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R. Starosta
Gdynia Maritime University, Mechanical Faculty, Department of Marine Maintenance

PROPERTIES OF THERMAL SPRAYING Ni-Al ALLOY COATINGS

ABSTRACT

The article presents the results of testing of Ni-Al alloy coatings with different chemical and phase composition, which might replace currently used electrolytic chromium coatings. Crust chromium coatings are suitable for reconditioning of machine parts because of their very good maintenance properties. However, due to toxicity of electrolytic chromium bath, their application tends to be restricted. Thermal flame and plasma spraying technologies were chosen for nickel aluminium coating application. Obtained coatings were distinguished by significant porosity of structure and surface roughness. The thickness of coatings ranged from 440 to 683 μm. Microhardness of coatings was not related to applied metal plating technology but to chemical and phase composition. The more aluminium content in coating the harder the coatings were. The hardness of coatings which resulted from NiAl phase was ca 250 HV 0.04. Flame spray coatings are distinguished by nearly 10 times higher corrosion current density compared comparatively with plasma spray coatings. The value of corrosion potential is influenced by structure and chemical composition of coatings. The more aluminium content caused the lower E_{corr}.

Key words: *thermal spraying, nickel-aluminium coating, corrosion, intermetallic coating*

INTRODUCTION

Exploational property of machine engine elements and marine devices can be improved by coatings application.

Parts of devices and marine machines worn in operation can be reconditioned by coating application. Crust chromium coatings deposited from electrolytic baths Cr (VI) are commonly used in industry. They are resistant to tribologic wear, electrochemical and high-temperature corrosion. They are used to coat parts exposed to complex operating conditions, e.g. piston rings, cylinder liner sliding surfaces and other parts of heat engines and compressors. Despite wide range of applications, engineering chromium coatings have become less common in use due to the following [1 - 3]:

- hydrating of basis,
- big tension forces of own stress in chromium coating,
- electrolytic bath efficiency for chromium plating amounts only 10-15%,
- engineering chromium coatings are distinguished by big and heterogeneous thickness thus require grinding to size,

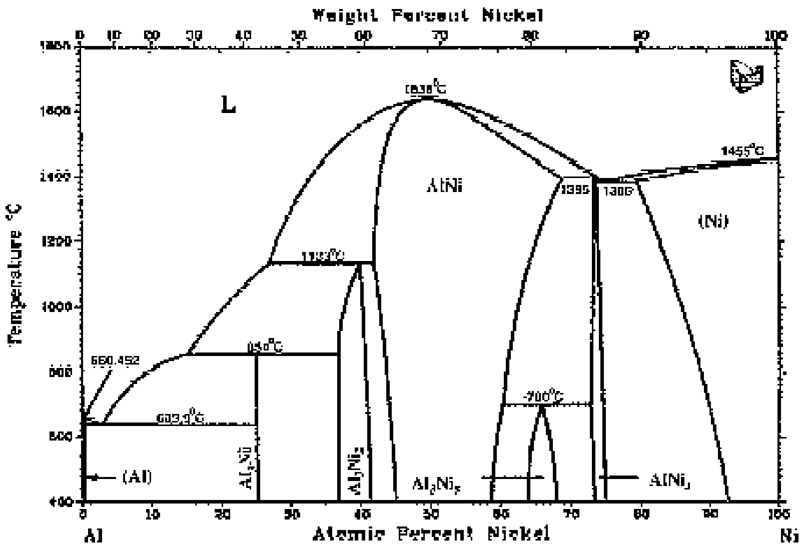


Fig. 1. The phase equilibrium diagram of Ni – Al system [4]

- electrolytic bath Cr (VI) is of high toxicity, environment-unfriendly, harmful and carcinogenic to human health,
- gas and chromium compounds (VI) emission pollute environment,
- growing insistence on environment protection in many countries resulted in increase of requirements referring to emission of Cr compounds (VI). For the time being in the European Union binding limit is 0.05 mg/ m^3 (MEL - maximum exposure limit), though the chrome limit value (VI) (Cr_2O_3) mg/m^3 proposed in the USA since 2004 is likely to be introduced by the European Union soon.

The reasons listed above will influence future designing and making of engineering superficial layers. For these reasons replacing electrolytic chromium coatings with nickel alloy coatings seems to be relevant. Nickel – chromium, titanium, iron and aluminium alloys are the most common [1, 2, 5, 6].

Nickel–aluminium alloys form system in which both solid solutions and ordered intermetallic phases can occur (Fig. 1). Two-component system Ni-Al forms five intermetallic phases:
Ni_3Al, Ni_2Al_3, NiAl, Ni_5Al_3 and Ni_2Al. Alloys containing NiAl i Ni_3Al phases are the most common.
These alloys are distinguished by the following [7-12]:
- resistance to oxidation and carburizing in temperatures up to 1100°C,
- good tensile, fatigue and creep strength in high temperature, very good abrasion resistance in high temperatures,
- transition from brittle to plastic state in the temperature range 300-600°C.

The work presents selected properties of Ni-Al coatings with various chemical composition which were produced by two thermal spraying technologies i.e. flame and plasma spraying.

SAMPLES PREPARATION

Flatbar 35 x 100 x 5 mm in size made of steel C45 served as basis metal. Before coating, the samples were degreased and prepared in vapour blasting to grade Sa3.

Alloy coatings including 5% aluminium (mass fraction).should be distinguished by two-phase structure consisted of solid solution of aluminium in nickel and Ni_3Al phase Coatings were applied by infrasound flame spraying and plasma spraying.

Intermetallic phase coatings NiAl (25 - 35 per cent mass of aluminium) and Ni_3Al (ca 15 per cent mass of aluminium) were obtained by plasma spraying of powder of granulation 45 µm and 150 µm respectively by Alfa Aestar.

Infrasound flame spraying was performed by means of 'Roto-Teck' burner manufactured by Castolin. The technological parameters of process were as follows:

- acetylene pressure: 0.7 MPa,
- oxygen pressure: 0.04 MPa,
- burner feed rate: 25 m/min,
- distance between burner and sprayed surface: 150 mm,
- number of layers: 6.

Both alloy coatings as well as composite ones were applied by two methods: 'cold ' and 'hot '. 'Cold ' spraying involved preheating of steel basis with burner to the temperature ca 100 ºC. Then the coating was sprayed so as not to exceed the temperature of the sample 250 ºC. Before 'hot ' coating application, the processed surfaces were heated up to 250 ºC and then in the spraying process the temperature of an object was maintained between 500 ÷ 600 ºC.

NiAl, Ni_3Al and Ni-5%Al coatings were thermally sprayed by plasma method by 'Plasma System' SA company. There were the following parameters of plasma spraying:

- current strength – 450A
- non-transferred arc voltage – 47V
- argon flow – 2000 [dm^3/h],
- hydrogen flow – 100 [dm^3/h],
- distance between nozzle and sample -70 mm

TESTING METHODOLOGY

Roughness of coatings and steel basis were measured with profile measurement gauge Hommel Tester T 1000. Measuring length was 4.8 mm, sample length 0.8 mm.

Microhardness was measured with hardness tester Vickers type by means of H type device mounted in a holder of metallographic microscope Vertival. Load used was 0.4 N in 10 sec in ambient temperature. Diagonal indentation lengths were measured with accuracy 0.2 µm.

The thickness of flame sprayed coatings was determined by microscopic method according to standards PN-EN ISO 2064 and PN-EN ISO 1463. An optical microscope Vertival with microhardness measurement instrumentation was used. The measurement was taken on sample cross-sections etched with nital to show the border between the basis and the coating. Five separate measurements along the microsection were taken determining local thicknesses of coating. Mean thickness was calculated from measurements of five randomly selected samples. Despite the measurement accuracy up to 0.4 μm , the values obtained were rounded to 1 μm due to standard recommendations PN-EN ISO 1463.

The thickness of plasma spray coatings was measured by means of an ultrameter Fischerscope MMS Permascope with EGAN probe.

Coating microstructures were assessed on cross-sections by means of metallographic optical microscope Zaiss Axio Vert 25.

Measurement of coatings corrosion resistance was taken by potenciodynamic method in three-electrode system. Degreased with acetone sample 1 cm^2 in size, an auxiliary electrode (polarizing) from platinized titanium and a reference electrode (saturated calomel electrode) were placed in a vessel filled with 500 ml 0.01 M H_2SO_4 solution of ambient temperature. The measurement was taken after 0.5 hour exposure of a sample in the electrolyte to stabilize corrosion potential. The electrolyte was being continuously stirred.

Testing involved registering of polarization curves i=f(E) in range ± 150 mV from corrosion potential. Cathode curve was registered first , then anode curve. Potential change rate in all occurrences equaled 10 mV/min.

It computer program ‘Elfit - corrosion polarization data fitting program’ the value of corrosion current density was made calculation. The ‘Elfit’ evaluated corrosive parameters using equation [13]:

$$I = \frac{I_{da}}{\left(\frac{I_{da}}{I_{corr}} - 1\right) \times \exp\left(\frac{-2{,}303 \times (E - E_{corr})}{b_a}\right) + 1} - \frac{|I_{dc}|}{\left(\frac{|I_{dc}|}{I_{corr}} - 1\right) \times \exp\left(\frac{2{,}303 \times (E - E_{corr})}{b_c}\right) + 1}$$

I – current density [$\mu A/cm^2$],
I_{ccor} – corrosion current density [$\mu A/cm^2$],
I_{da} – limiting anodic current density [$\mu A/cm^2$],
I_{dc} – limiting cathodic current density [$\mu A/cm^2$],
E – potential [mV],
E_{corr} – corrosion potential [mV],
b_a – anodic Tafel coefficient [mV],
b_c – cathodic Tafel coefficient [mV].

RESULTS OF TESTING

Coatings were distinguished by highly developed real surface which the results of roughness illustrated in Fig. 2. The value of parameter R_a depending on chemical composition and thermal spraying technology ranged from 5.3 μm for intermetallic phase NiAl coating to 13.6 μm for alloy coating with 5 % aluminium content obtained by ‘hot ‘ flame method. High mean values R_a are probably related to porous and heterogenous, layered coating structure. Machine parts of so high roughness shouldn’t operate in tribologic spots. IN Fig 3. Ni-5%Al ‘cold” and Ni-5%Al plasma coatings surface topography were presented.

Coatings should be further treated in order to obtain better stereometric surface.

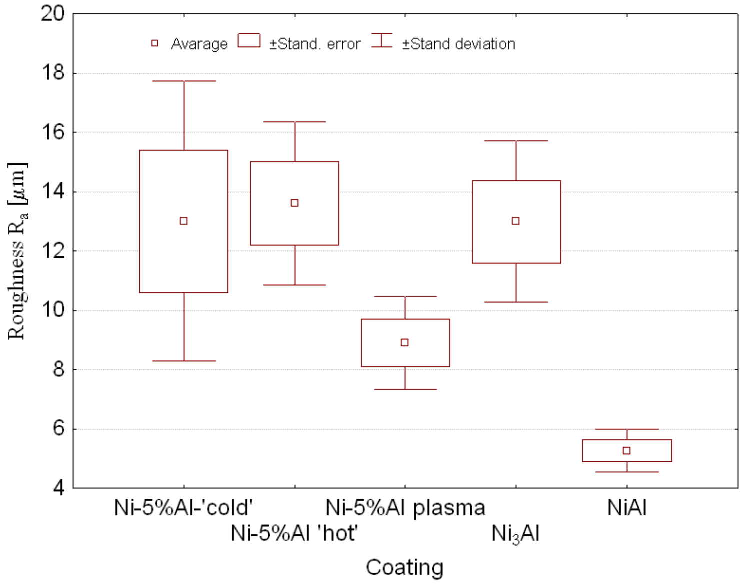
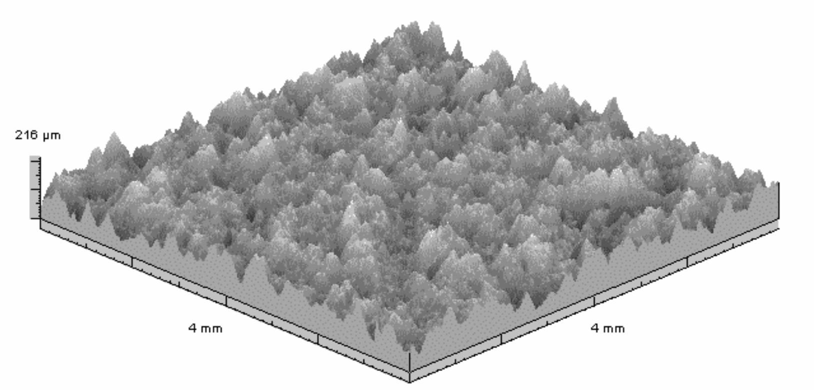


Fig.2. Coatings roughness

a)



b)

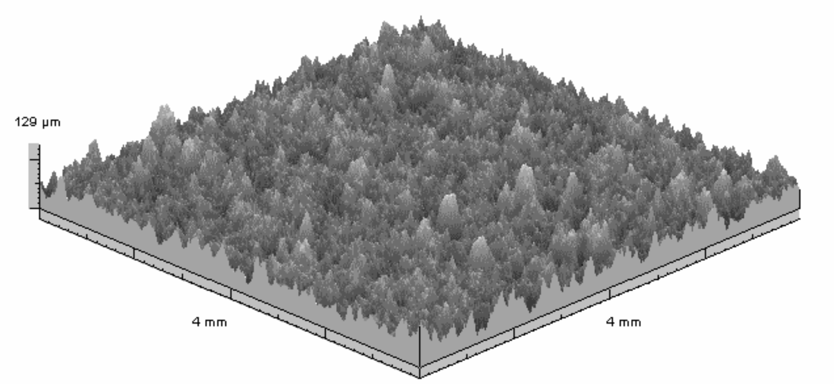


Fig. 3. Surface topography of a) Ni-5%Al 'cold" and b) Ni-5%Al plasma coatings [14]

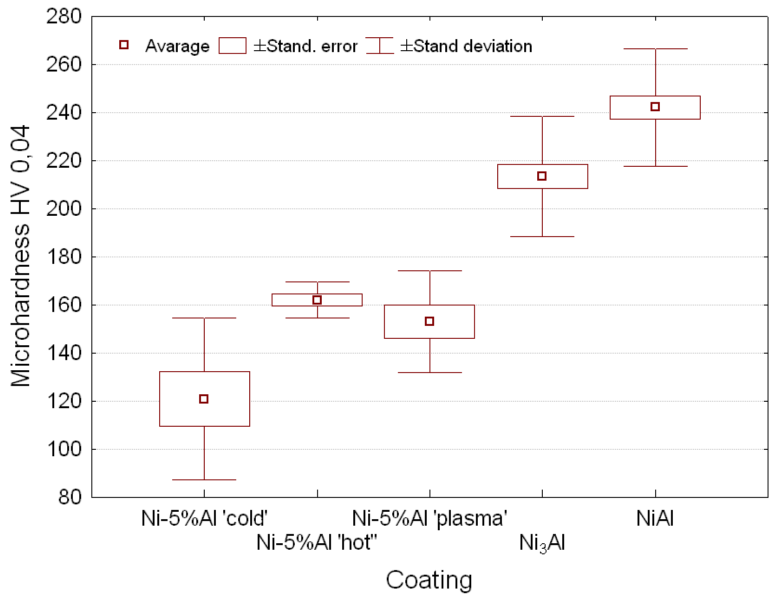


Fig. 4. Microhardness of thermal spray coatings
(microhardness of micro-cracked chromium deposit equal 500 -1000 HV)

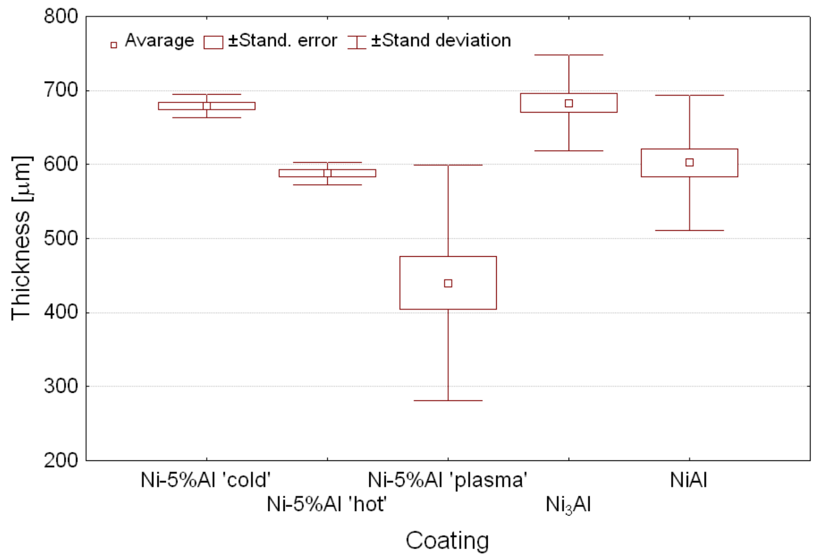


Fig. 5. Thickness of thermal spray coatings

Thermally spray alloy coatings Ni-5 %Al from powder material ProXon 21021 depending on applied technology had average microhardness from 121 HV 0.04 to 162 HV 0.04 (Fig. 4).The lowest average microhardness value was obtained in ‘cold ‘ flame spraying technology occurrence. The average value was determined from 9 measurements. Obtained measurement results ranged between 70 to 158 HV 0.04. Measurement spread equalled 88 HV 0.04, standard deflection 32 HV 0.04, error of determining average value (standard error) 11.3 HV 0.04. Such a big spread of measurement results was probably caused by high roughness of coatings. In some cases Vickers indenter could have met coating surface under which pores occurred.

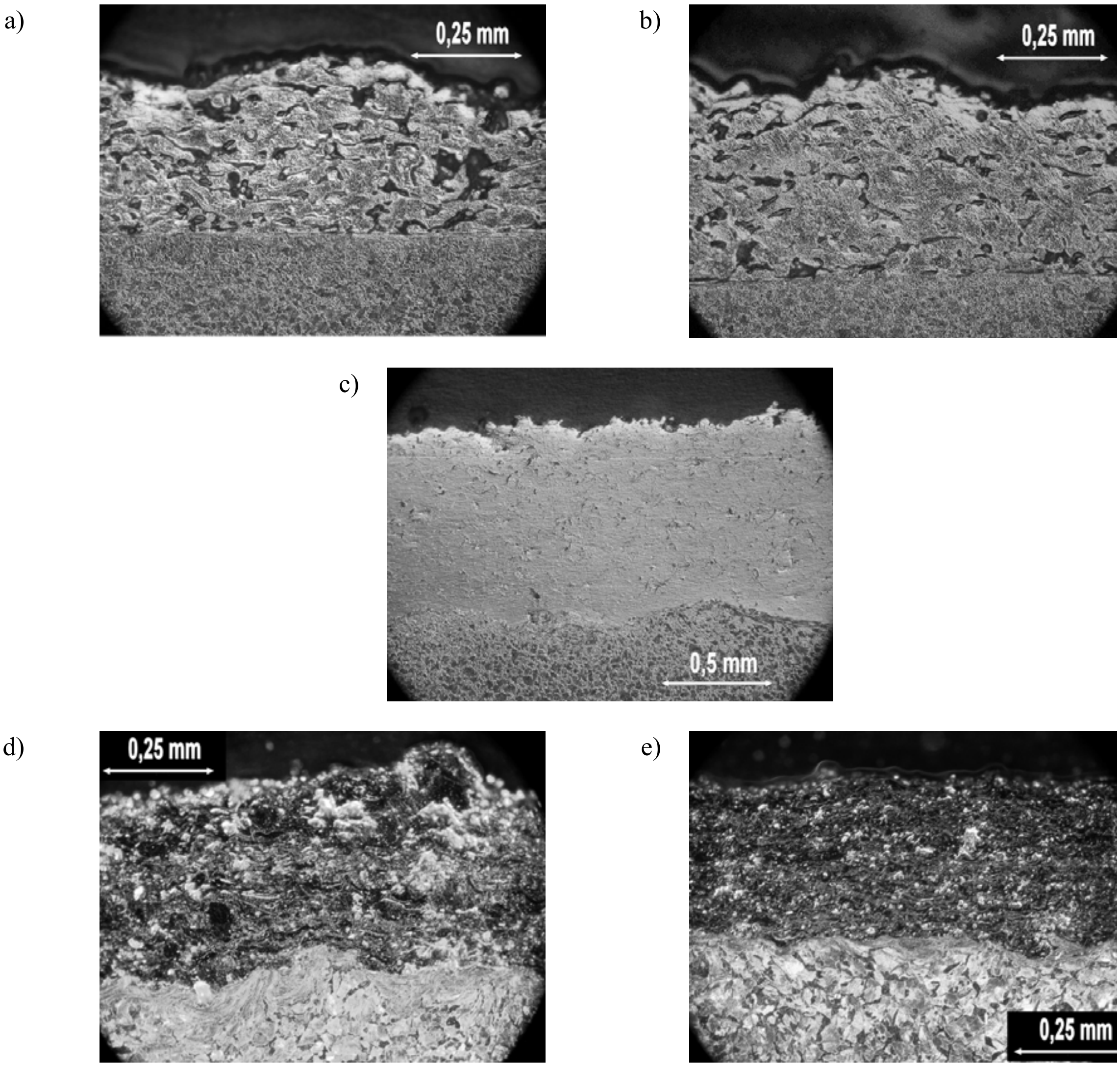


Photo 1. Alloy coatings structure NiAl thermally sprayed. a)'Cold ' flame spray Ni-5%Al coating (bright field), b)' Hot' flame spray Ni-5%Al coating (bright field), c) Plasma spray Ni-5%Al coating (bright field), d) Plasma spray Ni_3Al coating (dark field), e) Plasma spray NiAl coating (dark field)

Alloy coatings Ni-5%Al plasma sprayed were the least thick among coatings of such a chemical constitution. Higher temperature of the process and higher rate of spraying the coating material allow for reduction in coatings roughness, consequently reduction in their thickness.

The structure of alloy coating Ni-Al applied by flame and plasma spraying is shown in Photo.1. The coatings obtained are considerably porous. The analysis of coatings structure in cross-sections proved that the number and size of pores are affected by coating technology and their chemical constitution. Coatings of this chemical composition Ni-5%Al applied by 'cold ' flame spraying were the most porous. The least number of pores was found in coatings obtained by plasma method.

Among coatings applied by plasma spraying, layers obtained in intermetallic phase Ni_3Al were considerably porous. It is probably connected with the change of structural constituent volume that occurs during phase changes in solid state. Nickel and aluminium alloy containing ca 85% Ni solidifies, forming of eutectic mixture consisting of intermetallic phase NiAl and solid solution of aluminium in nickel.

Table 1. *The influence of chemical composition and processing on corrosion current density I_{corr} [A/cm^2]*

Coating	Average	Minim. value	Max. value	Stand. deviation	Stand. error
Ni-5%Al 'cold'	257	239	280	16	5,33
Ni-5%Al "hot"	249	237	258	7,35	2,45
Ni-5%Al plasma	27,7	20	33	6,81	3,93
Ni_3Al	40	35	46	5,57	3,21
NiAl	28,33	22	32	5,51	3,18

Table 2. *The influence of chemical composition and processing on corrosion potential E_{corr} [mV]*

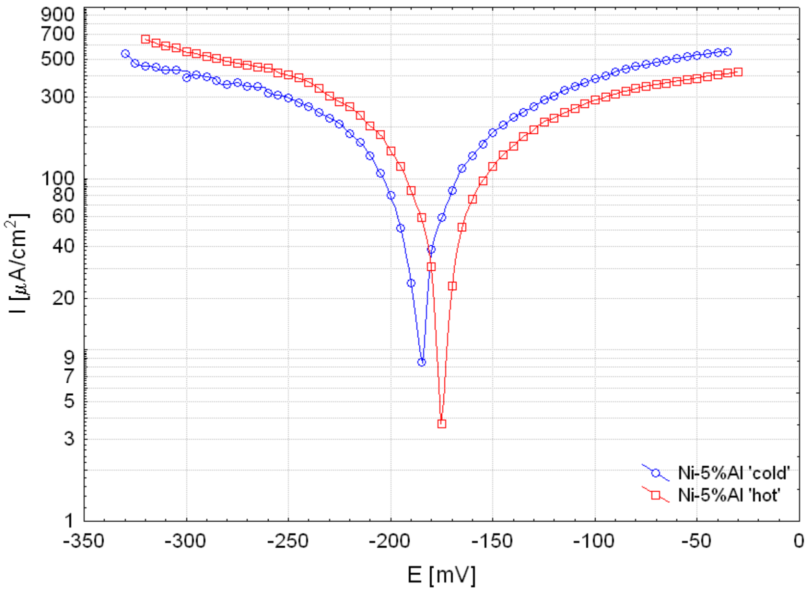
Coating	Average	Minim. value	Max. value	Stand. deviation	Stand. error
Ni-5%Al 'cold'	-173	-185	-160	12,58	7,26
Ni-5%Al 'hot'	-188	-215	-175	23,09	13,33
Ni-5%Al plasma	-103	-120	-90	15,27	8,82
Ni_3Al	-166	-173	-162	6,08	3,51
NiAl	-196,	-200	-195	2,89	1,67

Statistical analysis, Anova Kruskal-Walis test and median test for Ni-5%Al coatings at assumed relevance level α= 0,05 cannot exclude null hypothesis of no medians differences between variables. It can be maintained with 95% probability that applied technologies don't influence significantly the hardness of spraying alloy coatings with 5% aluminium mass fraction.

However, the hardness is affected by aluminium content in coating. In tested concentration range, growth in coatings hardness related to growing amount of aluminium content in a coating.

Tested coatings were structured from 6 layers. Depending on applied technology and chemical constitution, their average thickness varied from 440 to 683 μm (Fig. 5). Plasma spraying coatings in 'Plasma System SA' were distinguished by high spread range in obtained results of thickness measurements, e.g. thickness of Ni-5%Al coating varied from 227 to 668 μm, which made standard deflection 159 μm. Such a considerable spread in measurement results was presumably caused by partial overlapping of beads while spraying flat surface. Coatings applied by ' hot ' flame spraying method were less thick than those treated by ' cold ' method.

a)



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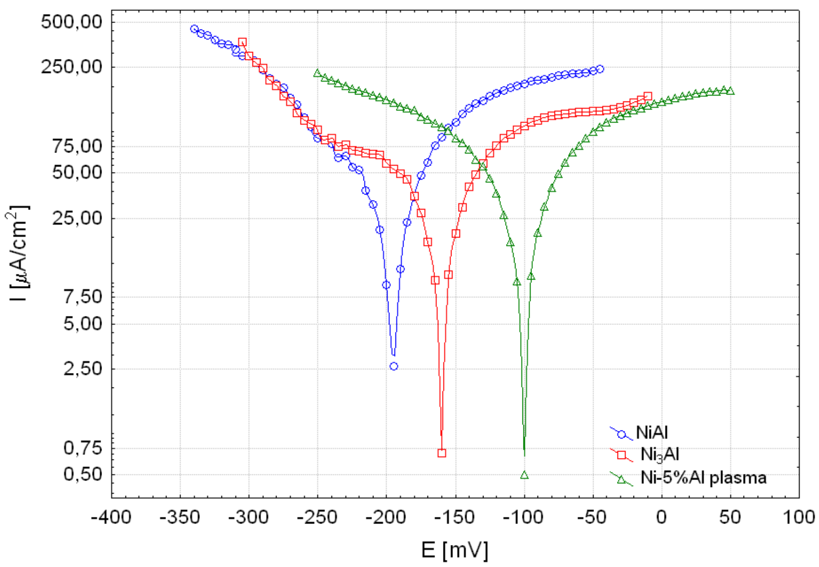

Fig. 6. The polarization curve samples of flame (a) and plasma (b) thermal spraying coatings

Coatings Ni-5% Al flame sprayed had around 10 times higher corrosion current density values (Table 1), thus they are several times less resistant to corrosive wear than coatings obtained by plasma method. This can be resulted from high roughness and porosity of these coatings, which is connected with highly developed real surface of tested samples. There is also probability of electrolyte penetration through pores to the steel basis surface. The influence of aluminium concentration on corrosion current density was not observed.

The polarization curve samples of flame and plasma thermal spraying Ni-Al alloy coatings was presented in Fig 6.

However, observed influence of aluminium content and phase structure on corrosion potential of plasma spray coating was significant. The bigger aluminium concentration has an effect on the bigger corrosion potential (Table 2). Presumably it is connected with much lower normal potential of aluminium when compared to that of nickel. Due to relatively high corrosion potential values of assessed coatings applied on steel basis, in case of electrolyte penetration through pores or mechanical damages, they will be cathodes. Steel basis will corrode. Technological process of applying these coatings must be assisted by their sealing by melting or impregnation with linseed oil.

CONCLUSIONS

1. Ni-Al alloy coatings applied by flame and plasma spraying are distinguished by considerable roughness of surface.
2. Microhardness of coatings increases with aluminium content.
3. The kind of thermal spraying method doesn't influence microhardness significantly.
4. Porosity of coatings is related to treatment technology and coatings composition. Flame spray coatings are more porous than coatings obtained by plasma technology. Increase of aluminium content increased porosity.
5. Corrosion properties depend considerably on applied technology. Plasma coatings have very low corrosion current density values.
6. In case of spray coatings, increase of aluminium concentration causes corrosion potential drop.
7. The method which decreases the porosity of Ni-Al coatings needs to be worked out, because of lower corrosion potential value of steel substrate.

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