Digest Journal of Nanomaterials and Biostructures Vol. 17, No. 2, April - June 2022, p. 569 - 577

Using High Voltage Electrochemical Oxidation (HVEO) to obtain protective coatings, surface finishing on electronic materials

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Electronics and microelectronic components such as printed circuit board, capacitors, CPU heat sinks, hard drive, etc. commonly encounter harsh environmental conditions during their operational lifetime. To protect the electronics materials from conditions like corrosion, wear, humidity and contaminants, aluminium protective coating materials can be used. However, the behavior of materials in harsh environments and their effect on the reliability of electronics in industrial products has been studied only very little. Moreover, the changes in the parameters (current density, temperature and time) of commonly used aluminium under various conditions remain largely unknown. In this paper, High Voltage Electrochemical Oxidation (HVEO) was used to produce a high microhardness of 440HV and high surface thickness of up to 44μm oxide coatings on aluminum alloy AMg2 (analogues of 5052-H32 alloy) for electronic components protection. The process was carried out in electrolyte of tartaric acid and sulfuric acid as an electrolyte under constant duration for each sample and various anodizing temperatures and current densities. The samples used in the study were aluminum used for commercial electronics devices designed for use in harsh conditions.

(Received January 24, 2022; Accepted May 3, 2022)

Keywords: Electronic materials, Aluminum, High-voltage electrochemical oxidation, Protective coatings, Electrolyte

1. Introduction

Electronics industry is one of the fastest growing industries with seemingly inexhaustible possibilities of new applications. Printed circuit boards (PCB), capacitors, CPU heat sinks, hard drive and many more find use in applications for the home, automotive, telecommunications, military, aerospace, and especially in recent years for wearable electronics.To ensure the reliability of equipment it is necessary to ensure the protection of these electronic components and to prevent operability reduction or worse case complete destruction of device. From the perspective of the manufacturer, costs of product failures, costs for achieving required reliability and costs of competitiveness for the provision of guarantees are essential. Wide range of electronic application means many different environmental influences which can cause deterioration of electrical properties, for example due to absorption of atmospheric moisture, electrostatic attraction of dust or mechanical stresses in the form of shock, abrasion and vibration.Printed Circuit Boards (PCBs) are the heart of the communication and electronics industry [1]. The on-going miniaturization, increasing complexity, and use of PCBs in all kinds of environments are making them much more sensitive to corrosion. The copper tracks used in PCBs are highly susceptible to humidity and contamination: exposure to humidity can lead to corrosion of printed circuit boards and subsequent failure of the electronic devices and even a small amount of contamination on the PCB can result in the physical breakdown of a device [2–4]. Contamination, continuous exposure to humidity and condensation result in the formation of a thin electrolyte layer on the surface of PCBs that connects the adversely biased tracks on PCBs.Presence of an electric field in the surrounding

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https://doi.org/10.15251/DJNB.2022.172.569

causes the migration of dissolved ions on the anode toward the negatively biased electrode (cathode) and this phenomenon is called electrochemical migration [3–5].Finding solutions for protecting printed circuit boards is crucial. Several surface-finishing methods have been introduced on an industrial scale, such as covering the tracks using Electroless Nickel immersion gold (ENIG), Organic Solderability Preservatives (OSP), and immersion silver (ImAg). However, most of these methods have some complications, such as the difficulty of the process due to the daily increase of complexity and sensitivity of the integratedcircuits, the presence of surface defects, or a short lifetime [6–8].Despite a large number of studies in this area, only a few works have been reported regarding the application of protective polymer films in electronics [9, 10]. Various plasma deposition methods are adapted to apply a conformal plasma-polymer layer on different materials. Plasma treatment or plasma polymerization is a very versatile surface treatment technique. It allows modification of a substrate's surface without affecting the bulk properties. Plasma treatment is gaining a great deal of interest due to the miniaturization of items (e.g. electronics) in industries which requires surface modification without affecting the functionality of these items. Plasma polymerization process allows deposition of thin organic coatings from several angstroms up to several microns. The possibility of using a wide range of gasses or their combinations enables full customization resulting in unique surface properties needed for different applications. In this study, the effect of protective coatings on electronic materials was studied using high voltage electrochemical oxidation. The influence of anodizing current density and temperature on highly anodic alumina with adjustable characteristics was investigated and obtained using the high voltage electrochemical oxidation (HVEO) method. The material used in the study wasaluminum alloy AMg2 (analogues of 5052-H32 alloy). In addition to the reliabilityof the devices tested, material parameter changes during testing were also studied.

2. Material and experimental methods

Aluminum alloy AMg2 (analogues of 5052-H32 alloy) was used as an experimental anode material. Specimens with areas of 0.5dm^2 and 0.2 dm^2 were cut from sheet material 1.8 mm thick and used for tests. The initial hardness of AMg2 alloy was 72HV and roughness of Ra=0.446 μm. Before subjecting the aluminum to anodizing, it went through the preliminary stages of surface treatment. The quality of the pretreatment largely determines the future properties of the anodic coating. Chemical preparation of aluminum parts includes the following operations: degreasing, etching, and bleaching. The quality of cleaning the surface of products is determined equally by three factors: the composition of the solution, temperature and processing time. This means that when switching to low-temperature degreasing and etching, it is necessary to increase the intensity of these three factors, i.e. enhance the effectiveness of the solution, for example, by introducing a strong surfactant into the solution, increasing the mechanical effect and the duration of the process. Washing of the aluminum parts after chemical preparation is an essential role in surface preparation. Insufficient rinsing can lead to defective coatings.Flat rectangular plates made of aluminum alloy (A5052) with a total area of 1 dm^2 were used as samples. The first stage of preparation is degreasing in an aqueous solution of trisodium phosphate and sodium carbonate at a component concentration of 4% and a process temperature of 50-60 °C. Etching was carried out in an aqueous 10% sodium hydroxide solution at a temperature of 15-25 ° C for 10 minutes. Subsequent clarification was carried out in a 40 wt% nitric acid solution for 30-40 seconds, with final washing in cold running water. For carrying out HVEO process, an aqueous solution of tartaric acid ($C_4H_6O_6$) with concentration of 80 g/l and addition of sulfuric acid (H_2SO_4) at concentration of 40 g/l were used. The electrolyte temperature was maintained at the range between 5 to 20 °C with difference of 5°C. The temperature was regulated by a refrigerator "TBT–1" with accuracy of ±0.5^{o}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) [11]. The optical microscopic measurement is the best exact method for measuring the thickness of coating, it is time consuming but more correct results are obtained. The microhardness of the sample was measured by using an AFFRI MVDM-8 instrument with a load of 25g and delayed the indentation for 11 secs. Microhardness measurements were made in two ways on the ceramic layer formed: 1. after a slight polishing on the surface subjected to HVEO, and loading the indenter in a direction normal to the interface of oxide - AMg2 alloy substrate, 2. in the direction along the interface - after the preparation of transverse section. The surface morphology of samples prior to HVEO and after treatment was investigatedwith the use of a Surtronic 25 (TaylorHobson) profiler/profilometer and an SEM 515 scanningelectron microscope. DRON 3 was used for X-ray diffraction analysis [11].

3. Results and discussion

One of the advantages of HVEO over the traditional hard anodizing 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. The experiments were performed in order to check the influence of electrolytetemperature and current density on the thickness and properties of oxide films. 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 temperature and current density influences not only on mechanical properties but also on color of the surface samples. It was observed (see the Fig2) that, the lower the electrolyte temperature the darker the surface layer. But in temperature 5 °C there wasn't much change in the color of the samples because the chemical activities were low thus, affecting only the roughness of the samples.

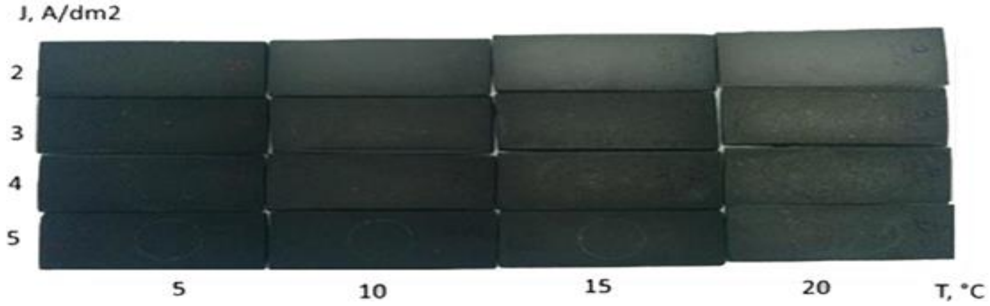

Fig.1. Photo of the 16 oxidizedsamples of aluminum alloy AMg2 obtained in different electrolyte temperature T and current density J.

The darkening that is seen (Fig. 1) on some of the samples is due to as an increase in coatings thickness. The effect of chemical etching component of the process of the oxide coating is not great, and as such, the diffusion of oxygen and aluminum are slowed [11].

3.1. Current density dependence of oxide coating thickness

Figure 2 above shows photographs that allow you to visually trace the change in the thickness of the oxide film depending on the processing current density.

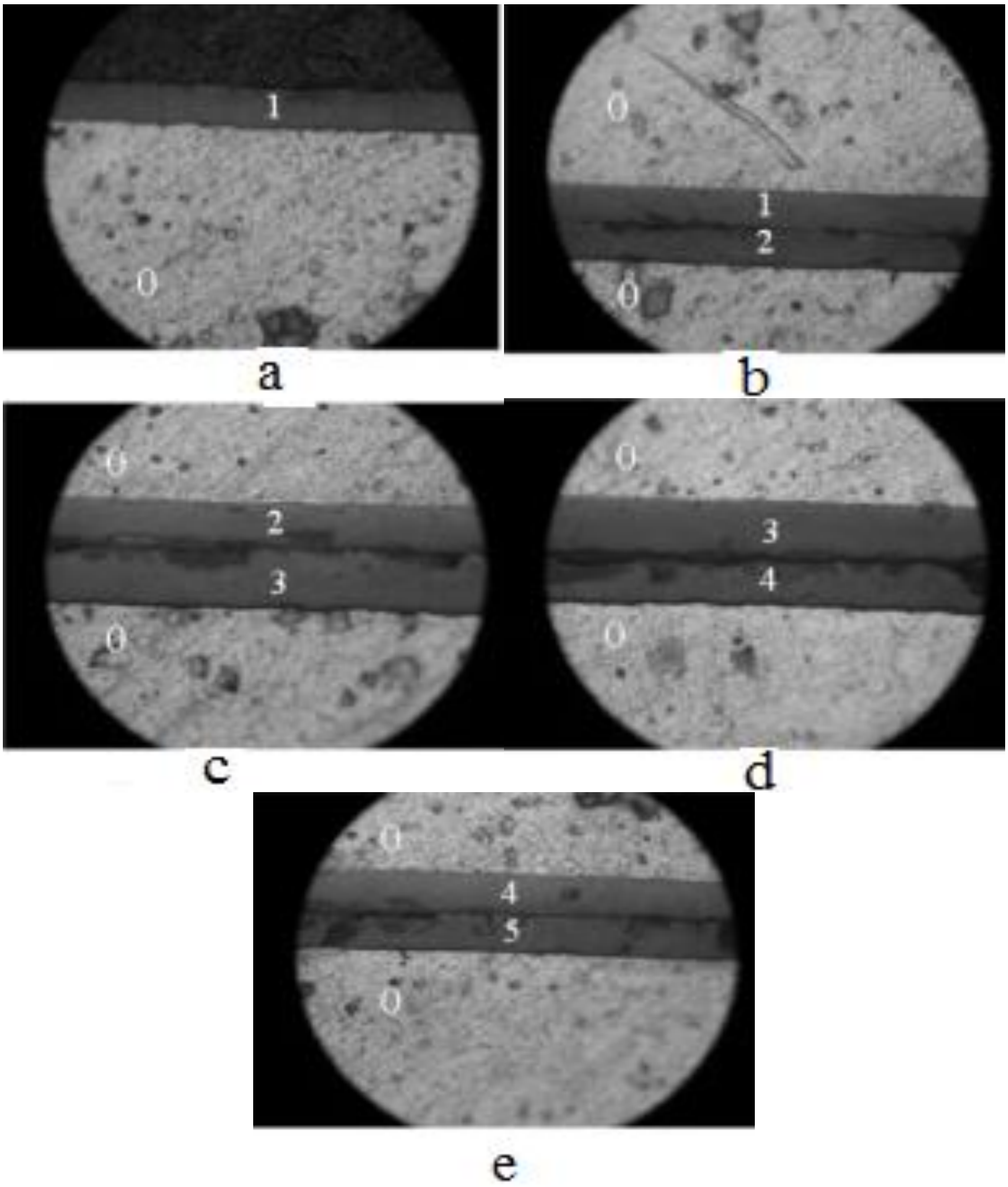

Fig. 2. Thickness of the oxide filma - current density 1 A / dm^2, b - current density 1 and 2 A / dm^2, c - current density 2 and 3 A / dm^2, d - current density 3 and 4 A / dm^2, e - current density 4 and 5 A / dm^2.1, 2, 3, 4, 5 - oxide film; O - metal base.

Numerical evaluation of the film thickness, carried out metallographically, showed that at a current density of 1 A / dm2, the film thickness is ~ 37 microns (Figure 2 a). As the current density increases, the film thickness increases to 39 microns and 44 microns at a current density of 2 A / dm^2 and 3 A / dm^2, respectively (Figure 2 b, c). A further increase in the current density leads to a decrease in the thickness of the oxide film to 40 µm and 38 µm (Figure 2 d, e).A graphic illustration of the resulting dependence is shown in Figure 3.

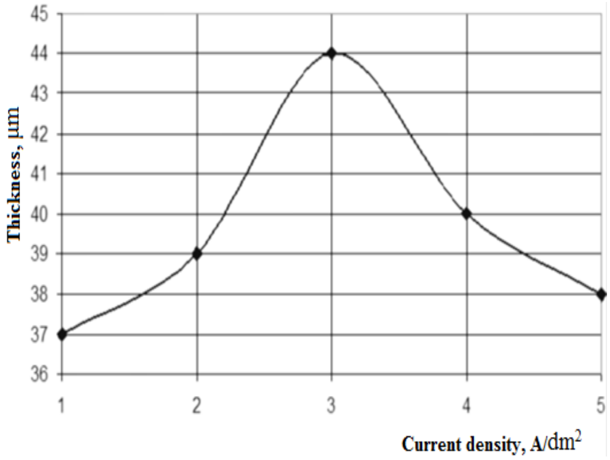

Fig. 3. Dependence of the thickness of the oxide film on the current density of high-voltage electrochemical oxidation.

The film thickness increases in proportion to the current density, reaching a maximum value at a current density of 3 A / dm^2. The subsequent drop in the curve is explained by an increase in temperature at the electrolyte-oxide layer interface and by the chemical activity of the electrolyte. The rate of etching of aluminum oxide by the etching component of the electrolyte increases - the thickness of the oxide film decreases. The general regularity of the dependence of the hardness of the oxide layer on the working current density is that the growth rate of the oxide layer linearly depends on the current density. The higher the current density, the higher the growth rate. In this case, more energy is released with local heating of the surface layers. With an increase in temperature near the interface, the chemical activity of the electrolyte increases, the rate of etching of aluminum oxide by the etching component - oxalic acid, increases. As a result, the number of pores and their diameter increase [11].The main defect in alumina ceramic films obtained by high-voltage electrochemical oxidation is the formation of uncontrolled micro-discharges, called burn-through spots. The number of defects formed depends on the current density and the quality of the starting material. The presence of burrs, high roughness and defectiveness of the surface of the base material increases the risk of burn-through during the formation of films of alumina ceramics.An increase in the surface quality of the base material can be achieved by using the technology of electrolytic-plasma treatment for preliminary preparation of aluminum samples instead of chemical treatment. Advantages of electrolytic-plasma processing - high speed of the process, reduction of the roughness parameter Ra of the processed material, removal of material surface defects. The electrolytic-plasma treatment of aluminum samples was carried out in an electrolyte with a concentration of oxalic acid electrolyte components and chlorine ions up to 3 wt%. Electrolyte temperature 60-90 °C, process voltage 260-300V. The processing time is 1-3 minutes. After electrolytic-plasma treatment, aluminum samples were washed in running water, followed by transfer to an electrolytic bath for high-voltage electrochemical oxidation.

3.2. Temperature and current density dependence of oxide coating microhardness

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 [12], the microhardness 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 microhardness 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 of the applied current density. As a result, there were formed and afterward–evaluated anodic oxide coatings with larger coating thickness, which influences the final value of microhardness and wear resistance [13–15].Based on the review of published studies on the mechanical properties of anodic oxide layers, focusing particularly on the microhardness, 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 microhardness and the higher the temperature the lower the micro–hardness of the sample surface (Fig. 4). This article presents the results of measurements of coatings microhardness, which were carried out in line of the `coating-substrate` interface after the preparation of transverse section.

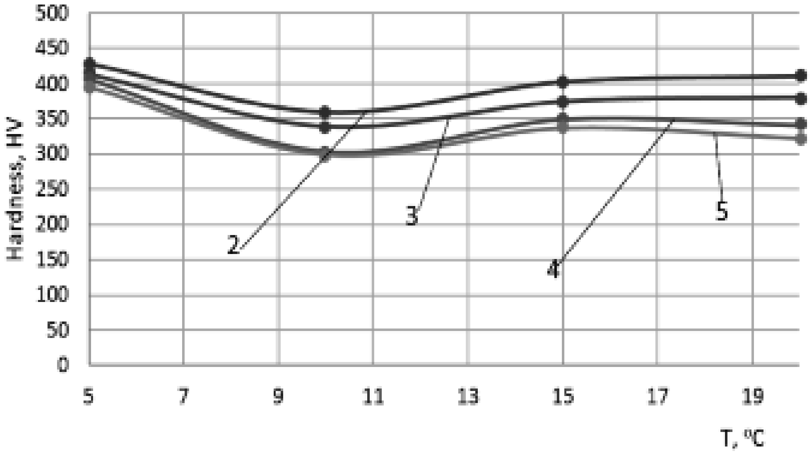

Fig. 4. Temperature dependence of oxide layer microhardness on aluminum alloy AMg2 at different current densities: curve 2 – 2 A/dm^2, 3 – 3 A/dm^2, 4 – 4 A/dm^2, 5 – 5 A/dm^2.

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 microhardness.Fig. 5 presents the relationship between the microhardnessof the oxide layer and the anodic current density. As can be seen, high microhardness values of the oxide layer were obtained at low temperatures. Highestvalues of the microhardness were obtained at low temperatures and current densities of about 2 A/dm^2. The microhardness of oxide layers slightly decreased with increasing current density.

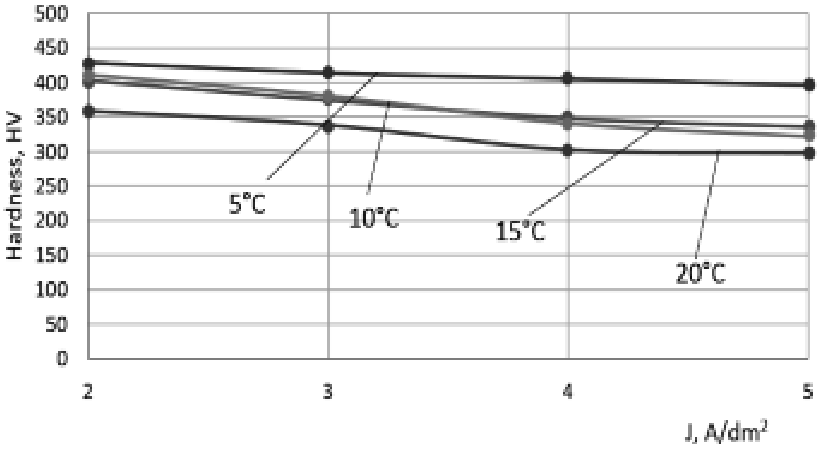

Fig. 5. Current density dependence of oxide layer microhardness on aluminum alloy AMg2 at different temperatures.

3.3. Temperature and current density dependence of surface roughness

Fig.6 is a graph that analysis the dependence of roughness on electrolyte temperature at 2–5 A/dm^{2}current density. The initial average roughness of all samples was Ra = 0.446 µm. When current density of 2 A/dm^{2}was applied, it was observed that the surface roughness increased at 5 and 10 °C and decreased at 15 °C but went up at 20 °C. This was due to the film growth rate that is low, the low passage of current also affected etching of the sample properly [11].When using 3, 4 and 5 A/dm^{2}current densities, it was observed that the coating growth rate was high and there was enough amount of current for the process. In this case, the lower the electrolyte temperature the lower the roughness and the higher the electrolyte temperature the higher the roughness of the sample.

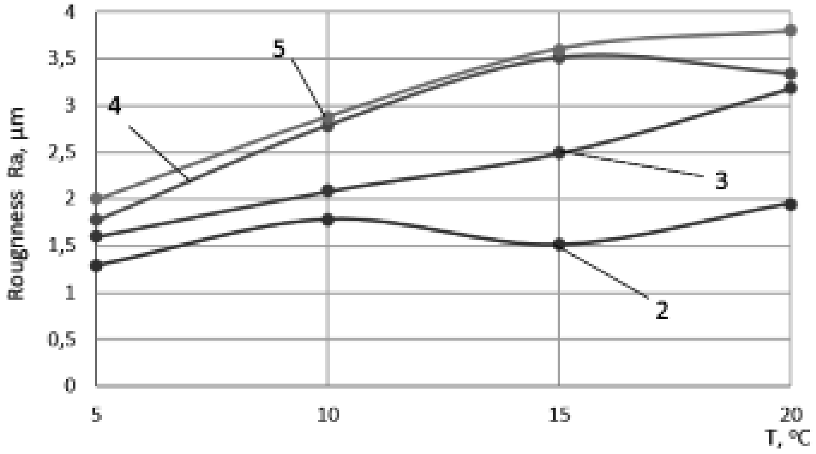

Fig.6. Temperature dependence of oxide layer surface roughness on AMg2 alloy at different current densities: curve 2 – 2 A/dm^2, 3 – 3 A/dm^2, 4 – 4 A/dm^2, 5–5 A/dm^2.

When current density is 4 or 5 A/dm^2, the current was very high and this led to very high surface roughness. This is happening because of high temperature near the surface of the sample. As current density is increased above 3 A/dm^2, the coatings are formed more quickly with relatively less dissolution by the electrolyte, consequently the coating is harder. 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. Fig. 7 presents the relationship between the roughnessof surface layer and the anodic current density.

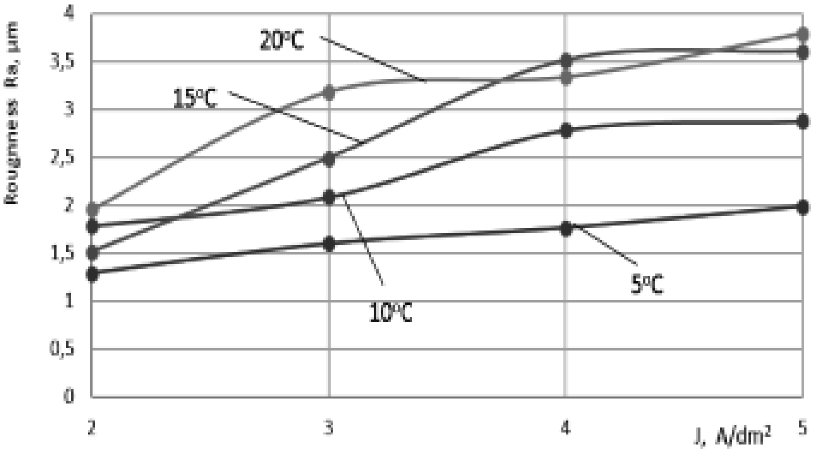

Fig. 7. Current density dependence of surface roughness of oxide layer on aluminum alloy AMg2 at different temperatures.

As can be seen, high roughness values of the surface layer were obtained at higher temperatures. The lowest surface roughnessvalues were all obtained at 2 A/dm^2, while the highest surface roughness was obtained at 5 A/dm^2. The roughness of surface layers increases with increasing current density.The surface roughness of the sample increases with an increase in current density because the coatings growth is faster due to the excessive high current flow at local areas with overheating at such areas.

4. Conclusions

This work was able to replace multi-stage, labor-intensive preparatory operations for protective materials in electronic devices using high-voltage electrochemical oxidation, as applied to the manufacture of printed circuit boards and other electronic devices.In this study the reliability of commercial electronics devices with protective coatings materials was studied using high voltage electrochemical oxidation. Overall, three combinations of protective parameters were compared. This paper highlights the importance of the influence of electrolyte temperature and current density on the structure and mechanical properties of coated materials for electronics devices. The film thickness increases in proportion to the current density, reaching a maximum value at a current density of 3 A / dm^2.

The influence of the temperature of the oxidation process in the studied range of 5 to 20 °C shows that the ceramic layer thickness is much less noticeable. The surface roughness of the samples after HVEO process increases with an increase in temperature of the electrolyte and the current density from the initial average value Ra = 0.446 μm to 1.25- 2 μm (at a current density of 2 A / dm^2) and to 2 – 3.79 μm (at 5 A/dm^2). However, lower temperatures of the process dramatically increase less surface roughness. Significant growth roughness for thick coatings were due to more pronounced uneven formation of the individual elements of the columnar structure of coating. The microhardness of the ceramic layer does not experience significant changes by varying the oxidation regimes, it is maximal (400–430 HV) at electrolyte temperature of 5 °C. Carrying out the process with an increase in temperature reduces the microhardness at all current densities.

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