CORROSION OF Ni-5%Al AND Ni-5%Al-Al₂O₃ FLAME SPRAYED COATINGS OF "CastoDyn 8000" TORCH IN 0.01 M H₂SO₄ AND 3.5% NaCl SOLUTIONS

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Abstract

One of methods of regenerating parts of machines is flame thermal spraying, which can be used by ship engine room crew. This method does not require great skill of the operator and is not associated with expensive workstation equipment.

Flame sprayed coatings are characterized by porosity and the presence of oxide inclusions. The presence of pores affects negatively on the corrosion properties of coatings. There is a corrosive environment which may be passed through the pores of the coating to the substrate. This phenomenon is especially dangerous in case of applying cathodic coatings (copper, copper alloys and nickel alloys). The substrate corrosion may then proceed below coating.

In the paper researches results of corrosion properties of Ni-Al alloy and Ni-Al-Al₂O₃ composite coatings were presented. Coatings were obtained by flame spraying of "Casto-Dyn 8000" torch. The studies in 0.01 M H_2SO_4 and 3.5 NaCl (artificial sea water) environments were realized. Measurements were made following methods: polarization and impedance spectroscopy.

Rated coatings are more resistant to the 3.5% NaCl environment than the 0.01 M H₂SO₄. Corrosion current density for alloy coatings in artificial seawater was 7 μ A/cm² and 232 μ A/cm² environment acidic. Impedance spectroscopy studies showed that the alloy coatings are characterized by more than four times greater resistance in sodium chloride solution than in sulphuric acid solution. Curves flattened in the Nyquist plots may indicate that the appearance of products of corrosion coatings in the pores of the samples during exposure to sea water substitute. The value of corrosion potential in an environment of 3.5% NaCl is about 200 mV lower than 0.01 M H₂SO₄.

Composite coatings Ni-Al-Al₂ O_3 were characterized by a lower corrosion current densities and increased resistance than Ni-Al coatings. This is connected with the operation of non-conducting barrier electric particles of alumina.

Keywords: thermal spray coating, composite coating, corrosion, torque pomp

1. Introduction

Torque pumps are often used on ships to drainage of cargo bilge, emptying ballast tanks in engine cooling systems and water supply boilers. In some cases, a medium that is pumped, it is sea water. Due to the working conditions for the construction of such pumps are used materials resistant to wear and electrochemical corrosion cavitation caused by sea water. The pump shafts are made from steel resistant to corrosion. In practice the existence of shafts damages are observed. It is often stated the consumption of pins (corrosion, friction and surface fatigue) on-site stuffing-box (gland). In practice, the damaging shafts are exchanged for new or regenerated pins through turning or grinding, the imposition of galvanic chromium coatings and deposition on the damaged shaft sleeve. Currently, the basic material of a shell increasing durability of machinery parts is chrome. However, due to the toxicity of the bath and a small current efficiency process for obtaining electrolytic chromium coatings are looking for alternatives. One proposal is to apply the coating with nickel and nickel matrix composite obtained using various technologies such as plated or spray methods [1-3].

The technical composite coatings on a metal matrix are used to increasing the durability of machine parts in frictional pairs, or protective coatings. It is believed that through appropriate

selection of matrix material and reinforcing phase (e.g., ceramics) can be obtained from the shell of the most useful properties of optima [4, 7].

Effect of dispersion of inclusions on corrosion resistance of composite coatings is not unambiguous. In some publications presented data showing improved corrosion resistance of Ni- Al_2O_3 coatings, it is stated the lower value of corrosion current density, and hence the corrosion rate, which is assigned the action particles of ceramics, which do not conduct electrical current. Much of the authors, however, believes that the introduction of pottery can cause the formation of local electrochemical cells in which the anodic area is made around the cathodic ceramic inclusions will be underwent localized corrosion. The actual course of corrosion processes depends to a large degree on the type of warp, the kind of ceramics and the environment. It probably also depends on the share and size of the ceramic inclusions [5].

In this work, the application of Ni-5% Al alloy and Ni-5% Al-Al₂O₃ composite coatings for the regeneration pivots pump shaft are proposed by flame spraying. Matrix nickel coatings are characterized by high plasticity, adhesion to steel substrates, abrasion resistance and a passive state. A reinforcing phase of alumina particles with a diameter of $\phi = 60$ microns are used. Spraying method does not require great skill from the operator and is not associated with expensive equipment, workstation, so it can be used by ship engine room crew or repair brigade during the voyage.

2. Preparing of samples

Coating was applied to a degreased steel elements by flame (steel C45) with a surface roughness Ra = 3.5 mm and purity class SA3. Powder ProXon 21.021 (Ni- 93.45%, Al-5%, B-0.8%, Fe-0.34% Cr-0.18%, Si-0.15%, C-0.08%) and its mixture with powder MetaCeram 28020 (Al₂O₃-97.7% TiO₂-2.2%, SiO₂-0.1%) were used in flame spraying. The volumetric concentration of non-metallic materials in coating was obtained: 0, 15, 30, 45%. Spraying torch was used, "Casto-Dyn 8000", the company Castolin. The following flame spraying parameters:

- Acetylene pressure: 0.07 MPa,
- The pressure of oxygen: 0.4 MPa,
- Air pressure: 0.1 MPa,
- Speed torch: 25 m/min
- Sprayed distance: 150 mm,
- The type of flame: neutral,
- The number of superimposed layers: 6.

Coating spraying was obtained of pre-heated steel substrate to a temperature of 100°C. Then it was sprayed with a coating so that the temperature of the shell shall not exceed 250°. In the case of the first layer of composite coating was applied without phase dispersion, in order to improve adhesion of coatings to the steel substrate [5].

3. Methods

The structure of the coatings was evaluated on cross-sections, using metallographic optical microscope Zaiss AxioVert 25th

Microhardness measurement was performed using Vickers hardness tester using H-type device mounted in the holder Vertival microscope. It was used 0.4 N applied load-time 10 seconds, at ambient temperature. Length was measured diagonally fingerprints with precision of 0.2 microns.

The corrosion tests were performed in 0.01M H_2SO_4 and 3.5% NaCl (artificial seawater) solutions by two techniques. The specimen of 1 cm² surface was rinsed with acetone, and then put into the cell, in which the anode made of platinised titanium and reference saturated calomel electrode were also immersed in 0.01M H_2SO_4 and 3.5% NaCl at ambient temperature. The solutions were constantly stirred.

With the first potentiokinetic technique, the polarization curves were obtained at a 10 mV/min rate of potential shift, within the region $\pm 150 \text{mV}$ from corrosion potential after half hour of preexposure in the electrolyte. As the first the cathodic curve and then anodic curve were recorded. The corrosion current was determined.

The second technique, impedance measurements of the base–coating-electrolyte system were performed in range of current frequency from 100 to 0.01 kHz, by sequential induction by sinusoidal voltage signal in range of ± 10 mV from stationary potential. The ATLAS 053 EU&IA instrument was used. The obtained results were analysed by the Equivalent Circuit (Boukamp) software in order to determine the charge transfer resistance.

For each specimen at least three tests were made and means calculated.

4. Results

Flame sprayed coatings Ni-5% Al alloy and Ni-Al-5%-Al₂O₃ composite were characterized by porosity. Porosity of the coatings depended on the content of dispersed phase in the composite coatings. Structure of the coatings: alloy and composite are shown in Fig. 1. Increased alumina content embedded in the alloy matrix contributes to the increase in coating porosity. The results of microhardness measurements are shown in Fig. 2. Depending on the phase composition of the average microhardness value of the matrix ranged from 146 to 197 HV 0.04. In order to determine the effect of composition on the microhardness of coatings are used non-parametric equivalent analysis of variance, a statistical test Kruskal-Wallis. This method was used because of the large dispersion of measurements obtained for different types of coatings. Calculations computer software "Statistica 5.5" was used. The result of statistical analysis H (3, N = 36) = 22.39, for a given level of significance $\alpha = 0.05$, allows to reject the null hypothesis that there were no differences between the variables. Results of statistical analysis allows, with a probability of 95%, conclude that there is a statistically significant effect of alumina content on the microhardness of the alloy matrix of coatings.



Fig. 1. The structure of flame sparing coatings obtained by "Casto-Dyn 8000" torch: a) Ni-5%Al, b) Ni-5%Al-15%Al₂O₃, c) Ni-5%Al-30%Al₂O₃, d) Ni-5%Al-45%Al₂O₃



Fig. 2. The microhardness of Ni-5%Al alloys and Ni-5%Al-Al₂O₂ composites coating obtained by "Casto-Dyn 8000" torch

The effect of microhardness measurements can indirectly testify to the stress occurring in their coating. In turn, residual stress can affect the value of the corrosive potential of coatings. The greater the residual stress found in the material, the greater the tendency to proceed on the surface of corrosive processes, and thus should be observed to reduce the value of potential. Porosity of the coating may also contribute to changes in the value potential. Determined the value of the corrosion potential takes the value indirect, located between the potential of matrix material coating and the steel substrate potential. In an environment of sulphuric acid solution, it was found that 45% of alumina caused a reduction in the average value of the potential corrosion (E_{corr}) coatings to from about -250 mV to -180 mV for the alloy coating (Fig. 3). In sea water, there was no impact of the quantity of ceramic phase included in a metal matrix coating on the corrosion potential value. In seawater, the flame spray coatings adopt a lower value than the corrosion potential in an 0.01 M H₂SO₄. Coatings corroded in the environment of 3.5% NaCl solution under control and cathodic environment of sulphuric acid solution under anodic control. Fig. 4 shows the results of measuring on the corrosion current density. Mean values Icorr of environment of sea water are lower than in a solution of sulphuric acid. However, in the test environments were different effects of alumina concentration on the rate of corrosion. In the 0.01 molar solution environment of sulphuric acid were found positive effect of oxide inclusions on the corrosion resistance of thermally sprayed coatings. Layers with 45% Al₂O₃ concentration were characterized by a corrosion current density of at $I_{corr} = 74 \ \mu A/cm^2$, in the case of alloy coatings $I_{corr} = 232 \ \mu A/cm^2$. Significantly lower corrosion current density values were observed in the environment of sea water replacement. Corrosion current density ranged from 7 to 15 μ A/cm². The relationship between the amount of oxide phase and is proportional I_{corr}.



Fig. 3. The alumina oxide influence on corrosion potential values E_{corr} coatings in a) 0.01 M H_2SO_4 and b) 3.5% NaCl environments



Fig. 4. The alumina oxide influence on corrosion current density values I_{corr} coatings in a) 0.01 M H_2SO_4 and b) 3.5% NaCl environments

The results of impedance (Tab. 1) also show greater resistance to corrosion coatings in the environment of the sea water than in a solution of sulphuric acid. In both acidic and alkaline conditions, it was found that the value of polarization resistance Rp increases with the oxide phase content embedded in the coating. In the case of 3.5% NaCl solution phase Al₂O₃ concentration increases the average value of resistance of coatings, and thus lower the rate of corrosion coatings process. Large values of resistance in the case of composite coatings of Ni-5% Al-Al₂O₃ can be caused by corrosion products in the pores or under coatings. It is evidenced by the flattened impedance spectrum (Fig. 5).

Tab. 1	. Polarization	resistance of j	flame sprayed	l coatings (average val	lues of t	hree measurements)
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Coating	$R_p [\Omega^* cm^2]$				
Coating	0.01 M H ₂ SO ₄ environment	3.5% NaCl environment			
Ni-5%Al	166.7	788.2			
Ni-5% Al-15% Al ₂ O ₃	179.6	1112.9			
Ni-5% Al-30% Al ₂ O ₃	233.3	1230.4			
Ni-5% Al-45% Al ₂ O ₃	256.9	963.5			



Fig. 5. The samples of impedance spectra of coatings in 3.5% NaCl environment

5. Summary

Thermally sprayed Ni-5% Al alloy and Ni-5% Al-Al₂O₃ composite coatings slower corrodes in a solution of 3.5% NaCl than in 0.01 M H₂SO₄ environment.

Corrosion potentials of coatings values are lower in an environment of sea water than in a solution of sulphuric acid.

In the environment of 0.01 M H_2SO_4 the presence of oxide phase decreases the value of corrosion current density and an increase in polarization resistance. Consequently, the participation of aluminum oxide in coatings reduces the corrosion rate.

In the solution of 3.5% NaCl there was a slight increase in corrosion current density of composite coatings compared to the alloy coatings.

Thermally sprayed coating of Ni-5% Al and Ni-5% Al-Al₂O₃ can be used as protective coatings and regeneration in sea water environment.

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