# Formation of composite coatings: morphology and composition studies

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**Abstract.** In this work, composite fluoropolymer-containing coatings were obtained on samples of AMg3 aluminium alloy, MA8 magnesium alloy, and VT1-0 commercially pure titanium treated by plasma electrolytic oxidation (PEO). Superdispersed polytetrafluoroethylene (SPTFE) and a solution of tetrafluoroethylene (TFE) telomers in acetone were applied onto preliminarily formed PEO layers by the spray-coating method. The obtained coatings contained a large amount of crystalline polytetrafluoroethylene embedded in the outer porous layer of the PEO coating and did not have visible defects, which indirectly indicates high protective properties.

## 1 Introduction

Plasma electrolytic oxidation (PEO) is one of the modern effective methods for modifying the surface of metals and alloys in order to increase their protective properties [1-12]. This method makes it possible to obtain ceramic-like coatings containing components of electrolyte and base material [1-12]. The coatings obtained by this method have high corrosion resistance, significant wear resistance, and high adhesion to the substrate due to the formation of chemical bonds between the coating and the base material [1-9]. Additionally, we note that the coatings synthesized by such plasma electrolytic treatment have a developed structure [10-12]. The presence of pores of micron size and smaller in the coating allows us to consider it as a suitable basis for the introduction of various substances that significantly improve the protective properties of the coating [10-12]. Thus, it is possible to create composite layers that significantly modify the surface of the base material, and there are many fields in which the PEO method is used in various modifications [1-12]. In particular, when introducing fluoropolymer substances into the pores of the PEO coating, it is possible to achieve an increase in the corrosion resistance of the processed products, sufficient for operation in harsh environmental conditions, which will significantly reduce economic costs of industry and shipbuilding [9-12]. The purpose of this paper is to study the composition and morphological features of composite coatings formed on non-ferrous metals and alloys by the PEO method followed by spraying of fluoropolymer substances.

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## 2 Materials and methods

Plasma electrolytic oxidation of MA8 magnesium alloy samples was carried out in an electrolyte containing 15 g/L $Na_2SiO_3{\bullet}5H_2O$ and 5 g/L NaF in the bipolar potentiodynamic mode. The samples made of AMg3 aluminium alloy were also oxidized in a bipolar potentiodynamic mode, but in the electrolyte contained 0.6 g/L NaF, 10 g/L $Na_2B_4O_7{\bullet}10H_2O$, 25 g/L $C_4H_4O_6K_2{\bullet}0.5H_2O$, and 10 g/L $Na_2SiO_3{\bullet}5H_2O$. PEO coatings on VT1-0 titanium samples were formed in an electrolyte containing 25 g/L $Na_3PO_4$ in a two-stage monopolar potentiodynamic mode.

As an organofluorine component of composite coatings, various types of such compounds were used: superdispersed polytetrafluoroethylene (SPTFE) and a solution of tetrafluoroethylene (TFE) telomers in acetone (obtained by radiation chemical synthesis at the Institute of Problems of Chemical Physics of the Russian Academy of Sciences). As a processing method, the spray-coating method was used. Preliminary tests made it possible to establish the optimal aerosol method for applying SPTFE and TFE telomers using a medium-pressure compressor and a spray gun [11, 12]. Spraying was carried out by air at a decreasing pressure from 0.6 to 0.4 MPa. Such values of pressure during surface treatment make it possible at the first stage to introduce polymer particles into the pores of the coating and provide a uniform layer due to the deformation of the particles. A gradual decrease in pressure is necessary so that the sprayed particles do not destroy the polymer that has already reached the surface, but are deposited on it, increasing the layer thickness. The distance between the nozzle and the surface of the workpiece is about 20 cm, while at least 90% of the sprayed fluoropolymers fall on the treated surface.

To study the morphological features of the samples, an EVO 40 (Carl Zeiss, Germany) scanning electron microscope was used.

The phase composition of the surface layers was determined in the "Far East Center for Structural Research" on a Rigaku X-ray diffractometer (XRD) (SmartLab, Japan), using $CuK_{\alpha}$ radiation.

## 3 Results and discussion

In the course of this work, studies were carried out on the effect of the volume of the sprayed substance on the composition and structure of composite coatings formed by the method described above. For this purpose, three types of coatings were obtained with different volumes of introduced dispersions on such non-ferrous metals and alloys as VT1-0 commercially pure titanium, AMg3 aluminium alloy and MA8 magnesium alloy (Table 1).

**Table 1.** Designation of the samples.

| Designation | CC-1 | CC-2 | CC-3 |
|---|---|---|---|
| The volume of sprayed dispersions, ml/cm$^2$ | 0.35 | 0.65 | 0.95 |
| Approximate weight of PTFE, g/cm$^2$ | 0.05 | 0.10 | 0.14 |

According to the analysis of SEM data, the formed coatings had no visible defects, except CC-3 on the titanium (Fig. 1). Analysis of SEM images of the surface of PEO and composite coatings revealed a complete filling of the coating pores with a small amount of the sprayed substance for aluminium and titanium materials (Fig. 2). However, at a volume of 0.95 ml/cm$^2$, defect formation was observed in the polymer film.

When evaluating the cross-sections of various composite coatings, no significant difference was found between them (Fig. 2). Data evaluation indicates the incorporation of the polymer into the porous part of the PEO layer (Fig. 2), from which it follows that the formed coatings are composite structures.

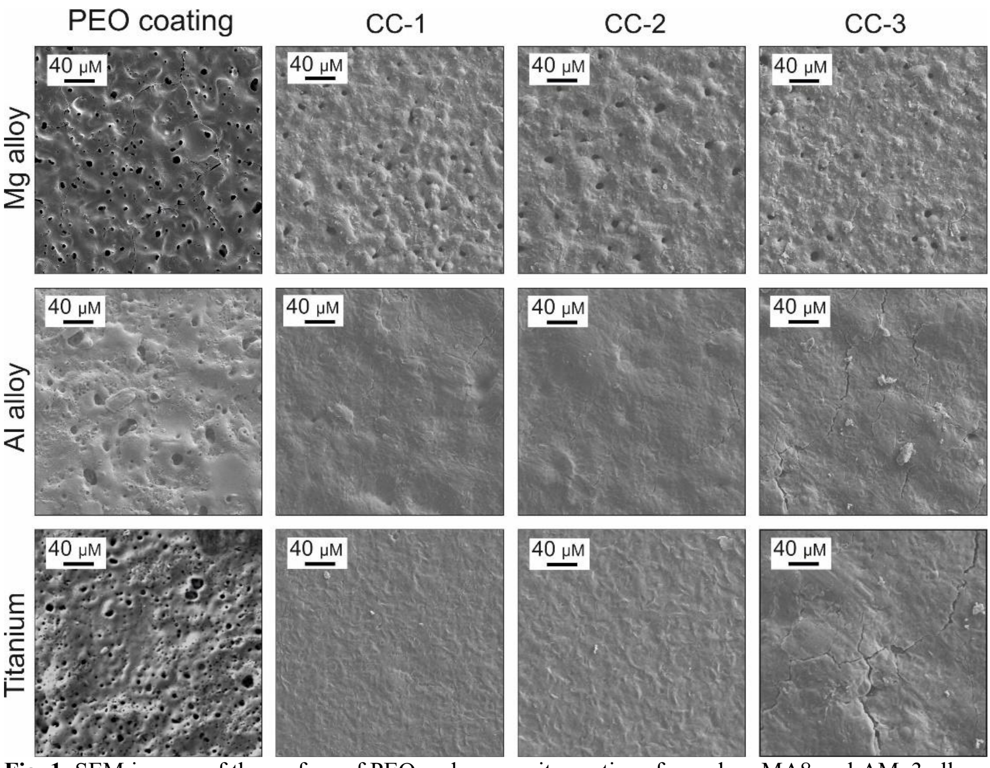


**Fig. 1.** SEM images of the surface of PEO and composite coatings formed on MA8 and AMg3 alloys and VT1-0 titanium.

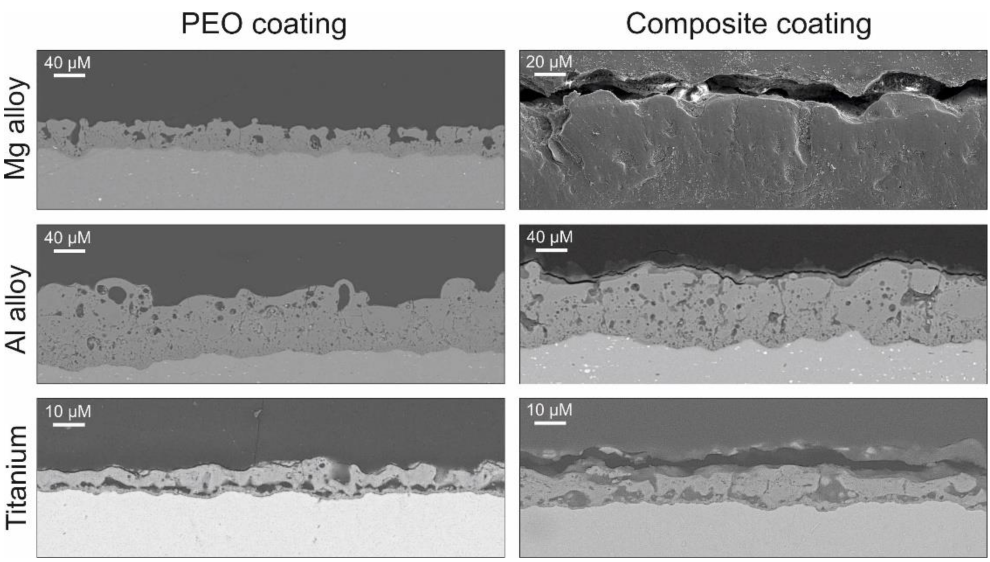


**Fig. 2.** SEM images of the cross-sections of composite coatings formed on MA8 and AMg3 alloys and VT1-0 titanium.

The phase composition of the formed coatings was determined by XRD analysis (Fig. 3). For composite coatings on all types of materials used, general trends were observed, namely, an increase in the intensity of the PTFE peak and a decrease in the intensities of the lines of the phases that make up the PEO coatings with an increase in the amount of sprayed substance. In particular, this is true for MgO and $Mg_2SiO_4$ in the case of a magnesium alloy (Fig. 3a), $Al_2O_3$ and $Al_6Si_2O_{13}$ in the case of an aluminium alloy (Fig. 3b), and $TiO_2$ for titanium (Fig. 3c).

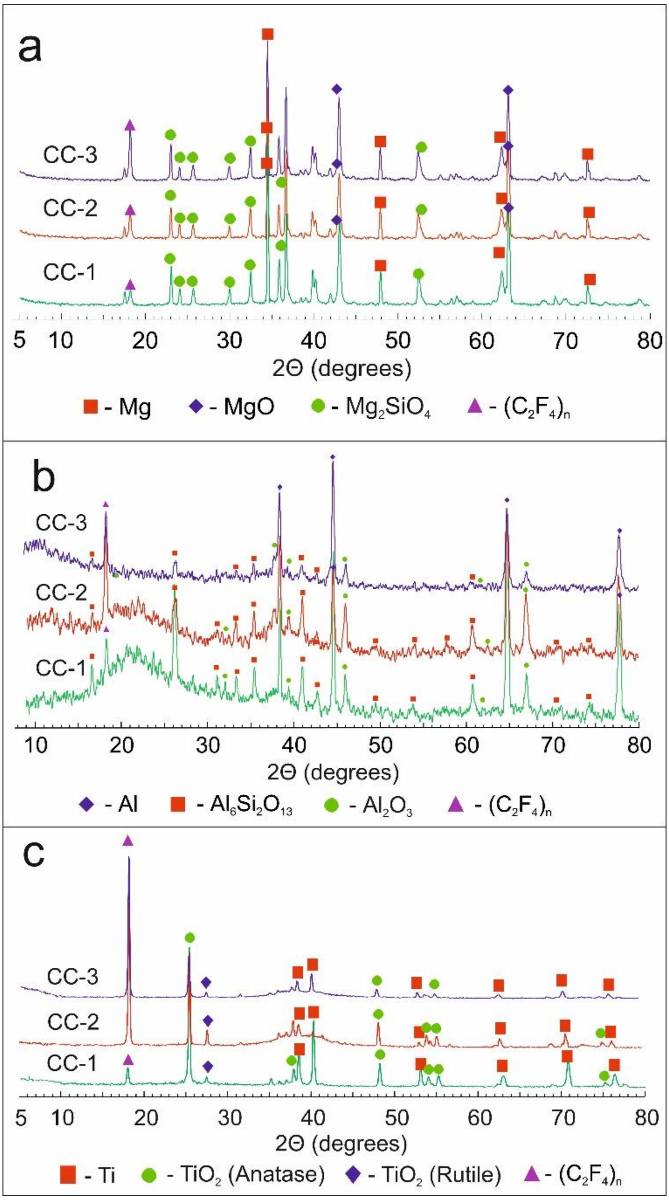


**Fig. 3.** X-ray diffraction patterns of composite coatings on magnesium alloy (a), aluminium alloy (b) and titanium (c).

## 4 Conclusion

Analysis of SEM data shows that a large amount of polytetrafluoroethylene embedded in the outer porous layer of the PEO coating, and surfaces of composite layers do not have visible defects, which indirectly indicates high protective properties of obtained structures. Summarizing the data of XRD analysis, we can conclude that the composite coatings consist of the metal oxides (MgO, $Al_2O_3$, $TiO_2$) and compounds formed during the interaction of substrate material with electrolyte components ($Mg_2SiO_4$, $Al_6Si_2O_{13}$), as well as a large amount of crystalline polytetrafluoroethylene .

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## References

1. D. V. Mashtalyar, K. V. Nadaraia, N.G. Plekhova, I.M. Imshinetskiy, M.A. Piatkova, A.I. Pleshkova, S.E. Kislova, S.L. Sinebryukhov, S.V.Gnedenkov, Mater. Lett., **317**, 132099 (2022).
2. S. Sikdar, P. V. Menezes, R. Maccione, T. Jacob, P. L. Menezes, Nanomaterials, **11**, 1375 (2021).
3. M. Kaseem, S. Fatimah, N. Nashrah, Y. G. Ko, Prog. Mater. Sci., **117**, 100735 (2021).
4. F. Simchen, M. Sieber, A. Kopp, T. Lampke, Coatings, **10**, 628 (2020).
5. T. W. Clyne, S. C. Troughton, Int. Mater. Rev., **64**, 127–162 (2019).
6. Y. Zhang, Q. Wang, R. Ye, C. S. Ramachandran, J. Alloys Compd., **892**, 162094 (2022).
7. R. Chaharmahali, A. Fattah-alhosseini, K. Babaei, J. Magnes. Alloy, **9**, 21–40 (2021).
8. L. Ren, T. Wang, Z. Chen, Y. Li, L. Qian, Metals, **9**, 170 (2019).
9. A. Fattah-alhosseini, M. Molaei, K. Babaei, Surf. Interfaces. **21**, 100659 (2020).
10. C. Lu, P. Shi, J. Yang, J. Jia, E. Xie, Y. Sun, J. Mater. Res. Technol., **9**, 12149-12156 (2020).
11. D. V. Mashtalyar, K. V. Nadaraia, E.A. Belov, I.M. Imshinetskiy, S. L. Sinebryukhov, S. V. Gnedenkov, Polymers, **14**, 4667 (2022).
12. V.S. Egorkin, D. V. Mashtalyar, A.S. Gnedenkov, V.S. Filonina, I.E. Vyaliy, K. V. Nadaraia, I.M. Imshinetskiy, E.A. Belov, N. V. Izotov, S.L. Sinebryukhov, S. V. Gnedenkov, Polymers, **13**, 3827 (2021).