

## Thin phosphate films on aluminum surfaces

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The effects of different factors such as concentration (2.0÷11 vol. %) and temperature (20÷70°C) on formations, compositions and morphologies of coatings obtained by treatment of aluminum (Al – 99.5 %) surfaces in solutions containing ammonium and sodium phosphates,  $\text{MoO}_4^{2-}$  promoting ions, buffers, softeners, inorganic activators, as well as surfactants, have been investigated. Gravimetric and electrochemical methods, optical microscopy, scanning electron microscopy with EDX-analysis and X-ray photoelectron spectroscopy have been used. The optimal operating conditions (concentration 4 – 7 vol. % and temperature range 50 – 70°C), under which dense and homogeneous coatings with thickness of about 1  $\mu\text{m}$  can be produced have been estimated. The coating contents include phosphorus, oxygen, molybdenum and nickel, and consequently a conjecture about probable chemical compounds

**Keywords:** aluminum, aluminum alloys, conversion coatings, phosphating.

### INTRODUCTION

Aluminum and its alloys are extensively encountered in materials used in aerospace, automotive, electronic, architectural and other industries due to their important properties such as low density, high ductility, high thermal and electrical conductivity, high mechanical strength as well as good corrosion resistance in neutral media [1-2]. Contacting solutions containing special complexing agents the aluminum undergoes to localized corrosion which invokes different protection methods against degradation processes of the metal and its alloys, to be developed.

Chemical conversion coatings are commonly produced on various engineering alloys, to improve paint adhesion and as adequate corrosion protection. Treatment in chromate [3-6] or chromate-phosphate [7-8] solutions has frequently been used to modify aluminum alloy surfaces in the past. However, chromate solutions have been widely associated with carcino – genesis [9-10], and its removal as a waste is a problem that should be resolved. Current environmental legislations are moving toward total bans on chromate-based treatments. Additionally, such treatments are not adaptable to the mixed steel-aluminum components frequently encountered in car body parts [2].

There is a strong incentive to explore and evaluate alternative treatments for aluminum surface modification. Recent studies [11-14] have shown that chemical conversion treatments in chromate-free phosphate baths are promising alternatives for the surface modifications of iron-aluminum components. It has long been recognized that phosphated metals exhibit substantially greater

corrosion resistances and paint adhesions. More importantly, this technique has advantages over chromate-phosphate treatment in terms of environmental effects [15].

Among these methods, the polymeric coatings with Zr or Ti metal addition and amorphous phosphate coatings should be mentioned. The amorphous phosphate coatings are widely used for steel and zinc-plated steel [16-17], but this method is insufficiently studied when applied to aluminum alloys [18-19].

The primary aim of this report is present results from studies where the characteristics of amorphous phosphate coatings on the aluminum surfaces, obtained in aqueous solutions of a newly developed process (KAF-50 FA) were examined.

### EXPERIMENTAL

#### *Materials and samples*

Disk shaped samples (26 mm, thickness 0.5 mm and working surface area 0.1  $\text{dm}^2$ ) cutted from an aluminum sheet (Al – 99.5 %) were tested. The electrochemical experiments were carried out with plate-shaped specimens prepared in accordance with ISO/FDIS 17475 (ISO 17475:2005) and a fixed working surface area of 1  $\text{cm}^2$ . In addition, square plates (10x10 mm) were used as specimens in case of all physical methods applied in the study.

#### *Solutions*

The working media represented aqueous solutions as follows:

- solution for cleaning;
- solution for brightening of Al surfaces on the basis of organic acids;

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- solution for phosphating, containing ammonium and sodium phosphates,  $\text{MoO}_4^{2-}$  promoting ions, buffers, softeners, inorganic activators, as well as surfactants, pH=4.0.

The working conditions for gravimetric method referred to:

Concentration values of 2.0 vol.%, 4.0 vol.%, 7.0 vol.% and 11.0 vol.%;

Temperature values of 20.0 °C, 30.0 °C, 40.0 °C, 50.0 °C, 60.0 °C and 70.0 °C;

Process duration: 1.0 min, 4.0 min, 8.0 min, 10.0 min and 15.0 min.

The working/model media used for the corrosion experiments is 0.6 M NaCl.

### Methods of investigation

#### Gravimetric method

The Gravimetric method was used for studying kinetics of forming and determining conditions of the processes for increasing of the coating's thicknesses depending on the influence of different factors. The method allows determining mass alteration of experimental samples after forming and removing coatings:

$$M = \frac{m_1 - m_2}{S},$$

where:  $M$ ,  $g\ m^2$  is mass or as accepted to call a thickness of the obtained coating,;  $m_1$  and  $m_2$  are the sample mass before and after coating,  $g$ ;  $S$  is the sample surface area,  $m^2$ .

#### Electrochemical methods

##### Open circuit potential determination

Metals immersed in liquid electrolytes media resulted in establishment of non-equilibrium, i.e. the so-called corrosion potentials. The corrosion potentials are not indicative with respect to the resistance attained but their values and time variations provide enough information about the character of the corrosion process, the behavior of both the metal and metal coating in different media under various conditions.

##### Potentiodynamic polarization method

The polarization curves recorded potentiostatically or potentiodynamically allow determination of various corrosion characteristics such as corrosion rate, corrosion potential, etc.

The experiments were carried out with EG&G Princeton Applied Research, *Potentiostat/Galvanostat, Model 263A*, provided with the specialized software package PowerCORR®.

### Physical methods

#### Optical microscopy (OM)

The microstructure of aluminum and the type of the corrosion attack were determined by optical microscopy, using a microscope OPTIKA® Model: B-500Bi.

#### Scanning electron microscopy (SEM)

The morphology and structure of the coatings were examined by scanning electron microscopy, using a SEM/FIB LYRA I XMU, TESCAN electron microscope, equipped with ultrahigh resolution scanning system secondary electron image (SEI).

#### Energy dispersive X-ray spectroscopy (EDX)

The energy dispersive spectroscopy is a local X-ray spectral analysis which permits qualitative and quantitative determination of surface micro volume contents of the order of several  $\mu\text{m}^3$ . Apparatus Quantax 200, BRUKER with spectroscopic resolution at Mn-K $\alpha$  and 1 kcps 126 eV is used.

#### X-ray photoelectron spectroscopy (XPS)

The chemical composition and the oxidation state of the elements on the surface being formed were studied using X-ray photoelectron spectroscopy (XPS). The XPS studies were performed in an Escalab II system with Al K $\alpha$  radiation with energy of 1486.6 eV and total instrumental resolution of ~1 eV. The elemental concentrations were evaluated from the integrated peak areas after linear background subtraction using theoretical cross-sections.

## RESULTS AND DISCUSSIONS

The data summarized in Table 1 shows the most important characteristics of the solution used in the phosphating experiments with aluminum specimens: density,  $\rho$ ; pH; conductivity,  $\sigma$  and total,  $K_o$  acidity.

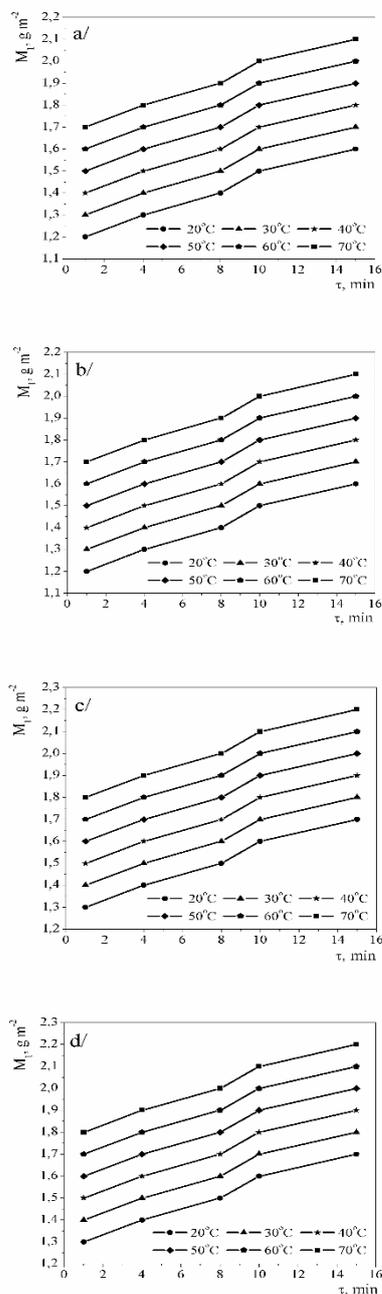
**Table 1.** Phosphating solution characteristics

Solution	$\rho$ $g\ cm^{-3}$	pH	$\sigma$ $mS\ sm^{-1}$	$K_o$
KAF-50 FA	1.23	4.29	64.3	208

#### Gravimetric investigations

The method was used to elucidate the effect of the operating conditions (concentration and temperature of the phosphating solution as well the duration of the process) on the coating thickness  $M_1$ . The plots in Figure 1 are the relationships  $M_1=f(\tau)$  in 2 (1a), 4 (1b), 7 (1c) and 11 (1d) vol.% aqueous solution of the KAF-50 FA agent under various conditions imposed by variations in the temperature

and duration of the sample treatment. These conditions were selected after preliminary tests.



**Fig. 1.** Effect of the phosphating duration,  $\tau$ , min on the thickness/mass of the phosphate coating obtained in KAF-50 FA,  $M_1$ ,  $\text{g m}^{-2}$ : a/ 2 %; b/ 4 %; c/ 7 %; d/ 11 %.

The curve behaviours reveal that the thickness/mass on films formed on the aluminum surfaces grows in time. The increase in the solution temperature from 20.0 to 70.0°C results in increased thickness/mass where the maxima are attained at 70.0°C. The similarities between the curves and the small differences in the values of  $M_1$  indicate that the solution concentration does not affect significantly both the mechanism and the rate of the phosphate film formations. The weak increase in  $M_1$  with

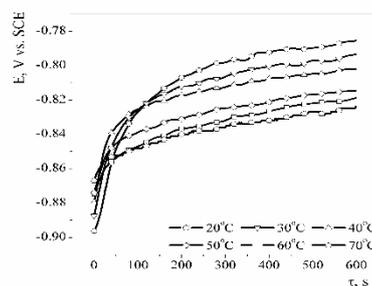
increase in the concentration reveals, actually, that it is more reasonable solutions with moderate concentrations to be used, that also have an economic impact, rather than film formations in high concentration solutions.

The phosphate coatings obtained are from pale to dark yellowish colors. The coatings with better distribution of thickness and color over the entire sample area were obtained at about 60°C and solution concentrations in the range 4–7 vol.%.

#### Electrode potentials measurement

The electrode potentials of the phosphate aluminum specimens were measured in the course of the coatings formation in the phosphating bath and after that they were tested in a model aqueous media 0.6 M NaCl.

The electrode potentials shown in Figure 2 are relevant to the process of amorphous phosphate coating formation by submerging of the samples in solutions with 7 vol.% (at 20.0, 30.0, 40.0, 50.0, 60.0 and 70.0°C) lasting 10 min. It is obvious that at all temperatures used the potentials shift in the positive direction: at the beginning approximately linearly and then followed by almost parabolic behaviour up to the moment when stabilization is attained.

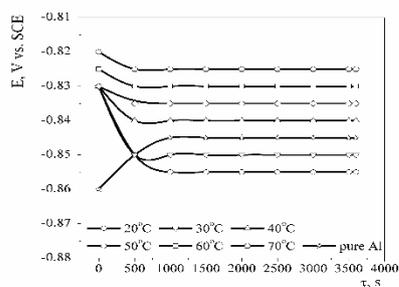


**Fig. 2.** Relationships potential-time during formation of the coating (open circuit): 7 vol.%; 10 min and different temperatures of obtaining

The corrosion resistance of the amorphous phosphate coatings was determined in model aqueous solutions of NaCl with 0.6 M concentration. The tests itself includes a submerging procedure for about 1 h of all samples in the NaCl solutions. The coating was determined as resistant if for 1 h (an empirically chosen time interval) no changes in the surface as color spots or colorization of the solutions occur. Meanwhile, in parallel to these tests the corrosion potential of the samples were measured that allowed to compare the behaviour with that of uncoated aluminum samples.

The potential behaviour shown in Figure 3 is relevant to the corrosion resistance of amorphous phosphate coatings in 0.6 M aqueous solutions of NaCl. The plots reveal that just after the sample

submergence in the corrosion medium the potentials shift sharply in the negative directions and after a certain accommodation time interval (about 500 seconds) a stable state is attained. In additions, with increase in the temperature of the phosphate coatings the potentials move in the positive direction. The corrosion potential of an uncoated aluminum sample is more positive than the phosphate coated ones at 20 and 30°C.



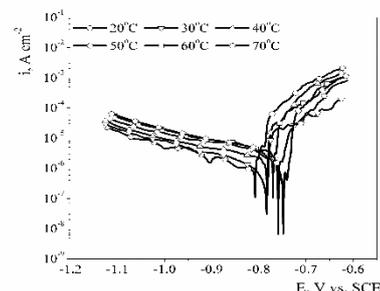
**Fig. 3** Relationships potential-time in 0.6 M NaCl (open circuit): 7 vol.%; 10 min and different temperatures of obtaining.

*Potentiodynamic polarization investigations*

The potentiodynamic polarization studies of the phosphate coatings were carried out at 20°C in model aqueous solutions of 0.6 M NaCl. The scanning rate of 10 mV s<sup>-1</sup> was chosen based on preliminary test

runs. The target of these experiments was to obtain information about the corrosion resistance of the phosphate coatings formed in the corresponding model media in course of their cathodic and anodic polarization and consequently to compare them.

The potentiodynamic polarization relationships of the phosphate coatings (see Figure 4) obtained in the model solutions of 0.6 NaCl allow estimating both the corrosion potentials and the corresponding currents, summarized in Table 2. It is obvious that in 0.6 M NaCl solutions the potentials shift in the positive direction with increase in the temperature and the corrosion current (it slightly varies) is the lowest in the range 40-60°C.



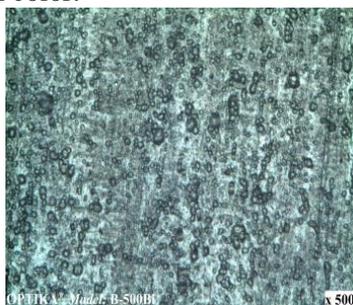
**Fig. 4.** Potentiodynamic polarization relationships of the phosphate coatings in 0.6 M NaCl: 7 vol. %; 10 min, scan rate 10 mV s<sup>-1</sup> and different temperatures of obtaining

**Table 2.** Corrosion parameters of the coatings in 0.6M NaCl

Corrosion parameters	Temperatures, °C					
	20°C	30°C	40°C	50°C	60°C	70°C
$E_{corr}, mV (SCE)$	-808	-785	-784	-760	-771	-749
$i_{corr}, A cm^{-2}$	$8.3 \times 10^{-7}$	$3.5 \times 10^{-7}$	$1.4 \times 10^{-6}$	$1.6 \times 10^{-6}$	$2.2 \times 10^{-6}$	$7.3 \times 10^{-7}$

*Optical microscopy*

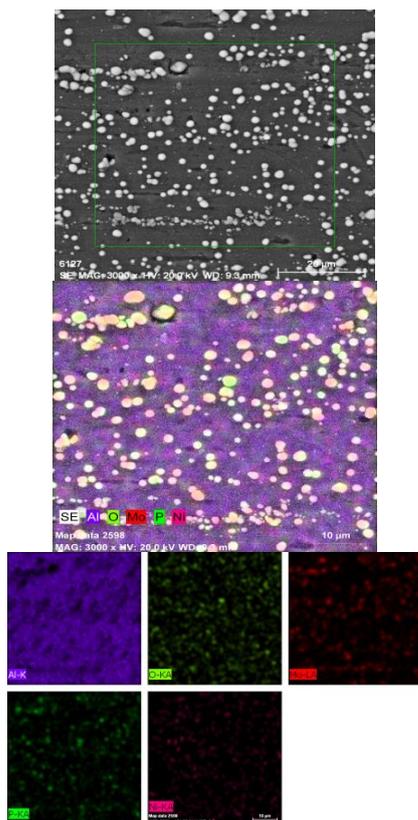
The micrographic picture in Figure 5 demonstrates surface of amorphous phosphate coating on an aluminum sample. The surface is almost homogeneous with dense fine film coating of gray bluish color.



**Fig. 5.** Optical microscopy of the phosphate coating: 7 vol. %; 60°C; 10 min.

*Scanning electron microscopy*

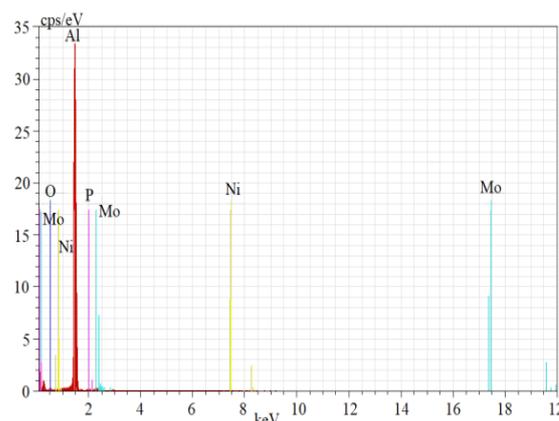
The microphotography in Figure 6a demonstrates an amorphous phosphate coating obtained on aluminum samples. The surface is covered with dense fine film with some small areas where spherical formations with white color emerge. The surface shown in Figure 6b and Figure 6c, in different colors, show the distribution of the elements in the coating content.



**Fig. 6.** SEM – microphotograph of the obtained coating: 7 vol.% 60°C; 10 min.

*Energy dispersive X-ray spectroscopy, EDX*

The EDX-analysis is performed on specimens treated in phosphate solutions again at 7 vol.%; 60°C; 10 min (see Figure 7). The basic elements contained in the coating determined by means of this analysis are Al, P, O, Mo and a little bit quantity of Ni. The results of EDX-analysis are presented in Table 3.



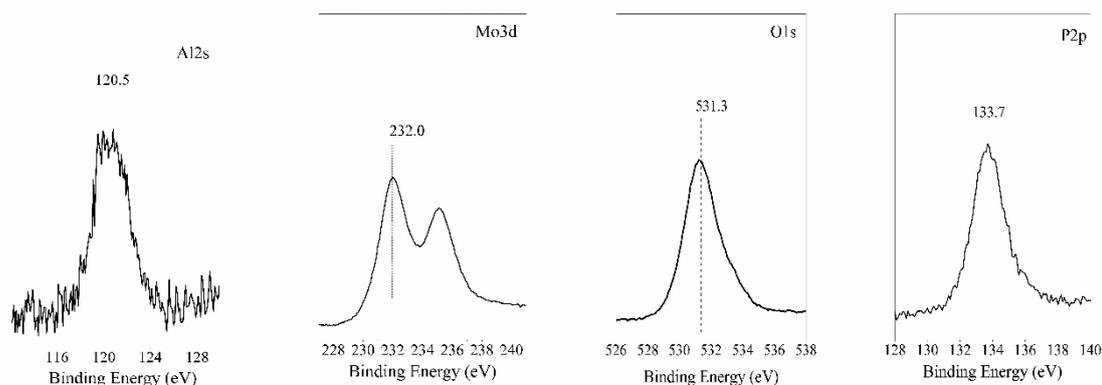
**Fig. 7.** EDX – spectrums of the elements in the coating: 7 vol.%; 60°C; 10 min.

*X-ray photoelectron spectroscopy, XPS*

XPS was used for determination of the chemical content of the coatings. Figure 8 presents the photoelectron spectra of Al2s, P2p, O1s and Mo3d, registered in the analysis of the phosphate coatings. The value of bonding energy of Al2s is 120.5 eV and it corresponds to the typical range related to Al<sub>2</sub>O<sub>3</sub>. The bonding energy of P is 133.7 eV and this value indicates that it is (V) valent state as PO<sub>4</sub><sup>-3</sup>. The obtained spectrum of O1s is characterized with wide half-wide and asymmetric shape in the direction of the higher bonding energy which may be attributed to formation of various oxides as well as hydroxides and phosphates.

**Table 3.** EDX analyse of the elements in the coating at the film surface

Concentration	Elements				
	Al	O	Mo	P	Ni
Atomic,%	84.91	10.70	3.24	0.78	0.37



**Fig. 8.** XPS – spectra of the elements in the phosphate coating: 7 vol.%; 60°C; 10 min.

The maximum value of the bonding energy of Mo3d is 232.0 eV. The shape and the large half-wide

of the registered peak suggest existence of Mo in various valent states at the coating surface.

Table 4 presents the quantity of the elements included in coatings determined by X-ray photoelectron spectroscopy in atomic percentages.

**Table 4.** XPS-analyse of the elements in the coating

Concentration	Elements			
	Al	O	Mo	P
Atomic %	4.9	76.0	12.0	7.1

### CONCLUSIONS

The effects of the operating conditions (concentration, temperature) on the thickness, content and morphology of coatings formed at aluminum surfaces in solutions containing ammonium and sodium phosphates (as well as molybdate, softeners and inorganic activators and surfactants) have been investigated by gravimetric, electrochemical polarizing methods X-ray and microscopic analyzes.

The studies carried out reveal that:

1. The mass/thickness of the coatings increases with increase in the temperature in all cases of the concentration variations.
2. SEM and optical analyzes reveal that the surfaces of the treated aluminum samples are coated by homogenous dense films and the better results were obtained with phosphating baths with concentrations 4-7 vol.% and temperature of about 60°C.
3. The coatings obtained are X-ray amorphous and the contents include phosphorous, oxygen, molybdenum, and nickel, forming chemical compounds in the structure of the coatings such as oxides, hydroxides and phosphates of aluminum, molybdenum and nickel.

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## ТЪНКИ ФОСФАТНИ ФИЛМИ ВЪРХУ АЛУМИНИЕВИ ПОВЪРХНОСТИ

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(Резюме)

Изследвано е влиянието на различни фактори като концентрация (2.0÷11 vol. %) и температура (20÷70°C), върху формирането, състава и морфологията на покрития, получени при третиране на алуминиеви повърхности (Al – 99.5 %) в разтвори, съдържащи амониеви и натриеви фосфати, MoO<sub>4</sub><sup>2-</sup> промотиращи йони, буфери, омекотители, неорганични активатори и ПАВ. Използвани са гравиметричен и електрохимичен методи, оптична микроскопия, сканираща електронна микроскопия с EDX-анализ, и рентгенова фотоелектронна спектроскопия (XPS). Определени са оптималните експериментални условия (концентрация 4 – 7 vol.% и температура 50 – 70°C), при които се получават хомогенни покрития с дебелина около 1 µm. В състава на покритията се съдържат фосфор, кислород, молибден и никел, които са под формата на фосфатни и оксидни съединения.