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CORROSION RESISTANCE OF PLASMA COATINGS BASED ON COMPOSITE POWDERS WITH FeAl INTERMETALLIC

N.V. Vihilianska[1], O.P. Gryshchenko[1], K.V. Iantsevych[1], Z.G. Ipatov[1], C. Senderowski[2]

[1]E.O. Paton Electric Welding Institute of the NASU
11 Kazymyr Malevych Str., 03150, Kyiv, Ukraine
[2]Warsaw University of Technology. Warsaw Polytechnic University.
Plac Politechniki 1, 00-661, Warsaw, Poland. E-mail: cezary.senderowski@uwm.edu.pl

ABSTRACT

The corrosion resistance of plasma coatings made of composite powders based on FeAl intermetallics in different corrosive environments was investigated. For deposition of coatings, powders based on FeAl intermetallics were used, which were produced by mechanochemical synthesis with the introduction of additional alloying elements of titanium and magnesium into their composition. Electrochemical tests of plasma coatings were performed by a potentiostatic method in a 3 % NaCl solution and in a 10 %` H_2SO_4 solution. It was revealed that the rate of the corrosion process of plasma coatings of the FeAl system depends on the nature of electrolyte and the mechanism of electrochemical process. Electrochemical studies of plasma coatings of the FeAl system showed that corrosion resistance in a 3 % NaCl solution is by an order higher than in a 10 % H_2SO_4 solution. It was found that introduction of alloying element of titanium to the composite coating based on FeAl intermetallics results in a 2–5 times increase in corrosion resistance of the coatings in a 10 % H_2SO_4 solution. It was shown that the plasma coatings based on FeAl intermetallics on a scale of corrosion resistance in a 3 % NaCl solution are in the "resistant" group. Electrochemical studies showed the ability of these protective coatings to operate in salty neutral solutions.

KEYWORDS: intermetallics, iron, aluminium, composite powder, plasma coatings, corrosion resistance

INTRODUCTION

Iron aluminides belong to the intermetallics that are the most studied and used in industry due to their properties, such as low specific weight, high wear and corrosion resistance, etc. [1]. In recent years, iron FeAl intermetallics have been widely used as materials of protective coatings due to high heat resistance (up to 600–700 °C) and corrosion resistance in different aggressive environments. The main advantage of these coatings is, first of all, the possibility of replacing expensive heat-strength and heat-resistant coatings based on nickel aluminide [2].

Studies in the field of thermal spraying of intermetallic FeAl-coatings have been considered in [3–8]. Most of the works are aimed at studying processes occurring in composite powders produced by the method of mechanical alloying or mechanochemical synthesis (MChS).

In [9–11] it was noted that FeAl-based coatings significantly increase the corrosion resistance of steel products during long tests in the solutions of a sulfuric acid and seawater. An additional increase in corrosion resistance of FeAl-based intermetallics is possible by introducing alloying elements, such as chromium, copper, etc. into their composition [12, 13]. Thus, the additional introduction of chromium into FeAl intermetallics reduces the corrosion current, accelerates the beginning of passivation in a 3.5 % NaCl solution. The introduction of 3–5 wt.% of copper to the composition of FeAl-coatings causes the formation of a dense passive film on the surface of the electrode, which allows 2–3 times increase in the corrosion resistance during long-term tests in a solution of sulfuric acid.

At the PWI for thermal spraying of protective coatings based on FeAl intermetallics, composite powders (CP) were developed and plasma spraying technology of protective coatings was mastered [14, 15].

The aim of this work was to study the corrosion resistance of plasma coatings based on FeAl intermetallics, the effect of alloying elements on corrosion resistance of coatings in different aggressive environments.

RESEARCH OBJECTS AND EXPERIMENT PROCEDURE

As starting materials for plasma spraying, composite powders based on FeAl intermetallics were used, produced by the method of mechanochemical synthesis [14] (Table 1).

The coatings with a thickness of 500 ± 50 μm were deposited on the specimens of St3 steel in the UPU-8M installation using the following modes: I = 600 A, U = 40 V, Q_{Ar+N_2} = 50 l/min, spraying distance is 80 mm.

The studies of electrochemical properties of plasma coatings were carried out by the potentiostatic method in the potentiostat P-5827M at a scanning rate of 2 mV/s at a temperature of 18–20 °C with the use of a clamping cell. The stationary potentials were

Table 1. Characteristics of MChS powders based on FeAl intermetallics

System	Composition, wt.%	Phase composition	Size of particles		
			D_{10}, μm	D_{50}, μm	D_{90}, μm
Fe_3Al	86Fe + 14Al	Fe_3Al	3.6	11.2	32.9
Fe–AlMg	86Fe + 14(Al5Mg)	Solid solution of Mg in Fe_3Al	2.8	14.5	29.8
Fe–TiAl	60.8Fe + 39.2(Ti37.5Al)	Solid solution of Al in FeTi ($Fe_{1-x}TiAl_x$)	2.6	8.7	29.7

measured relative to the chlorine silver electrode, platinum served as an auxiliary electrode. As an electrolyte for corrosion studies, a 3 % NaCl solution and a 10 % H_2SO_4 solution were selected. The selection of the mentioned acid was predetermined by its wide use in the chemical industry, the selection of salty solution — by its use in natural conditions. It is known that the presence of chlorine ions in the electrolyte (a strong depassivator) is very harmful to metals, the corrosion resistance of which is predetermined by the passive condition of its surface. Chlorine ions lead to local destructions of passive film that in turn can lead to pitting corrosion [16–18].

According to the experimental data, cathode and anode polarization curves were built in the coordinates $E_c = f(\lg i_c)$, where the E_c is the potential, V; i_c is the corrosion current, A/cm^2. From the polarization curves, using the graphic method, the corrosion current (i_c) and corrosion potential (E_c) were determined on the extrapolation of tafel tilts at cathode and anode curves until their mutual intersection. Using the values of corrosion currents determined from the polarization curves, the mass and deep corrosion indices of the coatings was calculated by the following formulas:

$$K_w \frac{iA \cdot 1000}{nF}, \quad (1)$$

where K_w is the weight corrosion index (g/m^2·h); A is the atomic weight of metal (iron); n is the valence of the metal ion, which has passed into the solution (Fe^{2+}, $n = 2$); i is the current density (A/cm^2); F is the Faraday constant, 26.8 A·h/mol.

$$K_i \frac{8.76}{\rho}, \quad (2)$$

where K_i is a deep corrosion index, (mm/year); K_m is the mass corrosion index (g/m^{2}h); ρ is the metal density, g/cm^3; 8.76 is the coefficient for the transition from mass corrosion index K_m to deep corrosion index K_i up to one year, calculated from the number of hours per year (24 h·365 = 8760 h) and divided into 1000.

For comparative characteristics of corrosion resistance, a ten-point scale evaluation was used based on the deep corrosion index (K_i) [16, 18].

RESULTS OF THE EXPERIMENT AND THEIR DISCUSSION

Examinations of microstructure (Figure 1) of the sprayed plasma coatings indicate that in the coatings based on FeAl intermetallics, a dense lamellar structure is formed; the porosity of the coatings does not exceed 7 %.

According to X-ray structural phase analysis [15], the plasma coating of the Fe_3A1 system consists of intermetallic Fe_3A1 and FeAl phases and contains traces of $A1_2O_3$ oxide; the coating of the Fe–AlMg system consists of a solid Al solution in α-Fe and complex $MgA1_2O_4$ and $MgFeAlO_4$ oxides; the coating of the Fe–TiA1 system in addition to the main Fe_3Al phase contains iron Fe_2O_3, Fe_3O_4 and FeO oxides, iron and FeTi phase.

The studies of the kinetics of electrode potentials of plasma FeAl-coatings allowed establishing that the value of the electrode potential will stabilize within 40–60 min during immersion of specimens with coatings in it. The measurements of stationary potentials

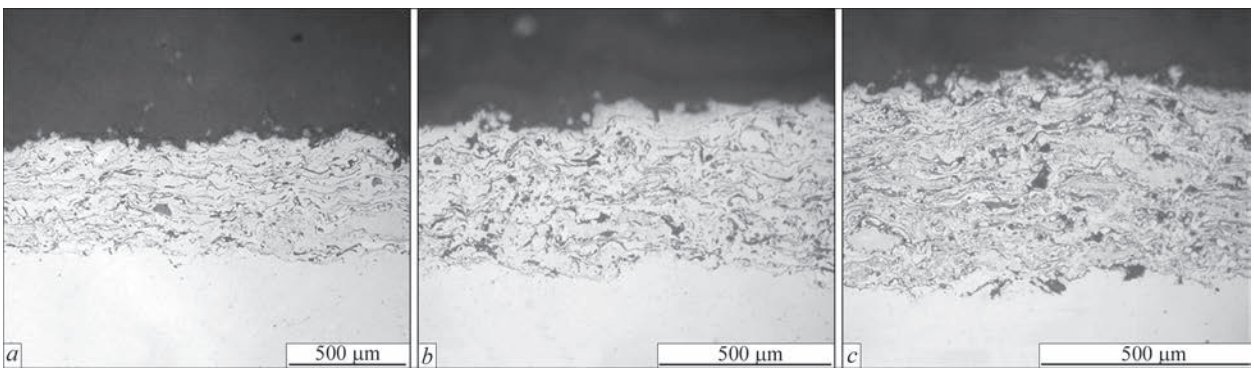

Figure 1. Microstructure of plasma coatings of the FeAl system: *a* — Fe_3Al; *b* — Fe–AlMg; *c* — Fe–TiAl

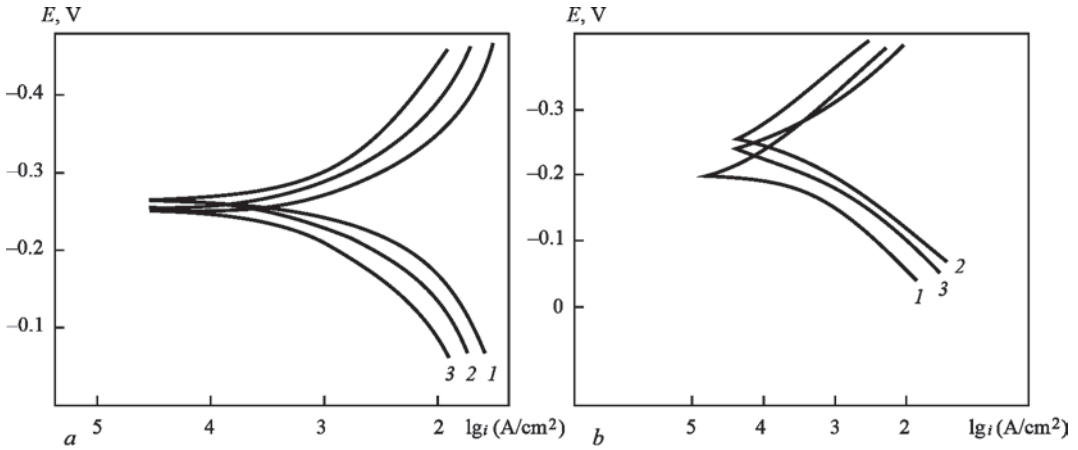

Figure 2. Polarization curves of plasma coatings of the FeAl system: *a* — in a 3 % NaCl solution; b - in a 10 % H_2SO_4 solution (*1* — Fe_3Al; *2* — Fe–AlMg; *3* — Fe–TiAl)

E_{st} of the specimens with plasma FeAl-coatings in the absence of current in an electrochemical system showed that regardless of the coatings composition in a 10 % H_2SO_4 solution and in a 3 % NaCl solution, the values of E_{st} amount to 0.34 and 0.32 V, accordingly.

The studies of electrochemical behaviour of the plasma FeAl-coatings have shown that at anode polarization on the polarization curves in a 3 % NaCl solution in the active region, the current depends linearly on the potential on the areas from –0.32 to –0.22 V and in a 10 % H_2SO_4 solution — from –0.34 to –0.2 V, and at the further increase in the potential, the saturation current is achieved and the current remains almost constant with an increase in potential, the areas of the passive state on the polarization curves are absent (Figure 2).

Deposition of plasma coatings of the FeAl system on St3 inhibits the corrosion process in a 3 % NaCl solution by a one order and in a 10 % H_2SO_4 solution — by two orders (see Figure 2). A different rate of the corrosion process is associated with different nature of anions (SO_4^{2-}, Cl^-) and pH value.

It is known that the nature of anions (SO_4^{2-}, Cl^-), which are present in the solution, significantly affects the anode dissolution and the rate of corrosion process [16, 17]. In the solution of a sulfuric acid, the corrosion process proceeds on electrochemical mechanism with hydrogen depolarization, according to which in the cathode areas $2H^+ + 2e \rightarrow H_2$ reaction occurs. The rate of the corrosion process of the plasma coatings of the FeAl system in the solution of a sulfuric acid (pH 1–2) is associated with a high activity of iron as the main component of the coating, which transfers into the solution in the form of Fe^{2+}. In the neutral medium, to which a 3 % NaCl solution (pH 7.0–7.5) corresponds, the corrosion process for the coatings proceeds on electrochemical mechanism with oxygen depolarization. In a 3 % NaCl solution, the rate corrosion process for coatings is inhibited due to the formation of a dense oxide Al^{3+} film, which inhibits the transition of iron to the solution [17].

The comparison of corrosion currents in the plasma coatings of the FeAl system (Table 2) determined by the method of extrapolation of tafel areas of polarization curves also showed that a corrosion current in a 3 % NaCl solution is by an order of value higher ($i_c = 10^{-6}$ A/cm^2) than in a 10 % H_2SO_4 solution ($i_c = 10^{-5}$ A/cm^2).

The carried out electrochemical tests indicated that introduction of alloying elements (Mg, Ti) into the FeAl system affects the corrosion resistance in the selected electrolytes in a different way. Electrochemical tests in a 3 % NaCl solution showed that when magnesium is introduced into the FeAl system, a slight shift in the corrosion potential into a negative value, inhibition of cathode reaction and acceleration of

Table 2. Results of electrochemical studies of plasma coatings based on FeAl

Number	Composition of coatings	Electrolyte					
		3 % NaCl			10 % H_2SO_4		
		E_{st}, V	E_c, V	i_c, A/cm^2	E_{st}, V	E_c, V	i_c, A/cm^2
1	Fe_3Al	–0.32	–0.28	$2.5 \cdot 10^{-6}$	–0.34	–0.26	$1.5 \cdot 10^{-5}$
2	Fe–AlMg	–0.34	–0.3	$3.5 \cdot 10^{-6}$	–0.28	–0.24	$3.3 \cdot 10^{-5}$
3	Fe–TiAl	–0.3	–0.28	$1.1 \cdot 10^{-6}$	–0.22	–0.18	$8.9 \cdot 10^{-6}$
4	Ст3	–0.54	–0.56	$6.5 \cdot 10^{-5}$	–0.28	–0.3	$2.5 \cdot 10^{-4}$

Table 3. Indices of corrosion resistance of plasma coatings based on FeAl

Number	Composition of coatings	Electrolyte			
		3 % NaCl		10 % H_2SO_4	
		K_m, g/m²·year	K_i, mm/year	K_m, g/m²·year	K_i, mm/year
1	Fe_3Al	0.05	0.056	0.13	0.14
2	Fe–AlMg	0.06	0.073	0.27	0.31
3	Fe–TiAl	0.042	0.046	0.061	0.06
4	St3	–	0.5935	–	0.3222

anode dissolution occur; corrosion current increases slightly (from $2.5 \cdot 10^{-6}$ to $3.5 \cdot 10^{-6}$ A/cm²) occurs. In a 10 % H_2SO_4 solution, the introduction of magnesium into the coatings increases the corrosion current (from $1.5 \cdot 10^{-5}$ to $3.3 \cdot 10^{-5}$ A/cm²), accelerates both cathode and anode reaction. A decrease in the protective properties of plasma FeAlMg coatings by 1.5–2.0 times (Table 3) is probably associated with the occurrence of a galvanic Fe–Mg couple and intensive dissolution of magnesium on the surface of the electrode in the process of corrosion studies.

Electrochemical studies of coatings in a 3 % NaCl solution and in a 10 % H_2SO_4 solution showed that alloying of FeAl intermetallics with titanium shifts the corrosion potential towards more positive values, inhibits the cathode process, reduces the corrosion current to $1.1 \cdot 10^{-6}$ A/cm² and $8.9 \cdot 10^{-6}$ A/cm², respectively. The corrosion resistance in a NaCl solution increases by 1.2–1.6 times and in a H_2SO_4 solution — by 2–5 times (Table 3). An increase in the corrosion resistance is probably related to the formation of FeTi phase in the coatings and a possible formation of the oxide film with TiO_2 composition on the surface of the electrode.

The values of corrosion currents found from the polarization curves allowed calculating the weight and deep corrosion index of the coatings (Table 3).

Corrosion tests have shown, that plasma coatings based on FeAl intermetallics, deposited on St3 in a 3 % NaCl solution and in a 10 % H_2SO_4 solution inhibit the corrosion process by 8–13 times and by 2–5 times, accordingly.

According to the used ten-point scale evaluation of corrosion resistance, the plasma coatings of the Fe_3Al, Fe–Al and Fe–TiA1 systems in a 3 % NaCl solution and the Fe–TiA1 system in a 10 % H_2SO_4 solution can be attributed to the "resistant" group and in a 10 % H_2SO_4 solution — the coatings Fe_3A1 and Fe–AlMg belong to the group of a "decreased resistance".

CONCLUSIONS

1. The conducted electrochemical studies have shown that the corrosion resistance of the plasma FeAl-based coatings depends on the composition of the electrolyte and pH value. In a neutral environment (3 % NaCl solution, pH 7.0–7,5), the corrosion resistance is by an order higher than in an acidic environment (10 % H_2SO_4 solution, pH 1–2), which is predetermined by different effects of SO_4^{2-} i Cl^- anions on the anode dissolution of coatings.

2. The introduction of alloying elements into the plasma coatings based on FeAl intermetallics showed that introduction of magnesium slightly reduces the protective properties of the plasma coatings in the studied electrolytes by 1.2–1.6 times, which is associated with the occurrence of a galvanic Fe–Mg couple on the surface of the electrode. The introduction of the alloying element of titanium to the composition of FeAl increases the corrosion resistance of the coatings in a 10 % H_2SO_4 solution by 2–5 times.

3. Plasma coatings based on FeAl intermetallics increase the corrosion resistance of carbon St3 steel by 8–13 times in a 3 % NaCl solution and by 2–5 times in a 10 % H_2SO_4 solution.

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ORCID
N.V. Vihilianska: 0000-0001-8576-2095,
O.P. Gryshchenko: 0000-0003-2640-8656,
K.V. Iantsevych: 0000-0002-3975-7727,
Z.G. Ipatov: 0000-0003-2209-408X,
C. Senderowski: 0000-0002-0331-3702

CONFLICT OF INTEREST
The Authors declare no conflict of interest

CORRESPONDING AUTHOR
N.V. Vihilianska
E.O. Paton Electric Welding Institute of the NASU
11 Kazymyr Malevych Str., 03150, Kyiv, Ukraine.
E-mail: pewinataliya@gmail.com

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