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TRIBOCORROSION RESEARCH OF NI-Al_2O_3/TIO_2 COMPOSITE MATERIALS OBTAINED BY THE METHOD OF ELECTROCHEMICAL DEPOSITION

Метою даного дослідження було проведення електрохімічного осадження і трібокоррозіонних досліджень композитних матеріалів на основі Ni-Al_2O_3/TiO_2. За час досліджень було виконано електрохімічне осадження різних композитних матеріалів, при цьому проводилося порівняння з базовими матеріалами, такими як дуплексна сталь і електрохімічно осаджений нікель. Були охарактеризовані робочі частки з використанням методів лазерної дисперсії, а покриття характеризувалися в SEM з використанням різних детекторів (Зворотне розсіювання і Вторинні електрони), EDX (енергодісперсная рентгенівська спектроскопія) і FIB (сфокусований іонний пучок). На основі виконаних знімків в SEM була визначена залежність кількості частинок в покритті від концентрації частинок TiO_2 в розчині і часу електрохімічного осадження покриттів. Також були проведені трибологічне дослідження матеріалів Сталь/Ni/Ni-TiO_2, трібокоррозіонне дослідження матеріалів Ni/Ni-TiO_2, порівняльна побудова профілів доріжок отриманих оптичним методом на основі конфокальної мікроскопії та визначення залежності висоти і ширини профілів від використовуваного матеріалу.

Ключові слова: композитні матеріали, трибологічні дослідження матеріалів

Целью данного исследования было проведение электрохимического осаждения и трибокоррозионных исследований композитных материалов на основе Ni-Al_2O_3/TiO_2. За время исследований было выполнено электрохимическое осаждение различных композитных материалов, при этом проводилось сравнение с базовыми материалами, такими как дуплексная сталь и электрохимически осажденный никель. Были охарактеризованы рабочие частицы с использованием методов лазерной дисперсии, а покрытия характеризовались в SEM с использованием различных детекторов (Обратное рассеяние и Вторичные электроны), EDX (энергодисперсная рентгеновская спектроскопия) и FIB (фокусированный ионный пучок). На основе выполненных снимков в SEM была определена зависимость количества частиц в покрытии от концентрации частиц TiO_2 в растворе и времени электрохимического осаждения покрытий. Также были проведены трибологические исследования материалов Сталь/Ni/Ni-TiO_2, трибокоррозионные исследования материалов Ni/Ni-TiO_2, сравнительное построение профилей дорожек полученных оптическим методом на основе конфокальной микроскопии и определение зависимости высоты и ширины профилей от используемого материала.

Ключевые слова: композитные материалы, трибологические исследования материалов

The purpose of this study was to perform electrochemical deposition and tribocorrosion studies of composite materials based on Ni-Al_2O_3/TiO_2. During the research, electrochemical deposition of various composite materials was carried out, while comparison was made with base materials such as duplex steel and electrochemically precipitated nickel. Working particles were characterized using laser dispersion methods and the deposits were characterized by SEM using different detectors (backscattered and secondary electrons), EDX (energy-dispersive x-ray spectroscopy) and FIB (focused ion beam). Based on the photographs taken in SEM, the dependence of the amount of particles in the coating on the concentration of TiO2 particles in the solution and the time of electrochemical deposition of the coatings was determined. Tribological studies of Steel/Ni/Ni-TiO_2 materials, tribocorrosion studies of Ni/Ni-TiO_2 materials, comparative construction of track profiles obtained by optical method based on confocal microscopy and determination of the height and width of profiles from the material used were also carried out.

Keywords: composite materials, tribological studies

The objective of the work was the preparation and modification of metallic surfaces for the experimental and theoretical tribocorrosion studies of composite materials based on Ni-Al_2O_3/TiO_2.

The main material in this study was duplex steel (duplex 2463). Duplex steel is a ferritic-austenitic stainless steel, which combines the most useful properties of ferritic and austenitic steels, also due to the high content of chromium and molybdenum, has very good resistance to pitting corrosion, crevice corrosion and corrosion resistance. Bi-directional microstructure of the steel provides high resistance to stress corrosion cracking and has high mechanical strength [1, 2].

For the experiment, five plates of duplex stainless steel with size of 100 mm by 40 mm by 3 mm were taken. Two plates were cut using a SiC disk into smaller ones with size 40 mm by 20 mm by 3 mm. Further, 40 by 20 by 3 mm plates were also cut using a SiC disk onto plates with a smaller dimension of 20 mm by 10 mm by 3 mm.

Initially, 40×20×3 samples were polished using SiC disks with grain sizes of 200, 400 and 1000. Finishing polishing was performed on a soft grinding wheel with a diamond atomizer. Later, this idea was rejected because there was no qualitative adhesion of the nickel coating on the samples. Subsequently, SiC grinding was carried out with disks with a grain size of 200.

After this, the samples were washed in running water, alcohol, distilled water and drying with compressed air.

From the stainless steel samples, the following parameters were taken: anode frequency impedance, cathode frequency impedance, cyclic voltammetry and open circuit potential [3].

The small and medium samples had different positions in the electrochemical deposition baths. For samples 40×20×3 (medium), the best conditions for the deposition of nickel are: the vertical position of the samples and a round platinum electrode located slightly lower and centered about the vertical axis of the sample. And for samples of 20×10×3 (small), the best conditions for the deposition of nickel are: the horizontal position of the samples and a special platinum electrode. Later it was decided to make the precipitation for medium samples in the horizontal position.

As is known, stainless steel is usually resistant to most corrosion effects, thanks to a thin oxide film on the surface. In this regard, it is quite difficult to obtain a coating with high-quality adhesion to the surface of the base metal. Accordingly, if this film is removed from the surface of the sample and held in such a state (while electrodeposition occurs), any galvanic metal can be applied to the stainless steel surface.

To remove the oxide film from the surface of stainless steel and to ensure good adhesion between the coating and the base metal, one of the chemical purification technologies described in the American Standard was applied [4].

The composition of the electrochemical bath and the parameters for the first treatment:

- Sulfuric acid (H_2SO_4) - 650 ml
- Water - to 1 l
- Potential (cathodic) - 10 V
- Temperature - room
- Time - 2 min

The composition of the electrochemical bath and the parameters for the second treatment:

- Nickel chloride (NiCl) - 240 g
- Hydrochloric acid (HCl) - 120 ml
- Water - to 1 l
- Temperature - room
- Time - 2 min
- Current density (cathodic) - 16,2 A/dm^2

For all time, 4 solutions for the electrochemical deposition of composite materials have been made. All solutions are based on a standard solution for nickel plating:

- Nickel sulphate Ni_2SO_4 - 300 g/l
- Nickel chloride $NiCl_2$ - 50 g/l
- Boric acid H_3BO_3 - 40 g/l
- Formalin - 1,2 g/l
- Methanol - 1,4 g/l

In the first solution, there were no additional (ceramic) components. The second solution contained aluminum oxide Al_2O_3 - 10 g/l in addition to the main components of the solution for the electrochemical deposition of nickel. The third solution contained titanium dioxide TiO_2 - 20 g/l. Initially, in the fourth solution, concentration of the TiO_2 was 10 g/l. Based on the fourth solution, 3 small samples were obtained. After that, the concentration of TiO_2 was increased to 30 g/l.

An attempt was also made to deposit the composite coating on the basis of Al_2O_3. During the investigation of the coating on the basis of Al_2O_3 in a microlaboratory, Al_2O_3 particles were not detected. A particle diameter of Al_2O_3 was also measured, which is 80 μm. In this connection, a decision was made to deposit TiO_2 particles instead of Al_2O_3.

Electrochemical deposition of coatings was carried out using Autolab and the Nova program [5] with the following parameters:

- Mode - Galvanostatic;
- Current range - 100 mA;
- Bandwidth - High stability;
- Apply current - 0.035 A/dm^2;
- Duration - 1800 s;
- Interval time - 0.1;

After each deposition, the thickness of the coating was calculated according to the Simpson's rule [6]:

$$\int_a^b f(x)dx = \frac{h}{3}[f(x_0) + 4f(x_1) + 2f(x_2) + 4f(x_3) + \ldots + 2f(x_{2n-1}) + 4f(x_{2n-1}) + f(x_{2n})] + R_T =$$

$$= \frac{h}{3}\left[f(x_0) + \sum_{k=1}^{n} 4f(x_{2k-1}) + \sum_{k=1}^{n-1} 2f(x_{2k}) + f(x_{2n})\right] + R_T = S_n + R_T$$

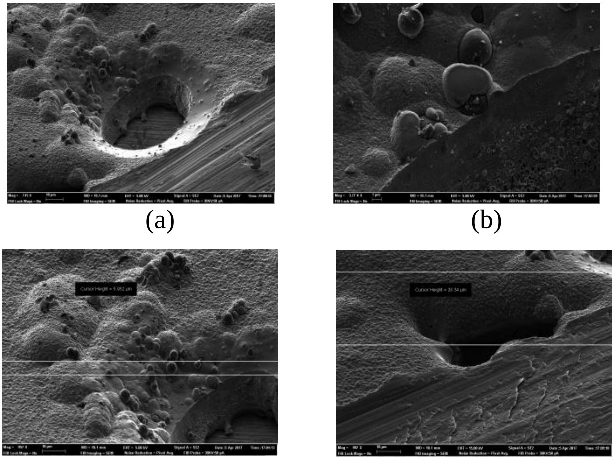
$$h = \frac{b-a}{2_n}$$

$$x_k = a + \frac{K}{2n}(b-a)$$

$$R_T = \frac{-(b-a)h^4}{180} f^{(4)}(\xi), a < \xi < b$$

Depending on the surface area, deposition time and concentration of TiO_2 in solution, the thickness of coatings was from 0.023 mm to 0.069 mm.

After deposition of the coatings on the samples, the coatings were examined in SEM, the results are given below (Figure 1).



(a) (b)

(c) (d)

Figure 1 – Study of the coating in a scanning electron microscope: (a) violation of the coating, (b) TiO_2 particles, (c) TiO_2 particle diameter measurement, (d) thickness measurement of coatings

Figure 1(a) shows a violation of the coating based on Ni-TiO_2 due to the emerging hydrogen bubble. Also in the figure 1(a), a trace (bottom right corner) of the coating cut is visible to determine its thickness and internal structure. In the figure 1(b), the TiO_2 particles included in the Ni structure are clearly visible.

In the figure 1(c), the TiO_2 particle diameter is measured, which is 5.952 µm. In the figure 1(d), the coating thickness is measured, which is 30.34 µm, which corresponds to the calculations.

In addition to the above, was made a study of the particle size of titanium oxide by the optical method (from 2728 nm to 5706 nm). The results correspond to the studies in SEM (Figure 1(c)).

A direct dependence of the amount of TiO_2 particles in the coating on the concentration in solution was determined using the method of graphical particle counting using images taken in SEM through the ESB filter and the ImageJ program [7-9]. The results are shown in the histogram below (Figure 2). The histogram was plotted against the initial particle size, time of deposition and concentration of particles in solution.

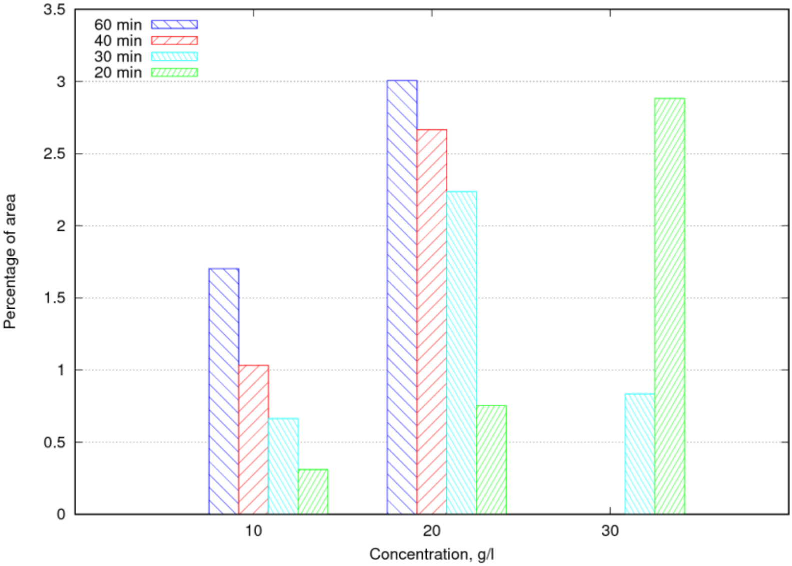


Figure 2 – The percentage of area occupied by the particles
as a function of the deposition time and concentration of TiO2
in the solution for the initial size of 0.50 µm

As can be seen on the histogram, there is a marked dependence on the amount of particles in the coating from the concentration of TiO_2 in the solution and the deposition time: the larger the particle concentration of TiO_2 in the solution and the longer the deposition time, the more particles in the coating.

It should be noted that in the histogram with 30 g/l for the columns of 20 minutes and 30 minutes there is some ambiguity. To resolve this ambiguity, additional studies with a solution of TiO_2 with a concentration of 30 g/l are necessary.

After that, tribological and tribocorrosive studies of the Steel/Ni/Ni-TiO_2 materials were performed using the reciprocating motion of a 3 mm ball of Al_2O_3 with different exposure time and load. The results are shown below.Tribological studies were carried out for Steel/Ni/Ni-TiO_2 materials with a load of 1 N and an exposure time of 10/20/30/40 minutes. After that, the construction of track profiles was carried out using a micro laboratory and an optical method based on confocal microscopy. Below are graphs for different materials and different time (Figures 3-6).

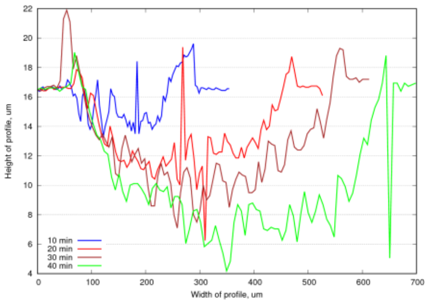


Figure 3 – Comparison of track profiles
for duplex steel
depending on the time of exposure

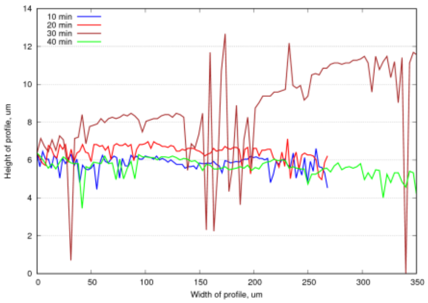


Figure 4 – Comparison of track profiles
for nickel
depending on the time of exposure

In the figure 3, the dependence of the shape of the track profile on the time of the load action is visible: with increasing exposure time, the height and width of the track profile increases rectilinearly.

Figure 4 shows that when comparing the profile of the tracks of nickel and duplex steel, the tracks are not clearly expressed regardless of the time of impact of the load. Also on the track with 30 minutes of load, there is some uncertainty, which is associated with a strong damage to the coating.

In the figure 5 it is noticeable that unlike the nickel tracks, the tracks Ni-TiO_2 are not very obvious and hard to identify

In the figure 6, there is a clear tendency to increase the height and width of the track profile for stainless steel, For Ni and Ni-TiO_2 do not change with increasing exposure time.

After tribological studies tribocorrosive studies were carried out for Ni and Ni-TiO_2 coatings. Tribocorrosion studies were carried out for 30 minutes at a load of 2/3/5/7 N in sulfuric acid H_2SO_4 0.5 M. Below are the comparative graphs of track profiles (Figures 7-9).

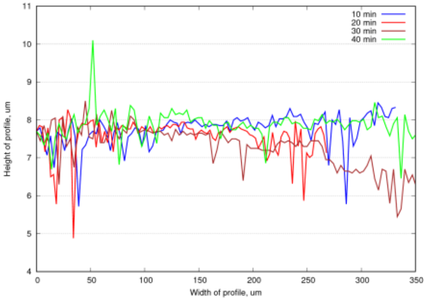


Figure 5 – Comparison of track profiles
for Ni-TiO_2
depending on the time of exposure

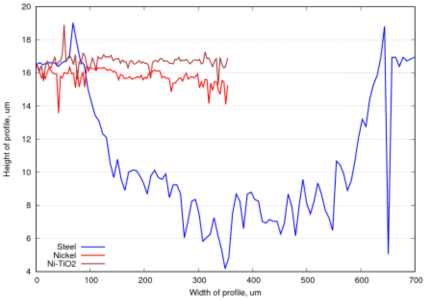


Figure 6 – Comparison of track profiles
for Steel/Ni/Ni-TiO2
in 40 minutes

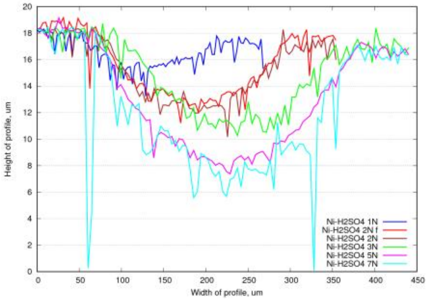


Figure 7 – Comparison of track profiles
for nickel
for 30 minutes
with different loads

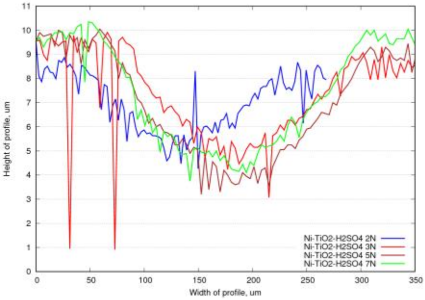


Figure 8 – Comparison of track profiles
for Ni-TiO_2
for 30 minutes
with different loads

In the figures 7 and 8, a relative construction of track profiles for Ni and Ni-TiO_2 coatings is performed. For Ni coating, it can be seen that the height and width of the track profile increases in direct proportion to the increase in load with an unchanged exposure time. At the same time, the track profile for Ni-TiO_2 coverage with increasing load and constant time does not change.

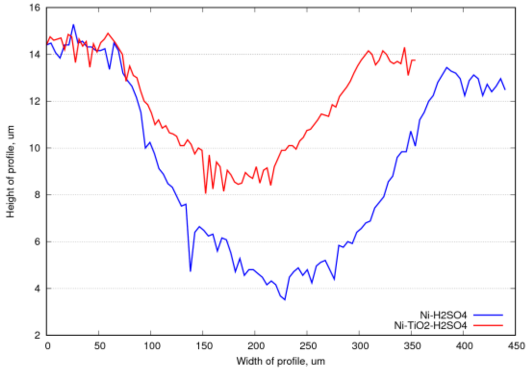


Figure 9 – Comparison of track profiles for Ni/Ni-TiO_2 coatings for 30 minutes and 5N load

Conclusions

During the period of research the following stages were performed. Samples were prepared for the electrochemical deposition of composite materials, which included cutting, grinding, polishing, and electrochemical cleaning before deposition. Four solutions were made for the electrochemical deposition of nickel and composite materials with the addition of additional ceramic elements - Al_2O_3 and TiO_2 in various concentrations. The precipitation itself was carried out directly on samples of duplex steel of various sizes, in different positions (vertical and horizontal) and with different particle concentrations of TiO_2 in solution. Studies of coatings in SEM have been carried out by various techniques, such as energy-dispersive x-ray spectroscopy, focused ion beam technique, transmission electron microscopy. The Al_2O_3 particle size was measured in a microlaboratory, as well as particles TiO_2 by a laser method. In addition, the dependence of the amount of particles in the coating was determined as a function of the concentration of TiO_2 in the solution by the graphic method using the ImageJ program. A tribological study of samples of various materials Steel/Ni/Ni-TiO_2 materials and comparative construction of track profiles was carried out. A tribocorrosive study of Ni/Ni-TiO_2 samples and a comparative construction of track profiles were also carried out.

The following main results can be singled out:

- there is a definite dependence of the amount of particles in the coating, depending on the concentration of TiO_2 particles in the solution and the time of electrochemical deposition of coatings. The greater the concentration and the longer the deposition time, the greater the amount of particles in the coating (for a concentration of 10 and 20 g/l). For a concentration of 30 g/l, additional studies are needed;

- after tribological studies of the materials, Ni-TiO_2, it was determined (confirmed) that Ni/Ni-TiO_2 coatings perform a protective function against mechanical abrasion under direct action on the base material;
- after tribocorrosive studies of Ni/Ni-TiO_2 materials, it was determined that for Ni coating, the height and width of the track profile is noticeably increased depending on the increase in load with constant exposure time. At the same time, the track profile for Ni-TiO_2 coverage with increasing load and constant time does not change. In this connection, it is possible to single out the positive influence of the TiO_2 particles in the coating, which increase the protective functions of the coating from mechanical abrasion, while the load for Ni-TiO_2 ceases to play such a significant role.

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