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THE QUANTITATIVE ANALYSIS OF THE EFFECT OF THE POROSITY, THE VOLUME OF FRACTION OF REINFORCING PHASE AND THE THERMAL SPRAYING METHODS, ON CORROSION PROPERTIES OF COMPOSITE COATINGS IN MARINE ENVIRONMENT

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Abstract

In the paper an assessment of the impact of the thermal spray methods, porosity and the volume fraction of reinforcing phase (aluminium oxide) on the corrosion properties (corrosion current density and corrosion potential) of Ni-5%Al alloy coatings and Ni-5%Al-Al_2O_3 composite coatings reinforced by particle dispersion was presented. The volume fraction of reinforcing phase in the coatings was 15, 30 and 45%. These materials would potentially be used in the shipbuilding industry as regenerative coatings for repair of marine pump shafts. The samples (substrates) were made of carbon C45 (0.45%C) steel. For thermal spray of coatings, two oxy-acetylene (Casto-Dyn DS 8000 and Roto-Tec 80) torches and one plasma gun (PN120) were deployed. The two distances 100 mm and 150 mm from the nozzle onto the substrate were used. In addition, the two substrate temperatures 150°C or 250°C were applied.

Corrosion properties of the coatings were tested in a replacement seawater (3.5% NaCl) by polarization curves method. It has been found that among the independent variables considered: a method of thermal spraying, fraction of reinforcing phase and porosity, the last mentioned has the greatest influence on the corrosion properties of thermally sprayed coatings on the matrix of Ni-5% Al. The value of the corrosion potential of coatings depended on the used thermal spray method. It has been found that the more modern method of producing coatings of the higher velocity of the coating material in a sprayed stream has a significant positive effect on the porosity of the coatings. The presence of the reinforcing phase (Al_2O_3) in composite coatings contributes to a reduction of value of the corrosion current density and increase of the corrosion potential value.

Keywords: *thermal spraying, corrosion property, composite coating*

1. Introduction

Construction elements of impeller and positive-displacement pumps and other devices operating on sea vessels are often exposed to seawater. Corrosion activity of seawater depends on a temperature and a chemical composition. The chemical composition of seawater primarily salinity mainly depends on the basins. Seawater contains dissolved salts (e.g. NaCl, $MgCl_2$), gases (primarily oxygen and carbon dioxide), organic impurities and traces of almost all elements. The salts concentration in seawater depends mainly on the intensity of the evaporation and the amount of flowing in freshwater. According to the findings of The International Council for the Exploration of the Sea, salinity is expressed using the labeled content of chloride ions (the Knudsen formula). The average salinity of ocean water is 3.5%, which correspond to 2% of the chloride ions. The salinity of the sea is more diverse, e.g. for The Baltic Sea is approx. 1%, and The Red Sea – approximately 4.5% [8].

Corrosion of metal matrix composites (MMC) under constant immersion in seawater is of electrochemical nature. Due to certain characteristics of the seawater environment resulting from the chemical composition and properties there of the corrosion process is characterized by [8]:

- high activity of micro and macro galvanic cells,

- negligible role of inhibition of the oxidation reaction of most metal alloys,
- essential role of inhibition of the reduction reaction,
- high tendency to local corrosion.

Impact of reinforced phase on the corrosion resistance of composite coatings has not yet been adequately elucidated. In some publications, the evidence of improved corrosion resistance of composite waiting reinforced by ceramic inclusions is presented. Lower a corrosion current density values or increase of charge transfer resistance was observed. Therefore, a slower rate of general corrosion was stated. This was attributed to the barrier action of ceramic particles, which do not conduct electric current or are semiconductors. The presences of oxides, carbides or nitrides in the metal matrix often change the course of corrosion. Composite coatings corrode with inhibition of reduction reaction. That is, the oxidation reaction occurs more readily than the reduction reaction [3, 12, 22].

Reducing the porosity of the coating contributes to the reduction of the anode current [10] and the corrosion current [21]. The usefulness of thermally sprayed composite coatings as protective layers in NaCl solution is determined by porosity. If the porosity is relatively small, up to 4%, the presence of a reinforcing phase improves the corrosion resistance of the Al-20%SiC coatings sprayed by Castodyn DS 8000 oxy-acetylene torch [4]. In our case, it was proposed to reduce the porosity of coatings by shortening the distance between the blowpipe and the workpiece surface or by plastic deformation [1, 2, 19]. The results presented in [9, 17] confirm the usefulness of plastic working to improve the corrosion properties of thermally sprayed Ni-5Al-Al_2O_3 composite and NiAl, Ni_3Al intermetallic coatings. In the case of the Al-SiC, coatings obtained by the flame spraying the reinforcing particles contribute to increased porosity as compared to aluminium coatings. Porosity is responsible for the permeation of the environment from surface of composite coating to the substrate (Mg-Al alloy), and there are formed galvanic cells [2, 4]. The subsurface corrosion was also found under layers of Ni-WC obtained by plasma spraying [11].

The presence of the ceramic phase in the metal matrix can cause the formation of local electrochemical cells, wherein the anodic zones around the cathodic inclusions of oxide phases will undergo localized corrosion [1, 6, 11, 12, 14, 15, 19-21], especially in environments where corrosion processes occur as a result of oxygen depolarization [20]. It is believed that the presence of the reinforcing phase makes difficult the passivation of composites coating with matrices of nickel [19] and aluminium [13], although there are data that contradict that thesis [12]. Improvement of the corrosion resistance of aluminium thermally sprayed coatings in a 3.5% NaCl is obtained by the anodic oxidation [5].

Tao studies [18] show no effect of the alumina on the corrosion of aluminium matrix composites coatings obtained by thermal spraying. Luczak [13] shows the negative effects of participation and particle size of reinforcement on corrosion resistance of the Al-Al_2O_3 composite.

The actual course of corrosion processes depend greatly on the type of matrix, reinforcing phase and the environment. The actual course of corrosion process of composites depends mainly on the type of matrix, kind of reinforcing phase and the environment conditions. The presence of reinforcing phase also effects the value of the corrosion potential. It probably depends also on the participation and the size of ceramic inclusions and porosity of coatings. The factor influencing the corrosion resistance is also the structure of matrix [1, 13, 14, 20, 21]. Trzaska [19] reported that nickel matrix composite coatings of amorphous structure are not subject to localized corrosion. Dobrzański [7] observes improving the corrosion resistance of aluminium matrix composites up to 15% percentage of Al_2O_3 phase. Above this percentage faster corrosion of composites was observed with, a simultaneous decrease of the value of corrosion potential. Homogenization of the matrix structure after heat treatment has a positive effect on the corrosion resistance of aluminium matrix composites. Composite coatings mostly take the cathodic potential as compared to the metal coating, rarely the anodic potential [13, 14, 19].

In this paper, a quantitative assessment of the impact of the method of preparation, the porosity and participation of the reinforcing phase on the corrosion properties of thermally sprayed Ni-

5%Al and Al-5%Ni-Al_2O_3 coatings is presented.

2. Sample preparation

Coatings, which were used to assess the impact of the technology of thermal spray on resistance to corrosion, were imposed on a flat bar made of C45 (0.45%C) steel. Surfaces of flat bar were cleaned of solid contaminants by abrasive blasting. The grade of cleanliness of steel surface preparation was Sa2 ½ (PN-ISO 8501-1:1988). The roughness of the metal surface was Ra = 3 μm. Immediately before thermal spraying the surface was degreased by flame treatment. For regeneration of machine parts of the shaft-type operating in seawater environment, the powder ProXom 21021 produced by Messer Eutectic Castolin was applied. This material is produced on the basis of nickel with the addition of aluminium in an amount of from 5% to 7% (w). EDS analysis of this material revealed the presence of molybdenum. Composite coatings were obtained using the mixture of ProXon 21021 and 28020 MetaCeram powders. Composition of the MetaCeram 28020 powder was as follows: α-Al_2O_3 – 97.7%, TiO_2 – 2.2%, SiO_2 – 0.1%. The volume fraction of reinforcing phase (Al_2O_3) in the sprayed material was 15, 30 and 45%. The coatings were prepared by thermal spraying. The two oxy-acetylene torches: Roto-tec 80, Castodyn DS 8000 and plasmatron PN 120 were used. The two distances 100 mm and 150 mm from the nozzle onto the substrate were used. Also, the two substrate temperature 150°C ("on cold") or 250°C ("on hot") were applied. The porosity of the thermal sprayed coating, depending on the applied method, was in the range of 9-47%.

3. Testing methods

The corrosion resistance of Ni-5%Al alloy and Ni-5%Al-Al_2O_3 composite coatings was estimated by electrochemical potentiodynamic (polarization) method. Electrochemical polarization studies belong to the classical methods of corrosion testing. It is well understood and relatively frequently used. The rate of measurement is high compared to the gravimetric methods. Electrochemical polarization allows both estimation of the instantaneous rate of corrosion and determination of the nature of the processes involved. The aim of studies of the polarization is to analyse the corrosion current with the aid of the following formula:

$$j = j_{corr}\left[\left(1-\frac{j_a}{j_{da}}\right)\exp\left(\frac{2.3(E-E_{corr})}{b_a}\right)-\left(1-\left|\frac{j_c}{j_{dc}}\right|\right)\exp\left(\frac{-2.3(E-E_{corr})}{b_c}\right)\right], \qquad (1)$$

where:
j – current density of polarization [mA/cm^2],
j_{corr} – corrosion current density [mA/cm^2],
E – polarization potential [mV],
E_{corr} – corrosion potential [mV],
b_a – anodic Tafel constant [mV],
b_c – cathodic Tafel constant [mV].
j_a – partial anodic current density [mA/cm^2],
j_c – partial cathodic current density [A/cm^2],
j_{da} – limiting anodic current density [mA/cm^2],
j_{dc} – limiting cathodic current density [mA/cm^2].

The polarization measurements in a three-electrode cell were performed. The test sample, platinum counter-electrode (CE), saturated calomel electrode (SCE) were placed in the vessel, in which was 500 ml of 3.5% NaCl solution (the so-called replacement seawater) at ambient temperature. The samples were exposed to the electrolyte for one hour.

During the study, the ATLAS 0531 potentiostat was used. The polarization curves of j = f (E) in the range of E_{corr} ±150 mV were recorded. Rate of change of the potential, in all cases, was 10 mV/min. In order to calculate the value of parameters characterizing the properties of corrosion (corrosion current density, corrosion potential, Tafel constants, limiting current density) of the test material the “Elfit – corrosion polarization data fitting program“ computer program was used. This program calculates the parameters of the process of corrosion of the equation (1).

To assess the impact of the method of spraying and the participation of reinforcing phase on the corrosion resistance of thermal sprayed coatings, calculated values of corrosion current density and corrosion potential were used.

For quantitative analysis of the effect: of the porosity, the volume of fraction of reinforcing phase and the thermal spraying methods, on corrosion properties of Ni-5%Al-Al_2O_3 composite coatings in marine environment the multiple regression was used.

4. Results

Tab. 1 shows the results of the multiple regression analysis of the effect of a thermal spraying method, and the volume fraction of reinforcing phase and porosity on the corrosion current density value of the coatings in replacement seawater environment.

The results of analysis of variance, $F(3, 8) = 2.6$, and t-Student's tests may indicate lack of sufficient statistical significance effect of analysed independent variables on the corrosion rate.

Due to low value of the correlation ($R=0.3$) between the independent variable (thermal spraying method) and the dependent variable (j_{corr}), and to the fact that the independent variable remains practically isolated, it was decided to exclude the independent variable from the analysis.

Tab. 1. The results of multiple regression analysis for the dependent variable j_{corr} ($F(3, 8) = 2.6$ – test of homogeneity of variance, $p < 0.12$ – the level of significance of the test of homogeneity of variance, $R = 0.7$- correlation coefficient, $R^2 = 0.49$ – R-square, SEE = 8.75 – standard error of estimate)

	BETA	B	p
Constant (intercept)	-	0.24	0.99
Thermal spraying method – value coded (m)	0.23	2.81	0.39
Volume fraction of reinforcing phase (u)	-0.79	-0.47	0.11
Porosity of the coatings (P)	0.99	1	0.03

where:

BETA standardized regression coefficient,
B regression coefficient in the equation,
p the calculated level of significance for the t-Student’s test,
m code of thermal spray method, discrete variable adopting the following values:

1 – Roto-Tec 80 – “on cold”,
2 – Roto-Tec 80 – “on hot”,
3 – Casto-Dyn DS 8000 – 150 mm,
4 – Casto-Dyn DS 8000 – 100 mm,
5 – PN 120,

u volume fraction of reinforcement phase in the sprayed material (in the range of 0 to 45%),
P relative volume of coating porosity (in the range of 5-47%).

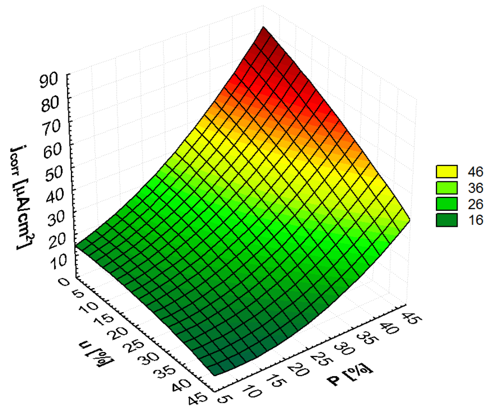

Fig. 1. Effect of volume fraction of reinforcement phase (u) in the sprayed material and coating porosity (P) on j_{corr} value of Ni-5%Al matrix composite coatings

Tab. 2. The results of multiple regression analysis for the dependent variable j_{corr}, excluding the independent variable – "thermal spraying method" (F (2,9) = 5.13, $p < 0.03$, R = 0.73, R^2 = 0.53, SEE = 7.99)

	BETA	B	p
Constant (intercept)	–	10.74	0.04
Volume fraction of reinforcing phase (u)	–0.82	–0.5	0.047
Porosity of the coatings (P)	0.93	1.06	0.01

The effect of coatings porosity (P) and volume fraction of reinforcing phase in coatings (u) on corrosion current density value was presented in Fig. 1. A porosity has the greatest effect on the protective properties of the Ni-5%Al matrix composite coatings in marine environments (Tab. 2). It was evidenced by the very high value of the standardized regression coefficient (BETA = 0.93). The variable P alone can explain nearly 86% ($BETA^2 \cdot 100\%$) variance of the dependent variable, excluding the impact of other independent variables. Porosity significantly reduces the protective properties of Ni-5%Al alloy coatings and Ni-5%Al-Al_2O_3 composite coatings. The participation of Al_2O_3 phase (BETA=-0.82) influences the density of corrosion current to a lesser extent. The relationship between u and j_{corr} variables is inversely proportional.

Multiple linear regression analysis leads the conclusion that the proportion of non-conducting reinforcing phase allows to obtain a composite coating with improved protective properties as compared to alloy coatings in a 3.5% aqueous solution of sodium chloride. The requirement for reducing the corrosion rate needs to reduce the porosity of the composite coatings. Due to the lack of a linear relationship between the independent variables and the dependent variable mathematical transformations of the independent variables were performed. The aim of the transformation was to obtain a linear relationship between the parameters. After taking into account the transformations of variable the multiple regression equation used to predict a corrosion current density values takes the form ($F(6,5) = 9.5$, $p < 0.01$, $R = 0.96$, $R^2 = 0.92$, SEE = 4.4):

$$j_{corr} = -270 + 136m + 0.21u + 0.6P - 15.68m^2 - 0.01u^2 - 0.05mP\,. \tag{2}$$

Tab. 3. The results of multiple regression analysis for the dependent variable E_{corr} (F (2,9) = 5.13, $p < 0.03$, R = 0.73, R^2 = 0.53, SEE = 7.99)

	BETA	B	p
Constant (intercept)	–	–278	$1 \cdot 10^{-6}$
Thermal spraying method – value coded (m)	–0.74	–37.84	$5.5 \cdot 10^{-5}$
Volume fraction of reinforcing phase (u)	0.54	1.35	0.01
Porosity of the coatings (P)	–0.76	–3,83	$2 \cdot 10^{-4}$

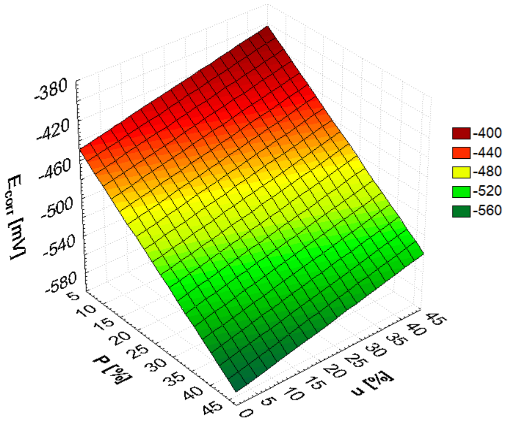

Fig. 2. Effect of volume fraction of reinforcement phase (u) and coating porosity (P) on E_{corr} value of Ni-5%Al matrix composite coatings

$$E_{corr} = -278 - 37.84m + 1.35u - 3.83P. \tag{3}$$

There is a high negative correlation (BETA = -0.76) between the porosity (P) and corrosion potential (E_{corr}) of coatings in an aqueous solution of sodium chloride (Tab. 3). There is displacement of E_{corr} values towards anodic potentials together with the increased number of voids in the microstructure of coatings. The increasing volume fraction of reinforcing phase including in the coating contributes to displacement of corrosive potential towards cathodic values (Fig. 2). This shows the rapid inhibition of the oxidation reaction occurring on the surface of the assessed composite coatings. The analysis of multiple regression (Tab. 3) showed a significant effect of the thermal spraying method on the value of the corrosion potential of coatings. The higher the particle velocity of the coating material (the more modern torch) colliding with the ground potential the greater the internal stresses present in the composite coatings. Consequently, the decrease the E_{corr} values was observed. The estimated value of the corrosion potential of Ni-5%Al-Al_2O_3 composite coatings in seawater can be determined from multiple regression equation (3).

5. Conclusions

1. Among the independent variables: thermal spraying methods, volume fraction of reinforcing phase and coatings porosity, this last mentioned has the greatest influence on the corrosion current density and corrosion potential of thermally sprayed coatings on the matrix of Ni-5%Al. The presence of these volume microstructural defects results in more intensive corrosion and in greater increment rate of the corrosion potential.
2. The applied technology of thermal spraying has a significant impact on the value of the corrosion potential of the alloy coatings of Ni-5% Al and composite coatings Ni-5%Al-Al_2O_3.
3. The presence of the reinforcing phase (Al_2O_3) in the composite coatings contributes to a reduction of corrosion current density value and increases the corrosion potential value.

References

[1] Arrabal, R., Pardo, A., Merino, M. C., Mohedano, M., Casajús, P., Merino, S., *Al/SiC thermal spray coatings for corrosion protection of Mg – Al alloys in humid and saline environments*, Surface and Coatings Technology, Vol. 204, pp. 2767-2774, 2010.

[2] Arrabal, R., Pardo, A., Merino, M. C., Mohedano, M., Casajus, P., Merino, S., *Corrosion of magnesium-aluminum alloys with Al-11Si/SiC thermal spray composite coatings in chloride solution*, Journal of Thermal Spray Technology Vol. 20, pp. 569-579, 2011.

[3] Baghery, P., Farzam, M., Mousavi, A. B., Hosseini M., *Ni-TiO_2 nanocomposite coating with high resistance to corrosion and wear*, Surface and Coatings Technology, Vol. 204, pp. 3804-3810, 2010.

[4] Campo, M., Carboneras, M., López, M. D., Torres, B., Rodrigo, P., Otero, E., Rams, J., *Corrosion resistance of thermally sprayed Al and Al/SiC coatings on Mg*, Surface and Coatings Technology, Vol. 203, pp. 3224-3230, 2009.

[5] Chang, C. H., Jeng, M. C., Su, C. Y., Chang, C. L., *An investigation of thermal sprayed aluminum/hard anodic composite coating on wear and corrosion resistant performance*, Thin Solid Films, Vol. 517, pp. 5265-5269, 2009.

[6] Charchalis, A., Starosta, R., *Effect of finishing on the corrosion properties of flame sprayed Ni-5%Al and Ni-5%Al-Al_2O_3 coatings*, Journal of KONES, Vol. 21(4), pp. 30-36, 2014.

[7] Dobrzański, L. A., Włodarczyk, A., Adamiak, M., *Wpływ obróbki cieplnej na odporność korozyjną materiałów kompozytowych o osnowie EN AW-2124 wzmacnianych cząstkami ceramicznymi Al_2O_3*, Kompozyty, Vol. 5, Nr 5, pp. 30-34, 2005.

[8] Domański, A., Birn, J., *Korozja okrętów i jej zapobieganie,* Wyd. Morskie, Gdansk 1970.

[9] Dyl, T., Starosta, R., *Effect of the ceramic dispersion in the nickiel matrix composite coatings on corrosion properties after plastic working*, Solid State Phenomena, Vol. 183, pp. 43-48 2012.

[10] Galvanetto, E., Borgioli, F., Galliano, F. P., Bacci, T., *Improvement of wear and corrosion resistance of RPS Ti-TiN coatings by means of thermal oxidation*, Surface and Coatings Technology, Vol. 200, pp. 3650-3655, 2006.

[11] Guozhi, X., Jingxian, Z., Yijun, L., Keyu, W., Xiangyin, M., Pinghua, L., *Effect of laser remelting on corrosion behavior of plasma-sprayed Ni-coated WC coatings*, Materials Science and Engineering, Vol. A460-461, pp. 351-356, 2007.

[12] Liu, S. L., Zheng, X. P., *Microstructure and properties of AC-HVAF sprayed Ni60/WC composite coating*, Journal of Alloys and Compounds, Vol. 480, pp. 254-258, 2009.

[13] Łuczak, K., Liberski, P., Śleziona, J., *Wpływ udziału objętościowego i wielkości cząstek na odporność korozyjną kompozytów aluminium-cząstki ceramiczne*, Kompozyty, Vol. 31, pp. 75-79, 2003.

[14] Spencer, K., Fabijanic, D. M., Zhang, M. X., *The use of Al-Al_2O_3 cold spray coatings to improve the surface properties of magnesium alloys*, Surface and Coatings Technology, Vol. 204, pp. 336-344, 2009.

[15] Starosta, R., *Corrosion of Ni-Al and Ni-Al-Al_2O_3 plasma sprayed coatings in 0.01 M H_2SO_4 and 3.5% NaCl solutions*, Solid State Phenomena, Vol. 199, pp. 390-395, 2013.

[16] Starosta, R., *Podstawy wytwarzania i obróbki powłok kompozytowych w procesach regeneracji elementów maszyn i urządzeń eksploatowanych w środowisku wody morskiej*, Wyd. Akademii Morskiej w Gdyni, Gdynia 2013.

[17] Starosta, R., *The influence of plastic strain on the corrosive properties of plasma sprayed intermetallic NiAl and Ni_3Al coatings*, Solid State Phenomena, Vol. 165, pp. 167-177, 2010.

[18] Tao, Y., Xiong, T., Sun, C., Jin, H., Du, H., Li, T., *Effect of α-Al2O3 on the properties of cold sprayed Al/α-Al_2O_3 composite coatings on AZ91D magnesium alloy*, Applied Surface Science, Vol. 256, pp. 261-266, 2009.

[19] Trzaska, M., Wyszyńska, A., Kowalewska, M., *Odporność korozyjna warstw kompozytowych z osnową niklową i dyspersyjną fazą ceramiczną*, Kompozyty, Vol. 2, pp. 338-341, 2002.

[20] Walczak, M., Bieniaś, J., Sidor-Walczak, J., *Badania korozyjne aluminiowych kompozytów zbrojonych SiC wykorzystywanych do produkcji tarcz hamulcowych*, Autobusy, Technika, Eksploatacja, Systemy Transportowe, Vol. 6, pp. 1-7, 2010.

[21] Xie, G., Lin, X., Wang, K., Mo, X., Zhang, D., Lin, P., *Corrosion characteristics of plasma-sprayed Ni-coated WC coatings comparison with different post-treatment*, Corrosion Science, Vol. 49, pp. 662-671, 2007.

[22] Xu, C., Du, L., Yang, B., Zhang, W., *The effect of Al content on the galvanic corrosion behaviour of coupled Ni/graphite and Ni-Al coatings*, Corrosion Science, Vol. 53, pp. 2066-2074, 2011.