Surface & Coatings Technology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Aluminum- and titanium-supported plasma electrolytic multicomponent coatings with magnetic, catalytic, biocide or biocompatible properties

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ARTICLE INFO

Article history:
Received 22 March 2016
Revised 19 July 2016
Accepted in revised form 20 July 2016
Available online xxxx

Keywords:
Plasma electrolytic oxidation
Titanium
Aluminum
Impregnation
Extraction
Sol-gel
Magnetism
Catalysis
Bioactivity

ABSTRACT

The paper presents some of the directions of developing the plasma electrolytic oxidation (PEO) technique to form the coatings with magnetic, catalytic, biocompatible or biocidal properties on the valve metals and alloys. It reflects the relationships between the structure, composition and functional properties of PEO coatings. The data presented suggest that PEO is an effective method of physicochemical synthesis on metals and alloys of the surface layers with different chemical composition and certain characteristics.

1. Introduction

In recent years, the plasma electrolytic oxidation (PEO) technique, that is anodization of valve metals and alloys in electrolytes at voltages of spark and microarc electrical discharges in the anode region, is rather actively explored for obtaining 'metal/coating' composites of different composition and purpose. Locally high temperatures and pressures in electric breakdowns zones, evaporation of the solution, partial melting of the oxide and, perhaps, of the metal – all these processes lead to the solid-state and gas-phase reactions [1–7]. From this perspective, PEO is an unconventional method of physicochemical synthesis of the surface layers of a certain chemical composition with various physical and chemical properties [3,5,8–14]. Meanwhile, the possibilities of PEO are underestimated. The works carried out are mainly focused on the application of PEO technique for obtaining protective coatings [13–19]. Only in recent years, some progress has been appeared in the direction associated with the use of PEO for obtaining the coatings of complex chemical composition with various functional properties. In this regard, one can note obtaining 'PEO coating / metal' composites, whose composition and structure make can them promising candidates for use in medicine as a biocompatible [20–24] or antibacterial materials [25–29], in photocatalysis [30–33], in catalysis of gas phase or liquid phase reactions [34–37], producing PEO coatings having ferromagnetic [38–41] or antiferromagnetic properties [42] and those with certain hydrophilic-hydrophobic balance of the surface, including superhydrophilic [43] or superhydrophobic properties [44]. The studies related to combination of PEO with other surface processing technologies to produce the coatings of certain chemical composition and functional purposes were initiated. Using combination of PEO with impregnating and annealing [37,45,46], extraction pyrolysis [47–49], deposition of corrosion inhibitors [50,51] and compounds imparting hydrophobic properties to the surfaces [44], template sol-gel synthesis [52–54] can be gives as examples.

Conducting the anodizing process under electrical discharges of various types such as spark, microarc, propagating ones (Fig. 1a-c) allows forming the coatings of complex chemical composition [55]. Depending on the electrolyte composition and processing modes, structures of three types can be obtained. The coatings may be built mainly of an oxide of the treated metal (Fig. 1d). In addition to the substrate oxides, the coating composition can involve crystalline inclusions and compounds based on the components of electrolyte or those of electrolyte and substrate (Fig. 1e). Moreover, the coatings may be multilayers

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http://dx.doi.org/10.1016/j.surfcoat.2016.07.060
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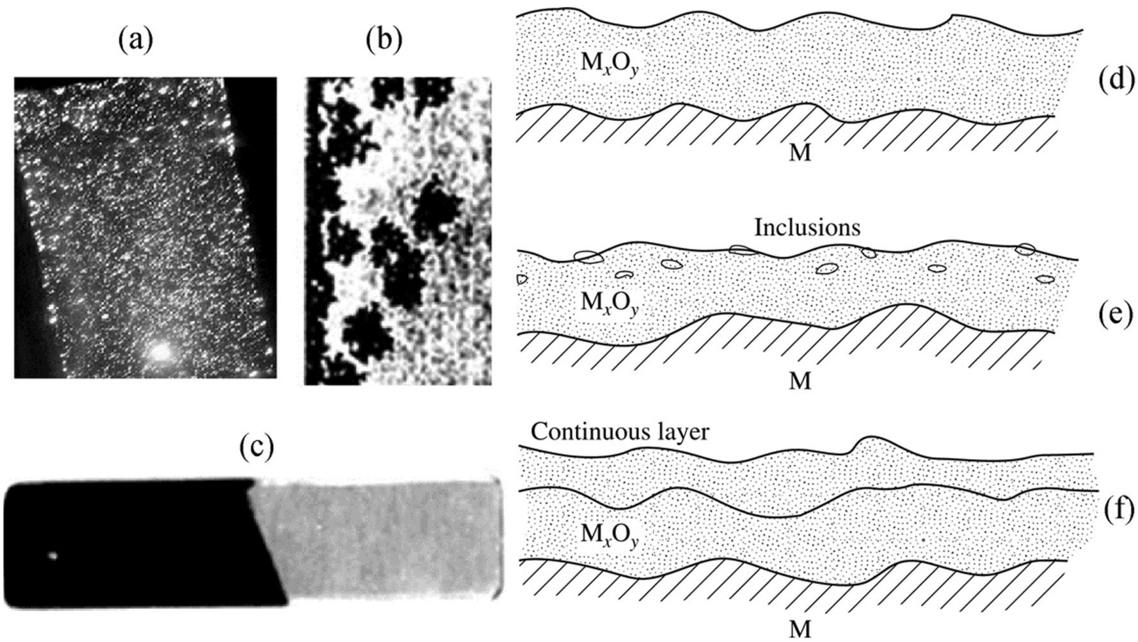

Fig. 1. Main types of electric discharges at anode during PEO treatment [55]: (a) an uniform ensemble of spark discharges transitioning over time into more powerful microarc ones; (b) the occurrence of isolated discharges which are subsequently concentrated along the perimeter of new phase areas (in the figure is painted black) increasing over the primary oxide layer; (c) the occurrence of a single discharge, which as a line or a spot migrates at the surface of the sample leaving behind an oxide film of a definite thickness (shown in black); and (d, e, f) the structures formed by spark and arc discharges.

with the external layer predominantly containing compounds based on the electrolyte components (Fig. 1f).

From a technological point of view, the following features of PEO technique are of interest to produce functional systems [2,4,5,7,11,13, 15,16,18,19]. The method allows (1) conducting the synthesis of high-temperature compounds on metal anode surface in an aqueous electrolyte under atmospheric pressure and average temperature not exceeding 100 °C during from a few to tens of minutes; (2) processing the products of complicated geometrical shape, including those with through narrow openings by pumping the electrolyte through them; (3) restoring the properties of the coating by re-treatment of the products; (4) forming the surface layers with high-temperature compounds on low-melting-point metals and alloys, such as aluminum and magnesium. Moreover, PEO technique (5) does not require a vacuum or gas protection and provides (6) good adhesion between the coating and the substrate, relatively low cost of the coating and processing, and (7) environmental acceptability of electrolytes (in most cases, aqueous solutions of inorganic salts).

The mechanisms of PEO coatings' growth and main ways of obtaining the coatings with specific composition, structure and functional properties have been the subject of discussion and analysis in a number of reviews and monographs, including [1–7,11,13,15–19]. However, as noted above, new areas regarding the application of both single-stage PEO technique and its combination with other methods of surface modification were formed in recent years to obtain compositions 'composite oxide coating/metal' with certain functional properties. The review deals with some directions and research results regarding obtaining PEO coatings with specific magnetic, catalytic, or bioactive properties. The authors believe that the review of publications in these areas can be useful for professionals working in these and similar research areas.

2. Coatings with certain magnetic characteristics

Scientific background of new methods for forming 'coating/metal' magnetic materials is very important. Application of PEO for these purposes is unconventional. The research in this area has been recently started [38–42,46,56–61].

The main approaches for fabricating the PEO coatings with certain magnetic characteristics are as follows: (1) using the electrolytes containing dispersed particles of Fe^0, Co^0 for obtaining ferromagnetic coatings [38,41]; (2) introducing the dispersed particles of iron oxides into electrolytes for producing antiferromagnetic coatings [42]; (3) the use of electrolytes containing metal-complex ions, for example, EDTA-Fe^{3+} [40] or $[FeP_6O_{18}]^{3-}$ [57] for ferromagnetic properties; (4) tribological application of nanoscale particles on the preliminarily formed PEO coating for ferromagnetic ones [41]; (5) using slurry electrolytes (suspension-electrolytes, sols) for introducing various metal oxides into PEO coatings for ferro-, ferri- and antiferromagnetic properties [19,39, 46,56–64]; (6) applying the impregnation of preformed PEO coatings in aqueous solutions of iron salts followed by annealing, resulting in ferromagnetic properties [46].

In [38], PEO coatings on an aluminum alloy were formed in a $Na_2WO_4 + Na_3PO_4$ electrolyte containing dispersed iron particles with sizes no larger than 5 μm. Coatings with an iron content of 10.2 at.% were produced. Scattered dispersed particles smaller than 5 μm in size were included in the coating surfaces. The authors believe that these are iron particles. The electromagnetic properties of the coatings were judged from the absorption of microwave radiation. The coatings were characterized by negligibly small dielectric loss tangents. The magnetic permeability of the coatings depended on the frequency of electromagnetic microwave radiation. Noticeable magnetic losses were observed at frequencies of 9.6 and 12.6 GHz. In the authors' opinion, the approach proposed makes it possible to create and synthesize microwave absorbers in an efficient and simple way.

Introducing Fe_2O_3 particles with a mean size of about 0.1 μm (in a range from 0.03 to 0.15 μm) in an alkaline silicate electrolyte enabled one to produce PEO coatings with a thickness up to 6–7 μm containing 16–19.5 at.% iron, which was homogeneously distributed over the cross section of the oxide layer, on a titanium foil [42]. The coatings involved the α-Fe_2O_3 (hematite) phase. According to the data of Mössbauer spectroscopy, the material of the coating was antiferromagnetic.

The authors of [41] studied magnetic characteristics of cobalt-containing coatings on titanium. Cobalt nanopowder with a mean particle size of ~70 nm was used for formation of the coatings. The powder