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Investigating the Porous Coating Produced on 6061 Aluminum Alloy in Sulfuric Acid Electrolyte at Different Temperatures

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Abstract

In this research, the effect of sulfuric acid electrolyte temperature on the surface properties of anodizing coating of 6061 aluminum alloy is investigated. For this purpose, anodizing was done in sulfuric acid environment and 4 different temperatures (-5°C, 5°C, 15°C and 25°C) on 6061 aluminum alloy. Characterization the structure and chemical composition of the coatings by the use of low-angle X-ray diffraction (GIXRD) and Energy-dispersive X-ray spectroscopy (EDS) results showed that the coatings have a non-crystalline structure with aluminum hydroxide as a result of atmospheric hydration of the anodized samples. The results of roughness measurement and Scanning electron microscope (SEM) images indicated that the porosity increased due to the higher corrosive power of sulfuric acid at higher temperatures. Examining the changes of anodizing flow over time determined that higher temperatures of the anodizing solution causes an increase in the anodizing flow and the dissolution rate of the coating. For this reason, the thickness and hardness of the samples, which have a direct relationship with the rate of dissolution and flow, decreased significantly with increasing temperature.

Keywords: aluminum alloy, temperature, anodizing, hardness, porosity.

1. Introduction

Various coatings are applied to aluminum parts with the aim of improving wear and tribological behavior through different methods, one of the best and most widely used of which is anodizing. This method is very popular due to its ease, reasonable cost and controllability of the process. Anodizing is a type of controlled corrosion process that can be used to create a sticky coating with suitable corrosion and wear properties on aluminum. This coating, which is oxide in nature, is porous, and it has been proven that the type of these pores, or in other words, the arrangement of holes in the oxide layer, will definitely affect the tribological behavior of the coating. However, the type of effect (direct or inverse) of this parameter is not constant due to the fact that the porosity of the coating is different in every acid solution in each voltage range. Therefore, considering the importance of the process, how the microstructure, holes and surface properties of this porous layer changes with process parameters such as electrolyte temperature is always an interesting subject for study. The effect temperature on the microstructure and properties of the oxide coating depends on the temperature ranges and acidic environment for the alloys, but the issue that has been pointed out in all the studies is the increase in the dissolution power of the anodizing electrolyte due to the increase in the process temperature [1]. This increase shows its effect on the porosity of the coating and finally the surface properties such as tribological properties of the oxide layer significantly [2]. In the study of the effect of temperature (in the range of 5 to 25 °C) and anodizing flow on the hardness of the anodizing coating produced on 1050 and 5754 alloys in an environment containing sulfuric acid by Gazmil et al., microhardness values for both alloys with increasing flow and decreasing anodizing temperature, increased, which was due to the compaction of the coating at low temperatures [3]. Also, the results of the study of the effect of sulfuric acid electrolyte temperature (in the range of 5 to 55 degrees Celsius) on the anodizing of 1050 aluminum alloy by Artes et al indicate that the diameter of the holes in the bottom and middle of the layer is constant and the diameter of the holes in the coating surface increases and as a result the hardness decreases due to the higher acid electrolyte temperature effect. [4]. In Niazbakhsh et al.'s study on the effect of anodizing temperature of 7075 alloy in oxalic acid-sulfuric acid mixture solution, the thickness and hardness decreased with increasing temperature in the temperature range of -5 to 5 degrees Celsius. They introduced the most important factor affecting the mechanical properties of the coating as the porosity of the produced oxide layers [5]. In general, it seems that the effect of the temperature of the anodizing process on the amount of and how the current changes during anodizing at constant voltage is very important. In fact, it is the effect of temperature on the current that determines the properties of the produced oxide coating.

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According to the mentioned materials, in this research, it is tried to evaluate how the temperature of the electrolyte in the environment of sulfuric acid affects the surface properties of the coating, including its morphology and hardness.

2. Materials and Methods

In this research, 6061 aluminum alloy was used with the chemical composition reported in Table 1. The solution used as an acidic electrolyte in the anodizing process was 165 g/l sulfuric acid, which is the most common industrial solution in industries and articles. The desired temperatures for anodizing the samples were considered to be -5, 5, 15 and 25°C, respectively. Anodizing was conducted for 60 minutes at a constant voltage of 35 V for all samples, and current changes during anodizing were recorded manually. Evaluation of the phases was done with use of low angle X-ray diffraction (GIXRD), chemical of the coatings was investigated with help of the Energy Dispersive Spectroscopy (EDS), and surface morphology of coatings was studied with Scanning electron microscope (SEM) images. Roughness of coatings was checked with help of Mitotoyo roughness meter and also thickness of coatings was analyzed with help of portable eddy current thickness gauge.

Table. 1. Chemical analysis of the 6061 aluminum alloy substrate used in the research in terms of weight percentage.

Cu	Si	Mn	Mg	Zn	Cr
0.190	0.510	0.120	1.60	0.210	0.160

3. Results and Discussion

Fig. 1 shows changes in anodizing current density at different temperatures. For more detailed analysis, initial holding times due to effective changes are displayed in this diagram. As it is clear, in all three temperatures, the trend of current changes during the anodizing process is same. In all samples, the current decreases at the beginning and the first seconds, which is due to the formation of a non-porous barrier layer that has a high electrical resistance. Then, by creating openings and grooves in this layer, the porous structure begins to form. In the future, these grooves grow by turning into holes, and finally, the growth occurs in the stable state of alumina oxide holes. In fact, it can be said that by carefully controlling the coating conditions, no more current changes are observed when reaching a stable current, and the growth of the oxide coating takes place at a certain rate [6, 7]. In Fig. 1, the diagram of each sample can be divided into 4 parts (for example, this division is done on the diagram related to anodized at 25 °C, and the rest of the samples are also divided into separate sections in the current-time density diagram). The most important parameter in the current-time density diagrams of anodizing aluminum and its alloys is the state current density (i_S). As it is known, as the temperature of the sulfuric acid solution used in the research has increased, this value has also increased, which indicates an increase in the rate of dissolution and electrochemical reactions of anodizing at the surface of the solution/oxide as well as the oxide/substrate. This issue can have a direct effect on the surface properties of the coating, such as the morphology, hardness and thickness of the oxide coating obtained at different temperatures, which will be investigated further. Also, with the increase in the temperature of the solution, the time to reach the state current is less, which is related to the increase in the acid strength of the electrolyte solution.

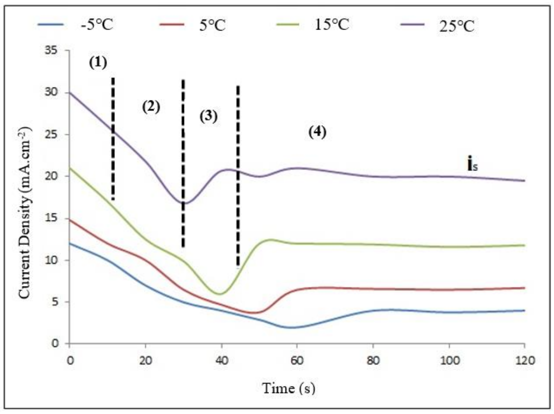

Fig. 1. The diagram of changes of anodizing current density -time for different samples.

The type of crystal structure of the anodized coating can affect the tribological properties of the coating due to its oxide and porosity. Fig. 2 shows the diffraction pattern obtained from the greasing test. The wide hill observed at angles of 20-30 degrees indicates the amorphous structure of the anodizing coating. The observed sharp peaks are related to aluminum, which due to the amorphous and porous nature of the coating, it can be said that these peaks are related to the aluminum substrate, because according to the reactions during the anodizing process, there is no separate presence of aluminum in the coating. This issue, i.e. the presence of the aluminum peak and the amorphous structure observed in the diffraction pattern, has also been mentioned in the studies of other researchers. Another point is the observation of very weak peaks of aluminum hydroxide, which is due to the atmospheric hydration of the anodized samples, which was also mentioned in the research conducted by Chadhuri et al. [7]. It should be noted that the crystal structure of the rest of the samples was similar to the anodized sample at -5°C.

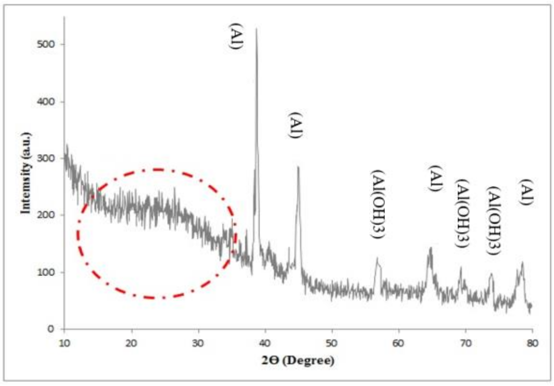

Fig. 2. X-ray diffraction pattern of anodized sample at -5°C.

The evaluation and analysis of the chemical composition of anodized coatings was done with the help of EDS analysis, and the results of this test for different samples are shown in Fig. 3. As can be seen, all coatings have an oxide nature of aluminum oxide. The presence of magnesium in the results of this analysis indicates the dissolution of the substrate and the placement of very small amounts of this element in the coating during the anodizing process, which is in agreement with other studies [8, 9]. The presence of sulfur is also due to the sulfuric acid solution used in the process. An important point that can be found in the comparison of the analysis results of anodized samples is the increase in the amount of sulfur in the coating as the temperature of the process increases. This issue shows the increase in the dissolution power of sulfuric acid solution and more penetration inside the structure, which is in line with the diagram of changes in current density during anodizing time (Fig. 1), because as the anodizing temperature increases, more current passes through the samples and this means that the dissolution rate is higher.

The scanning electron microscope images prepared from the surface of the coatings are shown in Fig. 4. Increasing the temperature and consequently the anodizing flow leads to an increase in exothermic reactions during the coating process, which can have a significant effect on the porosity of the coating. This issue can be fully proven according to Fig. 4, and the lowest and highest porosity is related to the coating obtained from anodizing at temperatures of -5 and 25 degrees Celsius, respectively. In fact, it can be said that at higher temperatures, due to the higher dissolution of the oxide coating, the rate of joining holes and porosity increases, which leads to higher porosity of the final coating at higher anodizing temperatures. In other words, it can be said that as the temperature increases, the non-uniformity of the porosity of the anodized coating increases (in some areas, large and connected and in some areas there is small porosity). Another point is the characteristic of the cellular microstructure of the coatings, which is shown in the scanning electron microscope images prepared at higher magnifications (Fig. 5) for example for the anodized sample at -5°C, , and is completely recognizable.

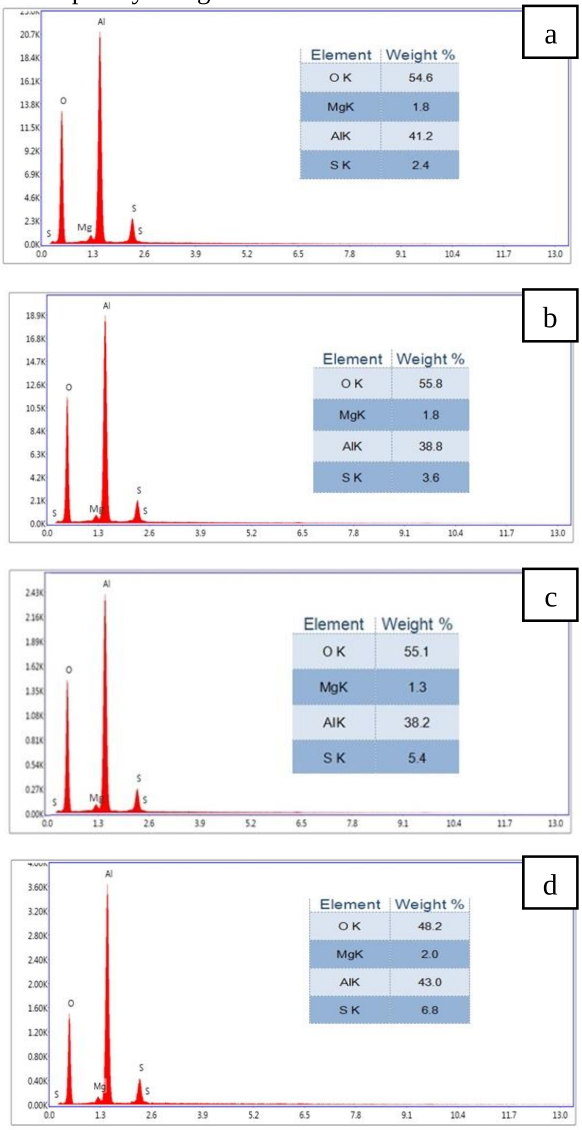

Fig. 3. The results of EDS analysis of the surface of the anodized samples at temperatures of a) -5°C, b) 5°C, c) 15°C and d) 25°C.

The images of the surface roughness of the coatings at different temperatures can be seen in Fig. 6, which shows that the roughness increases by increasing the temperature of the solution, because the pores have become bigger and somehow the heights detected by the tip of the roughness meter have increased. This is in agreement with the evidence obtained from the scanning electron microscope images.

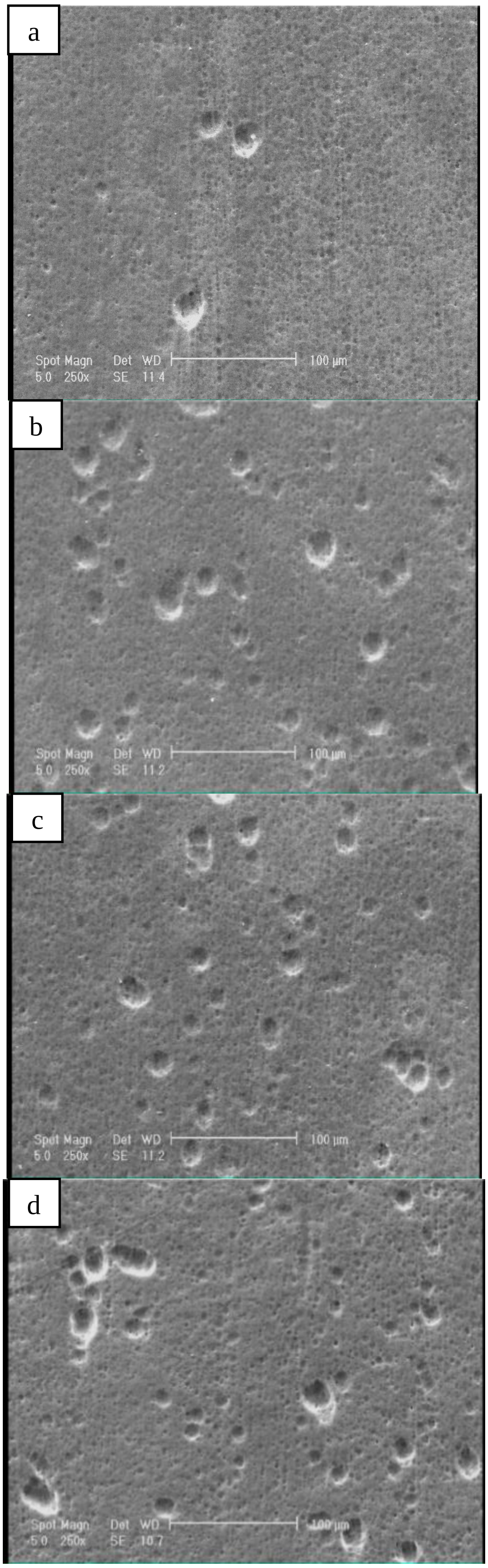

Fig. 4. SEM images of the surfaces of anodized samples at temperatures of a) -5°C, b) 5°C, c) 15°C and d) 25°C.

The changes in the thickness of the samples during the anodizing time are shown in Fig, 7-a. The thickness of the samples was measured by a portable thickness gauge. As it is known, the longer the anodizing time, regardless of the temperature at which the samples are anodized, the thickness of the coating increases, which indicates the continuation of the dissolution reactions and the formation of the oxide layer during the process at all temperatures. The hardness of the samples changes (Fig. 8.a) during the process and the microhardness of the samples increased with the thickness of the coatings, which shows the effect of the thickness on the hardness of the coating. It should be noted that anodizing for more than 1 hour reduces the hardness of the anodizing coatings due to the joining and enlargement of the pores [9-11] for this reason, the time used for anodizing in this research is 1 hr. The effect of temperature on the thickness and micro hardness is also shown in Fig. 7-b and 8-b, which shows that both of these parameters decrease due to the increase in the dissolution rate and the significant increase in the porosity of the coating, and if it is possible to lower the temperatures of the anodizing solution which is difficult due to the exothermic nature of the anodizing reactions, a hard coating can be achieved.

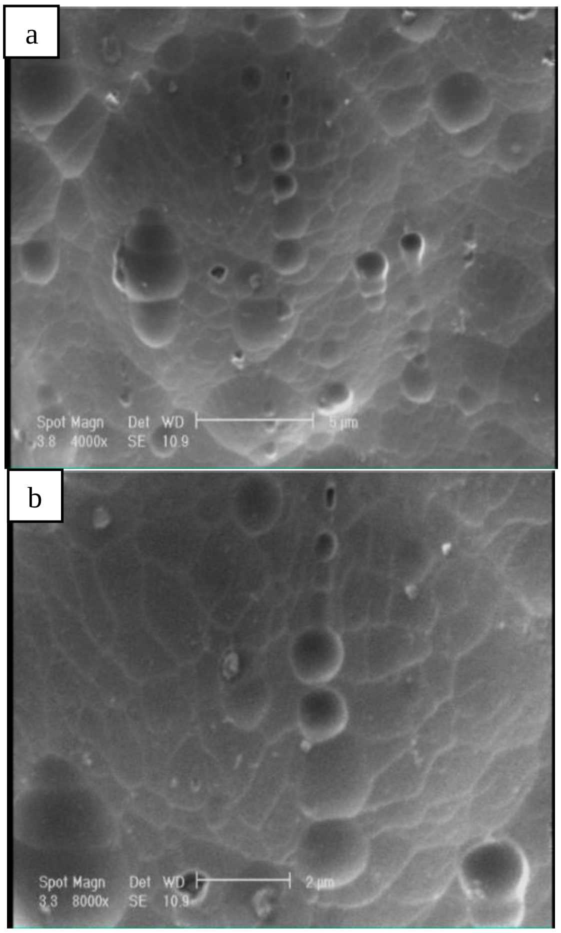

Fig. 5. SEM images with a) X4000 and b) X8000 magnification and cellular structure of the oxide coating of anodized sample at -5°C.

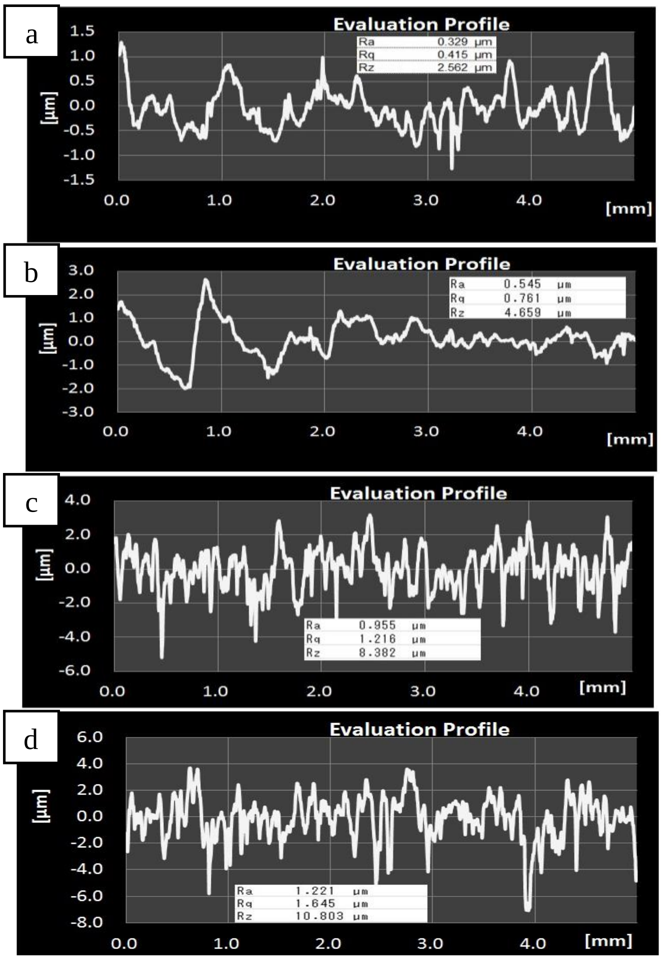

Fig. 6. Surface roughness of anodized coatings at temperatures of a) -5°C, b) 5°C, c) 15°C and d) 25°C.

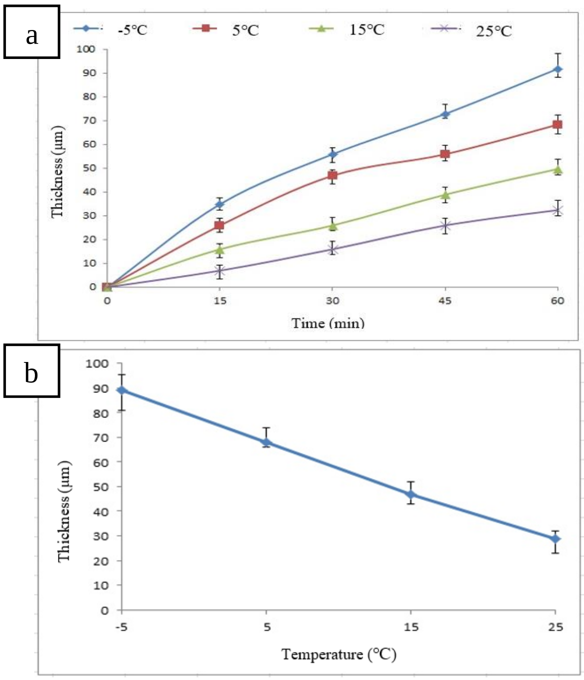

Fig. 7. Changes in the thickness of coatings a) based on anodizing time and b) based on changing the temperature of sulfuric acid solution.

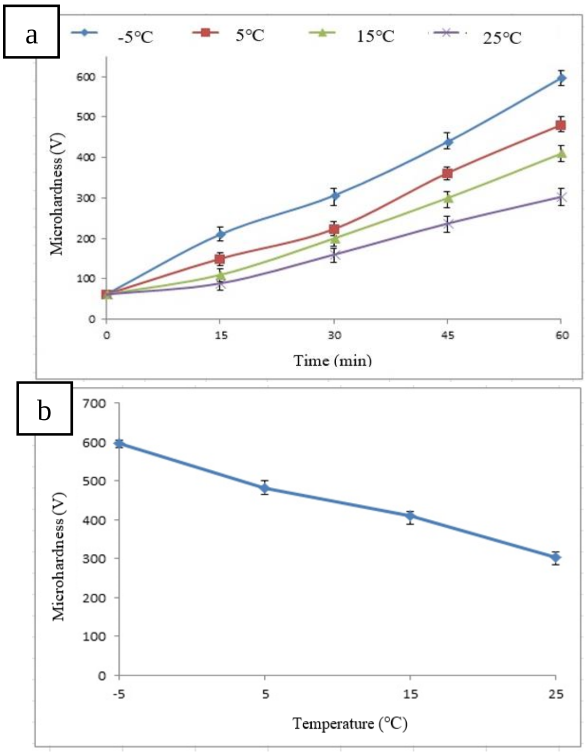

Fig. 8. Changes in microhardness of coatings a) based on anodizing time and b) based on changing the temperature of sulfuric acid solution.

4. Conclusion

1. Current changes during anodizing showed that the higher the temperature of the used solution, the higher the current will increase for the steady state.
2. As the temperature of the solution increases, the porosity of the coating increases due to the increase in the dissolution rate of the coating because of the increase in the acid strength of the sulfuric acid electrolyte.
3. Produced coatings are oxide and non-crystalline (amorphous). Also, the presence of sulfur in the coating increases with the increase in the temperature of the electrolyte solution due to the increase in the corrosive power of the acid solution.
4. The roughness of the coatings has increased with the increase in the temperature of the electrolyte, which is due to the connection and enlargement of the pores with the increase in the acid strength of the electrolyte. While the hardness and thickness of the oxide coating has an inverse relationship with the temperature of the electrolyte.

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