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INFLUENCE OF TEMPERATURE ON MECHANICAL PROPERTIES OF OXIDE FILMS USING HIGH VOLTAGE ELECTROCHEMICAL OXIDATION

The High Voltage Electrochemical Oxidation was used to produce an alumina ceramic film on aluminum alloy AMg2. The processing was carried out in oxalic acid as an electrolyte under invariable current and duration for each sample and various anodizing temperatures and current densities. The results were discussed in light of the rate of ionic current flow through the coating during anodic polarization measurements.

Keywords: *electrochemical oxidation, aluminum oxide, microhardness, roughness, electrolyte*

Introduction. Anodizing is an electrochemical process for producing stable oxide films on the surface of metals. Anodic coating can be produced on aluminum by using a wide variety of electrolytes with AC, DC or a combination of both. In order to generate an anodic film, the aluminum piece must be the anode and another suitable metal or alloy the cathode.

Anodic coatings are classified according to the solvent action of the electrolyte used to produce the anodic film. Some of them are of porous nature as for the example in phosphoric and sulphuric acid electrolytes. Others are essentially non-porous and are called «barrier layer» films and are generated in ″low solvents power″ electrolytes such as ammonium tartrate and ammonium borate [1].

Anodized aluminum products are suitable for a wild range of applications, not only in the standard field of machinery, aerospace, transport and building industry, but also for the potential use in the area of magnetic storage, photo voltaic solar cells, filters, chemical sensors, photonics and metallic nanowires [2].

Because of the high affinity of aluminum surfaces for oxygen, the metal is always covered with a highly resistant oxide film; the improvement of this natural oxide film to produce an anodic oxide film which is attractively finished, has excellent corrosion resistance and possesses other commercially desirable qualities, is the aim of the anodizing industry today.

The type of anodic oxide film that can be produced on aluminum when aluminum is the anode in an electrolytic cell depends on several factors, the most important of which is the nature of the electrolyte [3–5]. High voltage electrochemical oxidation (HVEO) was carried out in this experiment.

Material and equipment. In this work flat rectangular plates of aluminum alloy AMg2 (Al — 97 wt. %, Mg — 2,5 %, Si — 0,25 %, Fe — 0,4 %, Cu, Mn and Zn — 0,1 %) with a total area of 0,2 dm^2 were used. For carrying out the electrochemical oxidation at a high voltage an aqueous solution of oxalic acid with concentration of 40 g/l and addition of sodium silicate at concentration of 1 g/l was equally used. The electrolyte temperature was maintained at the range between 5 to 50 °C with difference of 5°C. The temperature was regulated by a refrigerator ″TBT-1″ with accuracy of ± 1 °C.

The process was carried out in galvanostatic mode with a pulsed anodic current. The operating voltage of the pulse reached 500 V. Treatment of the samples was carried out on HVEO laboratory installation (2,5 kW) [5, 6]. The schematic diagram of the installation is shown in Figure 1.

The experiments were performed in 50 different samples in different modes at 1–5 A/dm^2 current density, and duration of treatment of 20 minutes.

The micro-hardness of the sample was measured by using a PMT-3M instrument with a load of 100 g and delayed the indentation for 15 seconds as required by the standard 9450-76 to obtain the correct sizes of imprint. The roughness and surface profile were measured with the use of profilometer-profilograph 252.

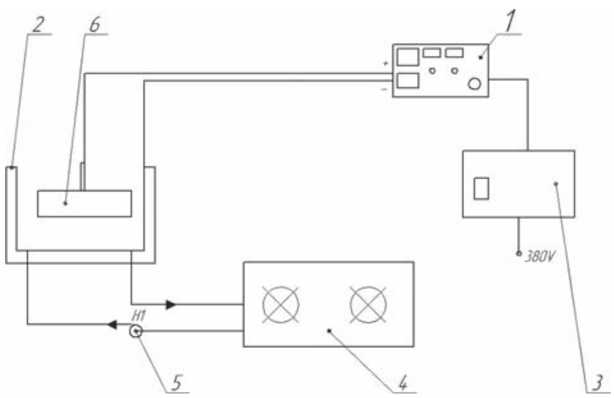

Figure 1 — The schematic diagram of HVEO installation:
1 — the control unit of power supply for the HVEO; 2 — working bath; 3 — power supply unit (current); 4 — refrigerator; 5 — pump; 6 — sample

Results and discussion. The HVEO takes place at the entire metal/oxide interface mainly by the migration of oxygen containing ions from the electrolyte. The dissolution and thinning of the oxide layer is mainly due to the hydration reactions of the formed oxide layers.

The experiment was performed in order to check the influence of temperature on the properties of oxide films. The study on the effect of HVEO thickness of oxide layers was not included in the scope of this study, their range was 10—35 mm.

The temperature influences not only on mechanical properties but also on color of the samples. It was observed (see the Figure 2) that, the lower the electrolyte temperature the darker the sample and vice versa the higher the temperature the brighter the sample surface.

The darkening that is seen on some of the samples is due to more pronounced amorphous structure, as well as an increase in film thickness. The effect of chemical etching component of the process of the oxide film is not great, and as such the diffusion of oxygen and aluminum are slowed [7].

Temperature dependence of surface roughness. Figure 3 is a graph that analysis the dependence of electrolyte temperature on roughness at 1—5 A/dm^2 current density.

When current density of 1 A/dm^2 was applied, it was observed that the film growth rate is low because the current is not enough for the electrochemical process. The low passage of current also affected etching of the sample properly. Therefore, 1 A/dm^2 current density is not proper for this process and needs to be adjusted. When using 2 and 3 A/dm^2 current densities, it was observed that the film growth rate was high and there was enough amount of current for the process. In this case the lower the electrolyte temperature the higher the roughness and the higher the temperature the lower the roughness of the sample. This is optimal parameters for mode of HVEO.

When current density is 4 or 5 A/dm^2, the current was very high and this led to breaking of the samples. This is happening because of high temperature near the surface of the sample. As current density is increased above 3 A/dm^2, the films are formed more quickly with relatively less dissolution by the electrolyte, consequently the film is harder and less porous. At a very high current density of 4 and 5 A/dm^2, there is a tendency of "burning"; this is the development of excessively high current flow at local areas with overheating at such area.

Thus, the current density of 200 to 300 A/cm^2 are optimal parameters for HVEO of the investigated AMg2 alloy samples.

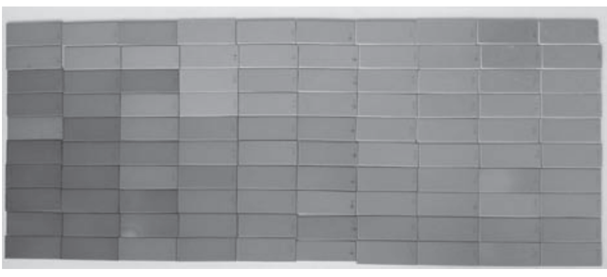

Figure 2 — Photo of the 100 samples of aluminum alloy AMg2

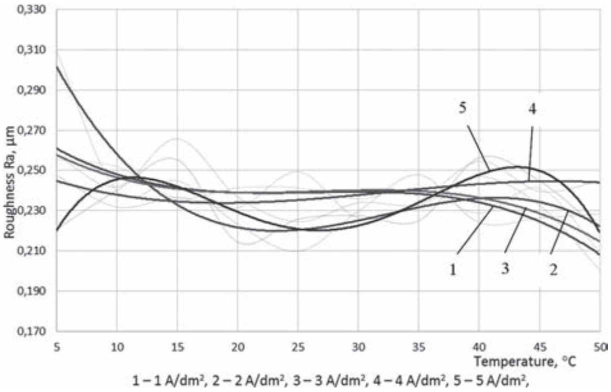

Figure 3 — Temperature dependence of surface roughness of aluminum alloy AMg2 at different current densities

Temperature dependence of aluminum alloy AMg2 surface micro-hardness. When anodizing at current densities of 1 to 8 A/dm^2 in a mixed sulphuric acid-oxalic acid electrolyte at temperatures of — 5 to + 20 °C [4], the micro-hardness and wear resistance were found to be almost constant in the temperature range of — 5 to + 5 °C, regardless of the applied current density. Furthermore, this study predicate that the value of micro-hardness gradually decreases with increasing electrolyte temperature, with the effect being more pronounced for the lower applied current densities.

This latter declaration should be handled with care because the anodizing time during this experiment process was always constant (45 min), regardless applied current density. As a result, there were formed and afterward evaluated anodic oxide films with larger film thickness, which influences the final value of micro-hardness and wear resistance [8—10].

Based on the review of published studies on the mechanical properties of anodic oxide layers, focusing particularly on the micro-hardness, we can state that there is very often an emphasis on the influence of temperature and applied current density without considering other factors.

Therefore it was observed that the lower the process temperature the higher the micro-hardness and the higher the temperature the lower the micro-hardness of the sample surface (Figure 4). This is because, when temperature are higher than 40 °C the chemical activities in the electrolyte becomes high, and the speed of oxidation becomes slower than the chemical reaction of etching of the oxide films. Therefore, for the process to be stable and to achieve the desired microhardness, temperature 5—40 °C has to be applied.

One of the advantages of HVEO over the traditional method of electrochemical oxidation is the ability to obtain more dense layers of metal oxide and an increase in the rate growth of oxide films.

It should be noted that when HVEO high voltage pulse go through the power, this feeding does not cause any micro-arcs, as in the case of micro-arc oxidation, and results in the formation of dense oxide layers with low roughness and relatively high micro-hardness.

Conclusions. The current density does not significantly influence HVEO roughness parameter *Ra* for the surface

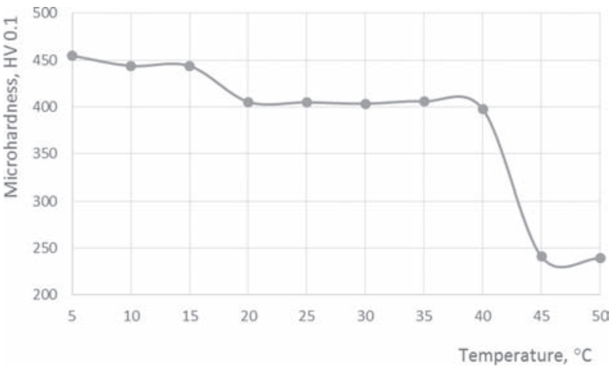

Figure 4 — Temperature dependence of micro-hardness of aluminum alloy AMg2 surface

of the oxide film. Thus, with an increase in temperature, there is a decrease of the roughness parameter reaching a minimum value (*Ra* ~ 0,22) at a current density of 1–3 A/dm^2. Subsequent increase in the *Ra* is due to the development of thermoelectric oxide film breakdown and oxidation instability modes at 4–5 A/dm^2.

The temperature effect on the micro-hardness of oxide films obtained by HVEO showed that wide operating temperature range is between 5 to 40 °C. Temperatures above 40 °C lead to a significant decrease in micro-hardness. Thus, the optimal HVEO mode is electrolyte temperature of 5 to 40 °C and current density of 1–3 A/dm^2.

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ВЛИЯНИЕ ТЕМПЕРАТУРЫ НА МЕХАНИЧЕСКИЕ СВОЙСТВА ОКСИДНЫХ ПОКРЫТИЙ, ПОЛУЧЕННЫХ ВЫСОКОВОЛЬТНЫМ ЭЛЕКТРОХИМИЧЕСКИМ ОКСИДИРОВАНИЕМ

Высоковольтное электрохимическое оксидирование применяется для обработки различных сплавов алюминия с целью получения высококачественной алюмооксидной керамики. В работе рассматривается влияние температуры электролита и плотности тока на механические свойства алюмооксидной керамики, сформированной на сплаве алюминия АМg2.

Ключевые слова: *электрохимическое оксидирование, оксид алюминия, микротвердость, параметр шероховатости, электролит*

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