

KOH vs. NaOH IN ELECTROLYTES OF THE PLASMA ELECTROLYTIC OXIDATION

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The plasma electrolytic oxidation (PEO) of different metals, their alloys and composites is carried out in electrolytes which contain the very different reactants, but fundamentally electrolyte contained the alkali. In this research the possibility influence of the species of alkali on the properties of the coating is studied. The two most commonly encountered alkalis, namely, KOH and NaOH, are chosen. The oxide layers obtained are studied using SEM, EDX, XRD, and a microhardness tester. The corrosion properties are determined using a potentiostat. The effect of the species of alkali in the electrolyte on the growth kinetics of the coating and its qualitative characteristics is discussed. It is shown that at describe the species of alkali in the electrolyte from NaOH to KOH, the rate of growth of the oxide layer increases from 20 to 30 $\mu\text{m h}^{-1}$ with significant variation of the phase composition of the coating. The greatest hardness of an oxide ceramic layer was obtained in the inner layer of the coating obtained with KOH than with NaOH (1570 HV₁₀ and 1288 HV₁₀, respectively). The most favorable combination of physical and chemical properties is observed in an electrolyte containing KOH.

Introduction

The plasma electrolytic oxidation of metals is a complex process that combines parallel processes of oxide film formation, dissolution, and dielectric breakdown. The probability of the domination of any of these partial processes in the overall process depends on the nature of both the metal and the electrolyte, as well as on the actual regime employed. The ultimate stage of the PEO treatment is a quasi-stationary state of persistent anodic microdischarges, which exhibit progressive variation of the characteristics of the material during the electrolysis. At high discharge temperatures and pressures (reaching about 2×10^3 to 3×10^3 °C and $\sim 10^2$ MPa, respectively [1]), solid electrolysis products and adsorbed gel layers are deposited on the metal surface in the form of high-temperature oxide phases or glassy ceramic coatings. Under those extreme conditions, which occur during the PEO process, oxides of base metals can crystallize in different crystalline forms of the oxide, under different conditions. Depending on the purpose of the oxidation, the PEO treatment is typically carried out for 5–180 min at current densities equal to 500–2000 $\text{A}\cdot\text{m}^{-2}$ and voltages up to 800 V [1, 2].

Various electrolytes are used for the oxidation of aluminum and magnesium alloys. They include electrolytes based on the silicate Na_2SiO_3 [3-8], the aluminates NaAlO_2 and $\text{K}_2\text{Al}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ [9, 10], the phosphates $\text{Na}_6\text{P}_6\text{O}_{18}$, and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ [4, 9, 10-12], the borates $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and $\text{K}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ [11, 13], acetates and tartrates [14, 15] etc. Many researchers work with basic electrolytes containing very different kinds of additives in the form of various soluble salts (Na_2WO_4 [11, 13], KF [15, 16], $\text{K}_2\text{Al}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$, $\text{K}_2\text{TiO}_3 \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{Cr}_2\text{O}_7$, KMnO_4 [9]) and in the form of insoluble dispersed particles (SiO_2 and Al_2O_3 [12], TiO_2 and ZrO_2 [9] etc.). The most popular are basic silicate electrolytes that have a lower alkali content (0.5–1.0 g/L of alkali) for the oxidation of aluminum alloys and a higher basicity (up to 10 g/L of alkali) for the oxidation of magnesium alloys.

Different researchers employ either KOH [2, 9, 13, 17] or NaOH [5, 10, 18] as the alkali for preparing the electrolytes used for plasma electrolytic oxidation. For this reason, it became necessary to conduct an additional investigation to evaluate the influence of the species of alkali on the properties of the coating obtained as applied to our electrolytes.

Experimental

Rectangular coupons $3 \times 15 \times 30$ mm in size made from 5052 aluminum alloy (2.5% Mg, 0.1% Mn, 0.08% Si, 0.05% Zn, 0.05% V, Al – balance [19]), were used. Prior to the PEO process, the samples were mechanically polished with #1000 abrasive SiC papers, rinsed in ultrasonic bath with distilled water, and cleaned in acetone. The homemade machine equipment with stirring and cooling systems was used to perform the PEO process with an applied current density $10 \text{ A} \cdot \text{dm}^{-2}$.

Oxide ceramic layers obtained in an electrolyte containing 0.057 M $\text{Na}_2\text{Si}_3\text{O}_7 \cdot n\text{H}_2\text{O}$ (water glass, $\rho = 1.38 \text{ g} \cdot \text{cm}^{-3}$) and 0.037 M KOH or NaOH were studied. After PEO treatment, the samples were rinsed in deionizer water and dried in vacuum desiccator.

Results and discussion

A YK-2005WA pH/CD meter was used to measure the conductivity and the pH of the electrolytes according to ASTM D1125 [20].

The conductivity of the electrolytes with KOH and NaOH was 4.53 and 5.03 μS , and the pH was 11.08 and 11.85, respectively.

Current and voltage wave profiles and trend plot of PEO process were monitored over the course of the process by a Fluke Scope Meter 199C (200 MHz/2.5 GS/s). Plots of the dependence of the formation voltage of the oxide layer on the oxidation time are presented in Fig. 1. As seen in Fig. 1, the forming voltage of the oxide layer is 15–20 V higher when

the electrolyte containing KOH is used, which determines the greater power of the microarc discharges. The latter leads to a change in its phase composition (Fig. 4.3), as well as an increase in the extent of diffusion of oxygen and, accordingly, in the thickness of the coating (Fig. 4, 5).

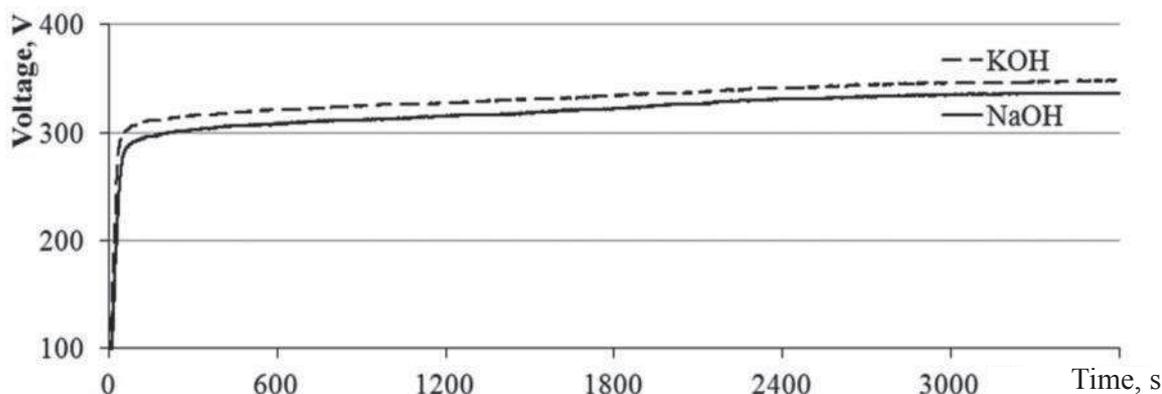


Fig. 1. Potential versus time responses for the PEO of the Al alloy Al5052 in electrolytes containing KOH and NaOH

Phase compositions of coatings were determined with a PANalytical X'Pert Pro X-ray diffractometer (Cu-K α radiation) in Grazing incidence mode, using a scan with a grazing angle Ω of 3° a step size in μ of 0.02° and a range of 2θ from 20° to 90° .

Fig. 2 presents diagrams that reflect the quantitative phase composition of the oxide ceramic layer. As is seen, in both cases the principal coating is η -alumina. However, after oxidation in the electrolyte

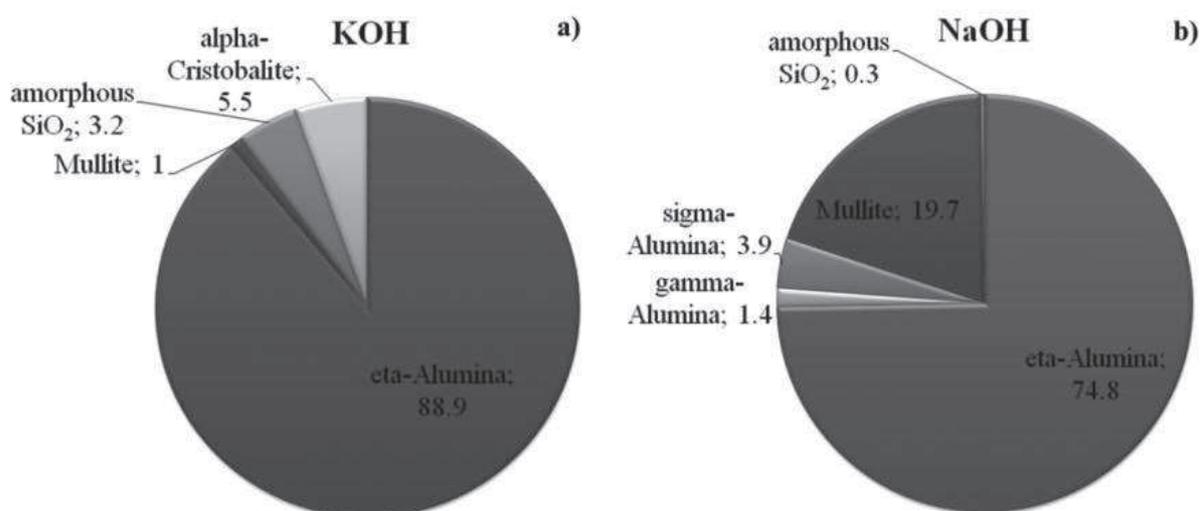


Fig. 2. Quantitative phase composition (%) of PEO oxide layers on aluminum 5052 (the electrolyte was 0.057 M SiO₂ with $n = 3$ (water glass)), which were obtained with the use of 0.037 M: a) KOH and b) NaOH as the alkali addition

containing NaOH, a larger amount of silicon-containing compounds and low-temperature modifications of aluminum oxide are present.

A Buehler Micromet 2100 microhardness tester was used to monitor the microhardness of the oxide layer on the cross section. The microhardness was determined according to ASTM E384, C1327, and B578 as the mean of five measurements for each sublayer under a load equal to 10–100 g.

The microhardness measurements performed revealed the greater hardness of the inner layer of the coating obtained with KOH than with NaOH (1570 HV₁₀ and 1288 HV₁₀, respectively). These measurements are confirmed by the phase composition of the coating – a larger amount of silicon oxide compounds in the coating lowers the hardness. The microhardness of the outer layer of the oxide ceramic coating was 1288 HV₁₀ and 1292 HV₁₀ for the electrolytes with KOH and NaOH, respectively, which are within the measurement errors.

The corrosion behaviours of specimens were investigated by potentiodynamic polarization tests in 3.5 wt. % NaCl solution, using an Autolab PGSTAT12 potentiostat/galvanostat with the General Purpose Electrochemical System (GPES) version 4.9 software. A three-electrode cell, with a stainless steel counter electrode and a saturated calomel reference electrode, was employed [21]. The polarization resistance of a sample was determinate at a scan rate of 1 mV/s, from 250 mV below the OCP.

How can we see reveals higher protective properties for the coatings obtained in the electrolyte containing KOH (Table 1). The Tafel plots are presented in Fig. 3.

Table 1

Corrosion characteristics of PEO layer on aluminum alloy Al5052 in KOH and NaOH base electrolytes

Alkali	Corrosion potential, V	Corrosion current density, $\mu\text{A}\cdot\text{cm}^{-2}$	Polarization resist., kOhm	Corrosion rate, $\mu\text{m}\cdot\text{year}^{-1}$
Base alloy	-1.126	15.99	0.145	230
KOH	-0.924	0.436	1.238	4.7
NaOH	-0.913	2.327	2.002	25.8

The surface and cross-section morphologies of the PEO coatings were examined by scanning electron microscopy (SEM) in a JEOL JSM-6510LV instrument with energy-dispersive X-ray spectroscopy (EDS, or EDX) – NORAN SYSTE 7. The Proza Phi-Rho-Z matrix correction algorithm was used for the quantitative analysis.

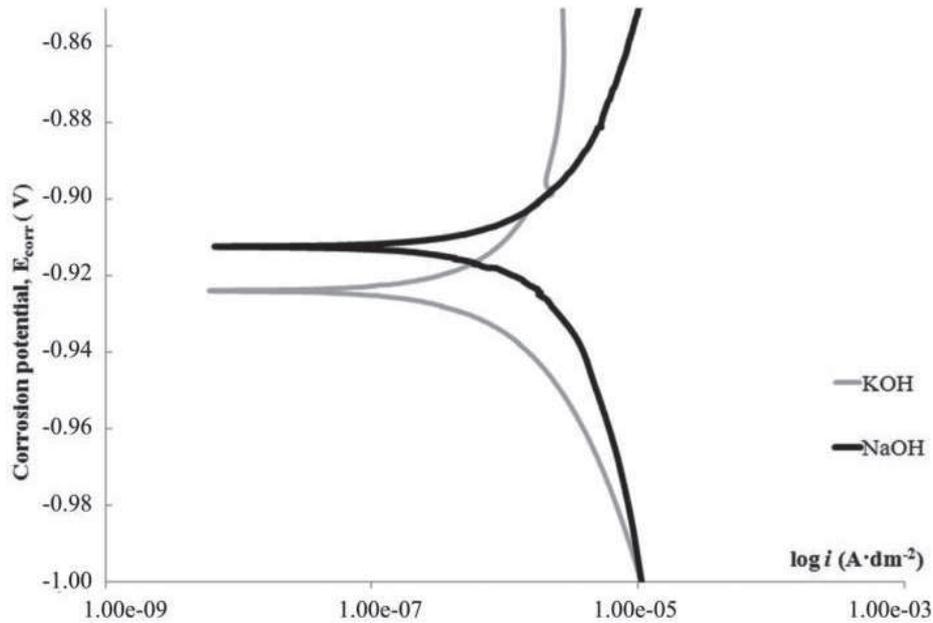


Fig. 3. Tafel plots of oxide ceramic layers obtained with KOH and NaOH in the PEO electrolyte

Photomicrographs of the cross section and surface of oxide layers, as well as data regarding their elemental chemical composition obtained by linear scanning using EDS, are presented in Fig. 4. On the figure is clearly seen that the coating consists of two sub-layers: internal and external. These layers have different microstructure, phase and chemical composition, microhardness, it is shown in the further text. The coating obtained in the electrolyte with KOH has a greater thickness and density of the oxide layer, and loose deposits of silicon-containing compounds are present on the surface of the “NaOH” coating.

On the basis of the investigations performed, the use of the electrolyte based on KOH is recommended for carrying out a plasma electrolytic oxidation process. The oxide ceramic layer obtained in this electrolyte has higher service characteristics (hardness, corrosion resistance, surface quality, etc.).

Conclusions

The choice of the alkali used in the plasma electrolytic oxidation electrolytes was substantiated. Potassium hydroxide ensures better technological properties for the oxide ceramic coating obtained.

The use of KOH (instead of NaOH) in the PEO electrolytes was substantiated. When KOH is used, the process takes place at a somewhat greater formation voltage of the oxide layer, which results in a change in the phase composition of the coating in the direction of an increase in the

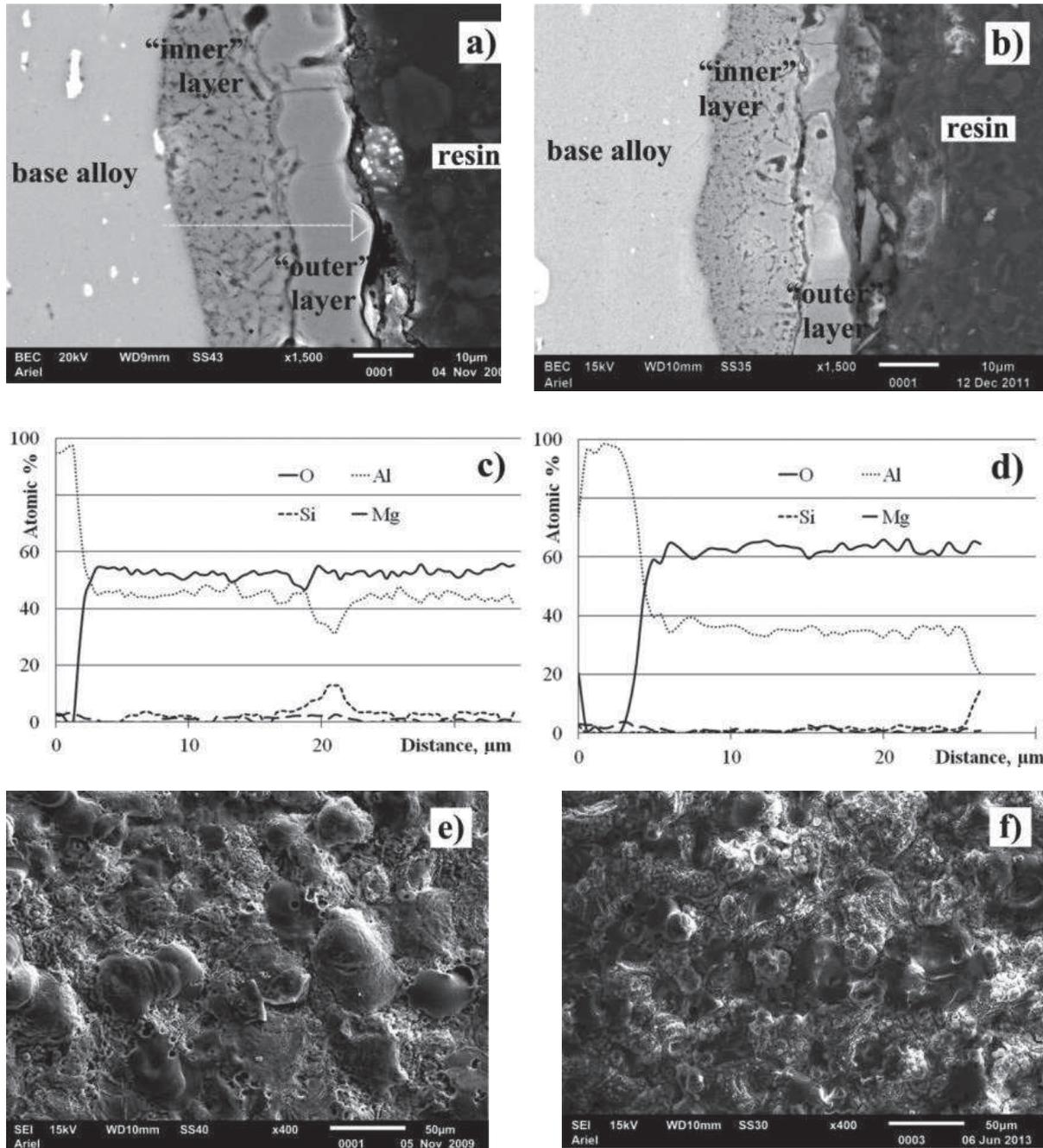


Fig. 4. Characterization of oxide layers obtained using KOH (a, c, e) and NaOH (b, d, f).
a, b – cross section of oxide ceramic layer (SEM, BEC, 1500×);
c, d – line scan of cross section (EDS);
e, f – surface of oxide ceramic layer (SEM, SEI, 400×)

content of aluminum oxides and thus in the microhardness (1570 HV_{10} as opposed to 1288 HV_{10}), as well as increases in the thickness of the coating and the corrosion resistance.

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