Investigation of the Corrosion Resistance of Porous Permeable Materials with Protective Coatings

Oleksandr Povstyanoy[1][0000-0002-1416-225X], Natalia Imbirovych[1] [0000-0001-8276-6349],
Volodymyr Posuvailo[2][0000-0003-0998-7588], Oleg Zabolotnyi[1] [000-0002-9169-9173],
Tatyana Artyukh[3] [0000-0003-3541-6690]
[1]Lutsk National Technical University, 75, Lvivska str., Lusk, 43018, Ukraine
[2] Physico-Mechanical Institute H.V. Karpenka NAS Ukraine,
5, Naukova street, 79060, Lviv, Ukraine
[3]Kyiv National Taras Shevchenko University
Vasilkivska str., 90A, Kyiv, 03022, Ukraine
`povstjanoj@ukr.net`

Abstract. It is known that porous permeable materials are subject to corrosion during filtration and cleaning of aggressive media, which leads to their failure. That is why the urgent task is to increase their corrosion resistance.

This article is devoted to the study of the corrosion resistance of PPM with combined protective coatings applied to their surface in the form of table salt and hydrochloric acid.

The corrosion resistance of PPM with combined protective coatings applied in solutions of sodium chloride and hydrochloric acid has been studied. Combined protective coatings were formed by the methods of electric arc spraying and aluminum alloy on the surface of PPM and subsequent plasma electrolytic treatment. As a result, a combined protective coating is formed on the surface of the PPM. Based on potentiodynamic mode established that the corrosion potentials in a solution of table salt move in the positive direction when a combined coating is applied to the surface of the PPM, which indicates a decrease in the corrosion activity of the surface. The corrosion currents of the combined protective coating for all the studied systems are reduced by 3 orders of magnitude, and an increase in the ratio of the cathode to anode current density reduces the rate of corrosion of the coating by another five times.

Keywords: Corrosion, Combined coating, Porous permeable materials, Corrosion current, Corrosion potential, Corrosive environment

1 Introduction

The current stage of development of materials science and powder metallurgy is accompanied by the emergence of new ideas for creating and improving the technology for obtaining porous penetrating materials (PPM), which, first of all, are aimed at achieving high performance characteristics and reducing their cost [1].

Porous permeable materials are subject to corrosion when used for cleaning aggressive media [2]. In order to solve this problem, it is necessary to apply a combined protective coating, which will significantly increase the corrosion resistance of PPM in the conditions of filtration and cleaning of aggressive media [3].

Corrosion of PPM causes significant damage when used for cleaning aggressive media. This damage is determined not so much by the cost of PPM, but rather by the cost of corrosion protection, the cost of repair work, as well as losses due to the temporary termination of the normal functioning of filter equipment. The relevance of PPM corrosion protection issues does not decrease from year to year, but rather increases.

In order to ensure timely and reliable protection of PPM from corrosion, it is necessary to pay more attention to conducting research on the assessment of the risk of corrosion and protection against it of PPM and improve the quality and reliability of protective coatings applied to them.

Currently, issues related to the process of interaction of verhons in contact in the process of their mutual movement are being considered. The creation and selection of tribotechnical materials is based on solving interrelated problems based on the study of friction mechanics and physico-chemical phenomena occurring on the surface.

2 Literature Review

The contact of solid interaction is observed only in certain zones, the size and density of which depend on the value of the applied load, as well as on the stress-deformed state of the contacts. These contacts depend on the geometric shape of the microroughness and the mechanical properties of the surface layer.

For the application of corrosion-resistant protective electrometallization coating on structural parts, the method of vacuum-arc spraying and plasma-electrolyte oxidation (PEO) is widely used, which is one of the most modern and promising methods for obtaining protective layers on the surface of metals and alloys with a complex of important characteristics. The properties of the obtained coatings are determined by the composition of the electrolyte and the modes of the PEO process.

The combination of coatings makes it possible to increase hardness, wear and corrosion resistance, ductility, resistance to contact, dynamic loads and vibrations. Thus, due to the chemical and phase composition and structure of ceramics, oxide coatings obtained on valve metals by the method of plasmoelectrolyte oxidation have high functional properties. The versatility of oxide-ceramic coatings contributes to their wide application in many industries, and the range of processed parts is constantly increasing. However, the possibilities of the method have not yet been fully explored. Work continues to improve the process of oxide-ceramic synthesis itself; new electrolytes are being developed, and new power sources are being created. However, a significant disadvantage of the PEO process is the limitation of the metals that can be coated.

Expanding the scope of application of the plasmoelectrolyte oxidation method for other metals and alloys is possible through the use of a complex technology of gas-thermal spraying of wires or aluminum-based powders, followed by plasmoelectrolyte oxidation. In addition, the use of such a comprehensive technology allows you to restore worn parts and extend the life of the equipment.

Plasma electrolyte oxidation (PEO) [4, 5], known as ANOF (Anodishen Oxidation unter Funkenentladung) in Germany [6, 7], ASD (Anodic Spark Deposition) in the USA, Europe and China [8, 9], MAO (microarray oxidation) in Russia, and REO (plasma Electrolytic Oxidation) in the UK. Switzerland [10, 11], has been developing in the last twenty years as a new intensive technology for metal anode processing. The process is carried out under conditions of surface spark discharges as a result of electro-and plasmochemical reactions and is used both for cleaning the surface of metal and for applying various coatings, the properties of which are determined by the composition of the electrolyte and the electrolysis mode. Being essentially a technology similar to traditional anodizing, PEO does not require either the use of deep cooling or the use of Vi-valence chromium compounds, which makes this method very environmentally attractive [12].

3 Researches Methodology

In this paper, samples made from steel powder BBS15 + graphite powder were studied. The powder was mixed in a mixer for four hours, after which the steel powder was pressed into the mold for one minute (**Fig 1**).

Fig. 1. Compressed samples of the composition BBS15+graphite

Then the blanks were placed in an induction furnace and sintered at a temperature of 1200C. Surface protection of samples from corrosion was carried out in two stages: an electrometallization coating was applied to the sample, then synthesis with PEO method was carried out.

The electrometallization coating was sprayed using a vacuum-arc method. The essence of this method of coating is that molten electric arc liquid metal jet of compressed gas (usually air) is sprayed into small particles that fall at high speed in the molten or plastic state on the prepared surface, deformed during impact, welded or stick to the surface, forming a coating [13].

The coating is sprayed using electro-arc method [14].

To implement the process of metal oxide synthesis, an installation was designed and manufactured, which consists of a power part, a control and measurement console, a diode-thyristor converter with a control circuit and working baths.

The PEO process takes place in an electrolytic plasma of spark (microarray) discharge in an electrolyte based on distilled water. Oxygen formed as a result of dissociation of water partially reacts with the metal and forms an oxide on its surface.

The coating formation process takes place in an electric field, which is an energy source for plasmochemical reactions at the working electrode. By increasing the voltage in the process: I-Faraday, II - sparking, III-micro-arc discharges (**Fig. 2**).

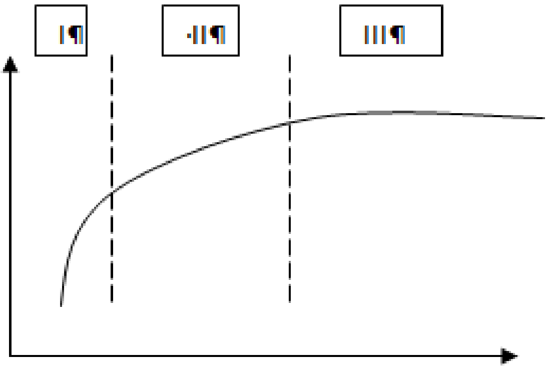

Fig. 2. Kinetics of the anode process:
I-Faraday part, II-sparking part, III-microarray discharge part

In the Faraday part, electrochemical processes known as anodizing take place. Oxygen involved in the synthesis of the oxide film is formed as a result of electrolysis. Breakdown is carried out due to the injection of electrons from the band gap into the conduction band under the action of an electric field.

This process can also be stimulated by electrons released as a result of electrochemical reactions at the anode. In the breakdown channel, the temperature increases strongly, the electrolyte dissociates and ionizes, and a plasma clot is formed, in which plasmochemical reactions of oxide synthesis are realized.

The PEO method makes it possible to create wear-and corrosion-resistant oxide-ceramic dielectric coatings with a thickness of up to 200 microns and a hardness of up to 20 GPA on parts and structural elements.

After the proposed surface treatment, a sample was obtained, the general view of which is presented on **Fig. 3.**

Fig. 3. PPM sample with combined coating

The corrosion properties of alloys and their coatings were studied according to polarization curves taken in potentiodynamic mode on potentiostats PY-50 and IPC-PRO+PK IBM PC according to a standard three-electrode scheme with a chlorinated comparison electrode and an auxiliary platinum (**Fig. 4.**). On the electrode, a working area was selected, the area of which was $S=1\times10^{-4}$ m^2, the remaining surfaces were insulated with epoxy varnish.

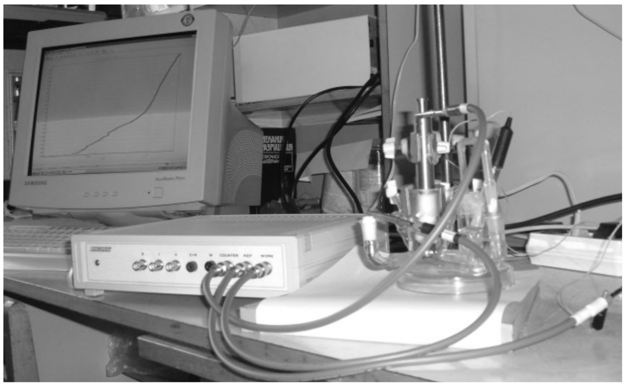

Fig. 4. General view of installation IPC-PRO+PK IBM PC

By building the polarization curves, the surface of the alloys was activated up to -2 B by the cathode. After cathodic polarization, continuous potentiodynamic polarization was immediately performed at a rate of potential change of 5 MV/s. the corrosive media were 10% NaCl and 10% HCl. Corrosion currents and potentials were determined to characterize the corrosion resistance. Polarization curves were recorded after the stationary potential was established. Corrosion currents and potentials were determined graphically. In addition, the samples were examined using a MIM-10 microscope with a computer surface fix.

4 Results

During the operation of anodized alloys in a corrosive environment, narrow channels with increased ionic conductivity are formed in certain areas of the cover in the PPM. Such areas become foci of local corrosion damage to the PPM [15]. Active anions (for example, chlorine and water) in these places penetrate through the anode film and interact with the alloy.

Plasmoelectrolytic coatings are inert. However, if there are pores in them that are channels of spark discharges, corrosion destruction of the metal or alloy is also possible. All this reduces the functional properties of the coating and reduces the service life of the alloy. In this regard, the corrosion resistance of plasma-electrochemical oxidoceramic coatings (OCC) on zirconium and titanium alloys in different corrosive media was studied and their corrosion currents were determined, which were used to judge the rate of corrosion in PPM.

The rate of electrode reactions that cause the corrosion process can be judged from electrochemical studies. In this regard, we studied the electrochemical behavior of

PPM in the initial state and with an oxide-ceramic coating in acidic media that are corrosive to PPM.

Of the solutions of table salt and hydrochloric acid used in corrosion studies, the medium containing sodium ions is more aggressive for PMT. After the formation of OCC, corrosion processes are significantly inhibited. In a hydrochloric acid environment, the corrosion current of the coating decreases by an order of magnitude compared to the matrix y. In a more aggressive environment of sodium chloride, the corrosion current decreases by two orders of magnitude, and the corrosion potential in the salt solution is shifted in the positive direction, which also indicates a decrease in the corrosion activity of the surface.

It is known that high corrosion resistance is achieved by the formation of a thin oxide film. However, in severe operating conditions and in the presence of particularly aggressive media (used in the work), these films, due to their small thickness and low hardness, do not provide high anti-corrosion properties.

The corrosion currents of the I_{cor} on the basis of which the corrosion rate was judge the rate of corrosion of the material, are reduced for all the studied systems, and the higher effect of creating OCC is manifested in more aggressive environments.

Analysis of the obtained polarization curves shows that the formation of OCC affects the electrochemical parameters of PPM corrosion, i.e. the values of corrosion currents decrease. This change is due to less dissolution of the alloy components.

The corrosion potential of corrosion-resistant PPM under the action of a 10% HCl solution has a negative value of -370 mV **(Fig.7.)**, and the corrosion current is 80 mA/m^2.

During the formation of the OCC PPM, the corrosion current decreases by 1...2 orders of magnitude depending on the composition of the electrolyte in which the coating was synthesized. Thus, the synthesized low-concentration electrolyte containing alkali and Liquid Glass has the lowest corrosion resistance of those synthesized in more concentrated electrolytes and has a value of 1,2.10-3 A/m2. With a further increase in the electrolyte concentration, the corrosion currents of i_{cor}OCC decrease (**Fig. 5.**).

The coating obtained in an electrolyte of the composition 10 g/l KOH + 15 g/l liquid glass (l.g.) has a corrosion current of 1.39.10-4 A/m2, and when introduced into the electrolyte of 10 g/l H2O2 reduces the isog to a value of 1.21.10-4 A/m2.

This result is obviously due increasing thickness of the coating on PPM [16].

In the more aggressive environment of table salt, the values of the current and corrosion potential of unprotected PPM are 0.82 A/m2 and -0.48B. Since the coating obtained in a low-concentration electrolyte did not perform well in the less aggressive environment of hydrochloric acid, it was impractical to study such a coating in further experiments.

So, we studied the covers, the modes of which are given in Table 1. according to the analysis of data, it was found that the corrosion currents of the OCC for all the studied systems are reduced by 3 orders of magnitude.

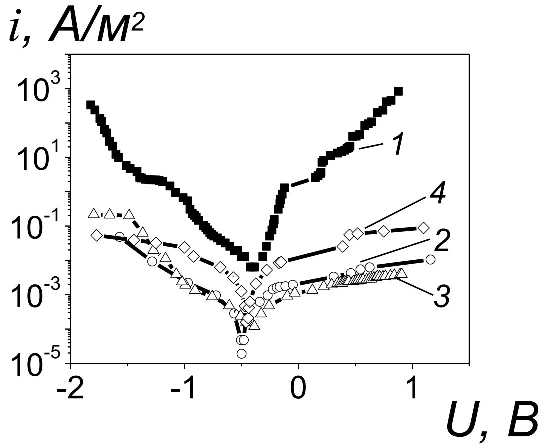

Fig.5. Polarization curves of PM (1) and its OCC (2, 3) in solution 10%HCl (see **table 1**)

Table 1. Potential and current of corrosion of the PMT and the coating on it under various oxidation modes

№	Corrosive environment	Electrolyte composition, g/l				I_a/I_c A/dm^2	τ, min	U_{cor}, B	i_{cor}, A/m^2
		KOH	p.c.	CrO_3	H_2O_2				
1	10%NaCl	-	-	-	-	-	-	0,48	0,82
2		10	15	-	-	20/20	20	0,41	$9{,}09 \cdot 10^{-4}$
3		10	15	-	-	20/30	40	0,24	$1{,}63 \cdot 10^{-4}$
4		10	15	0,1	-	20/30	40	0,26	$6{,}20 \cdot 10^{-4}$
1	10%HCl	-	-	-	-	-	-	0,37	$8{,}07 \cdot 10^{-2}$
2		10	15	-	10	20/20	30	0,41	$0{,}21 \cdot 10^{-4}$
3		10	15	-	-	20/20	30	0,50	$1{,}39 \cdot 10^{-4}$
4		3	2	-	-	20/20	20	0,45	$12{,}07 \cdot 10^{-4}$

The coating synthesized in an electrolyte of 10 g/l KOH + 15 g/l l.g has a corrosion current value of 9.09.10-4 A/m^2. However, increasing the ratio of the current density of the cathode to the anode reduced the rate of corrosion of the coating by another five times.

Adding 0.1 g/l CrO_3 to such an electrolyte did not significantly increase the corrosion current value (**Fig. 6., curve 4**).

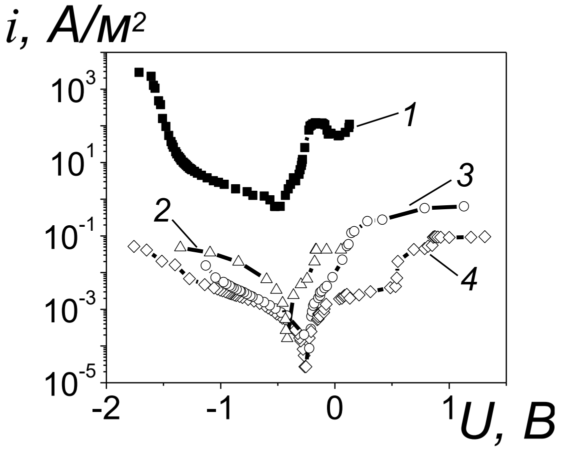

Fig.6. Polarization curves of PPM (1) and its oxide-ceramic coating (2, 3, 4) in solution 10%NaCl (see**Table 1.**)

Corrosion potentials in a solution of table salt move in a positive direction when all OCC are synthesized, which also indicates a decrease in the corrosion activity of the surface.

On **Fig. 7.** the PPM cover after corrosion in aggressive environments under anode polarization is shown. PMT undergoes co-destruction in aggressive environments. However, the cover, even from the assessment of appearance, does not obvious corrosive damage. The figure shows a photo of OCC after corrosion in a highly aggressive 10% NaCl environment. In a solution of hydrochloric acid, the general appearance of the cover does not change, and its properties can be studied in more detail using polarization curves.

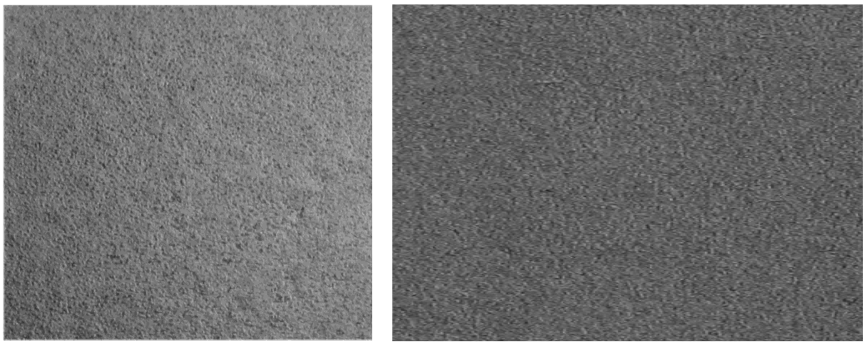

Fig. 7. General view of the oxide-ceramic coating on PPM after corrosion in media: a – 10%NaCl; b – 10%HCl.

Consequently, coatings synthesized in higher concentrations of electrolytes have better corrosion resistance [17]. The introduction of hydrogen peroxide into the electrolyte increases the resistance to corrosion, and chromium oxide significantly reduces it. The greatest corrosion resistance can be achieved by synthesizing a coating in an electrolyte of 10 g/l KOH + 15 g/l liquid glass at high current densities.

5 Conclusions

Based on the analysis of the data, it was found that the corrosion currents of the OCC for all studied systems are reduced by 3 orders of magnitude. The coating synthesized in an electric roll of 10 g/l KOH + 15 g/l l.g has a corrosion current value of $9.09 \cdot 10^{-4}$ A/m^2. However, an increase in the cathode-to-anode current density ratio reduced the corrosion rate of the coating by another five times.

Adding 0.1 g/l CrO_3 to such an electrolyte does not significantly increase the value of the corrosion current. Corrosion potentials in a solution of table salt move in a positive direction when all OCC are synthesized, which also indicates a decrease in the corrosion activity of the surface.

Consequently, coatings for PMM that are synthesized in higher concentrations of electrolytes have better corrosion resistance, i.e. the anticorrosive effect of coatings increases with increasing aggressiveness of the corrosive medium. The introduction of hydrogen peroxide in electrolite increases the resistance to corrosion, and chromium oxide significantly reduces it.

It was experimentally established that reducing the electrolyte concentration from 10 g/l KOH and 15 g/l l.g and 10 g/l H_2O_2 to 10 g/l of alkali and 15 g/l of liquid glass reduces the corrosion current of the coating by 5 times.

It is also found that at higher ratios of anode and cathode currents, the corrosion currents of the coatings are reduced by 6 times, and the greatest corrosion resistance can be achieved by synthesizing the coating in an electrolyte of 10 g/l KOH + 15 g/l of liquid glass at higher current densities.

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