the
samples significantly decreased after ca 50 hours of the test.
The \( E_{\text{corr}} \) 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 % Na₂SO₄ is –530 mV.

Taking into account the above-mentioned course of po-
tentials of the samples during the immersion tests, it is evi-
dent that the potentials measured at the beginning of expo-
sure 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 mea-
sured. 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 forma-
tion 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 val-
ues 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 macro-
scopic 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 anal-
ysis of the samples of the TiN coating deposited on the
steel substrates 11 523 and 19 830 after exposure in 1
% Na₂SO₄ have shown that the coating thickness and
the substrate type have dominant effects on the cor-
rosion properties of the TiN coating.
2. A decrease of the corrosion potential measured against
the saturated calomel electrode in the sulphate ion me-
dium confirms that the coating is dissolved in the points
of its defects, while the coating area on the sample sur-
face 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 coa-
ting and the substrate, corrosion of the anodic steel sub-
strate in the place of the TiN defect is stimulated by the
formation of the coating-substrate corrosion cell.

REFERENCES

[2] M. Hagarová: PhD, Thesis, Faculty of Metallurgy Technical Uni-
[3] V. Ballo: PhD, Thesis, Faculty of Metallurgy Technical Uni-