

MICRO-ARC OXIDATION PROCESS IN DIFFERENT ENVIRONMENTAL FRIENDLY ELECTROLYTES

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Abstract: Micro-arc oxidation is an environmental friendly process able to complete the electrolytic aluminium surface treatments by offering a new range of properties. By supplying the workpieces with a high amplitude alternative current, we cause the breakdown of the dielectric coating formed on the surface at the beginning of the process. This results in the creation of sparks on the whole surface, which allows the oxidation process to continue. Thanks to a specific AC power supply (Ceratron process [4]), films are elaborated which exhibit a wide range of interesting characteristics, such as good mechanical properties or a high corrosion resistance. Moreover, the treatment is achieved in different environmental friendly electrolytes, without any further surface etching and coating sealing process.

In this communication, we present the first results of the plasma characterisation by means of optical emission spectroscopy. This technique is used to determine and quantify the species present in the micro-arcs and their evolution with time. It allows us to get insights into the progress of the oxidation process and to improve the understanding of the growth mechanisms. The influence of different electrolyte compositions is also investigated.

Introduction

The anodising process allows to improve the properties of the aluminium alloys surfaces. Nevertheless, this kind of process has reached its technological as well as environmental limits. Actually, the insulating nature of the aluminium oxide coatings leads to a small thickness of the layer and a good corrosion resistance requires further steps of sealing and painting. Moreover, most of the electrolytes and sealing baths contain hexavalent chromium, which is known for its carcinogenic effects. A new process, based on anodising has been developed in the 70's to offer a new range of properties: it is known as micro-arc oxidation [1] (MAO) or plasma electrolytic oxidation [2]. Compared with anodising, the MAO treatments are achieved in an alkaline bath, using an ac power supply. The process is characterized by the development of plasma discharges at the metal/electrolyte interface. These plasmas appear as a number of discrete short-lived micro discharges moving across the metal surface. Owing to the liquid environment of the process, optical emission spectroscopy (OES) is the best suitable technique to characterize the micro-arc plasmas in order to study the species that are created in the gas bubbles and that interact with the sample surface. This paper deals with the first results of OES characterization of the MAO process.

Experimental procedure

The experimental setup is presented in figure 1. The workpieces are rectangular samples of 90 mm x 100 mm x 10 mm. In order to compare oxidation mechanisms according to the composition of the alloy, we performed treatments on two different aluminium alloys: the 1050 Al alloy (purity = 99,5 %) and the 7050 Al alloy (zinc, copper and magnesium).

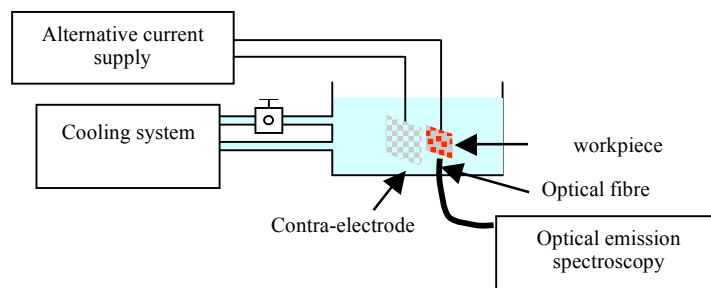


Figure 1 : experimental setup

The samples are processed in two kind of electrolytes:

- The first electrolytic solution consists of KOH and Na_2SiO_3 diluted in distilled water. (Na_2SiO_3 is introduced into the electrolytic solution to increase the growth rate and improve the tribological properties of the coatings [3]).
- The second one is composed of Na_3PO_4 and NaAlO_2 in distilled water [6].

The pulse power supply [4] allows to control the current density (about 600 A/cm²) and to work at frequencies ranging from 100 to 1000 Hz. Up to now, many works are realised at 50 Hz, but very different properties can be achieved with increasing the repetition rate. It is worth noting that the choice to impose a current rather than a voltage is necessary for a good control of the process. Indeed, the resistivity of the sample surface increases with time, owing to the growing insulating layer. Thus, working with a voltage supply would lead to a current drop as long as the process goes on. Such a current drop will result in a complete extinction of the micro-arcs and consequently will stop the oxidation process.

Although the MAO does not necessitate surface pre-treatment prior to the treatment process [5], the samples are cleaned with acetone before being processed to avoid poisoning of the bath and to ensure the same initial surface state for each sample.

Principle

During the early beginning of the treatment, we notice the fast formation of a first insulating oxide film by electrochemical way. By imposing a higher current than in anodising, it is possible to cause the breakdown of this superficial dielectric layer. The resulting plasmas appear as sparks moving rapidly across the specimen surface and allow the oxidation process to go on. The growing film induces the evolution of the plasmas, which become more energetic and less numerous. So the sparks become micro-arcs before changing to arcs. By this way, the process allows the fast formation of really thick, dense and hard ceramic layers. These layer properties are obtained with only one step of processing, contrary to the anodising process, which needs surface preparation before treatment and at least a further step of sealing. An-other advantage of the plasma electrolytic process is to work in an environmental friendly alkaline electrolyte.

Along the process, the evolution of the plasma colour and nature is typical of the change in the micro-discharge composition. The study of these plasmas could thus allow a best understanding of the growth mechanisms. In this paper, we present the first results of these electrolytic plasmas characterization. By using optical emission spectroscopy, we can investigate the species that are present in the arcs and study their evolution as well. In particular, we are interested in to the aluminium which is issued from the sample surface, and in the elements of the electrolyte (H, OH, Na).

Results

✦ Optical Emission Spectroscopy (OES)

Thanks to OES, we can determine the dominant species that are present in the arcs. We detect the main components of the aluminium alloy (Al, Cu, Mg), and those from the electrolyte (Na, H, OH, O, K for the case of a KOH – Na₂SiO₃ electrolyte) in neutral form (figures 3 and 4).

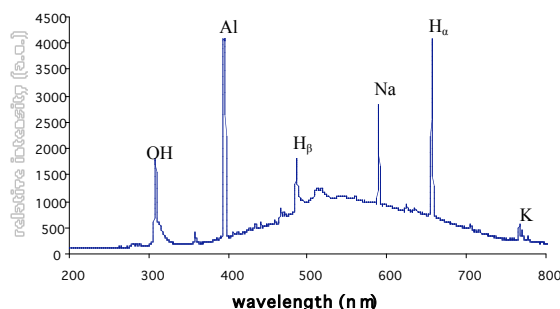


Figure 3: optical emission spectrum during a micro-arc process on a 1050 alloy

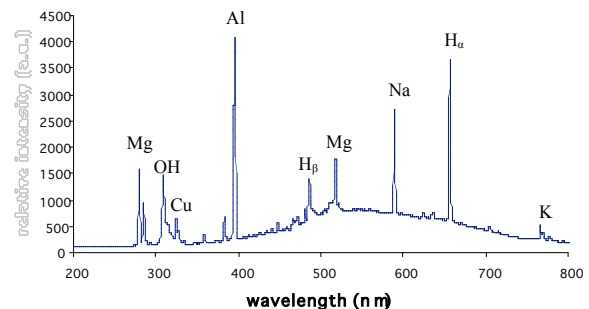


Figure 4: optical emission spectrum during a micro-arc process on a 7050 alloy

✦ Time evolution of the emission lines

As the ceramic coating grows, its resistivity increases, inducing changes in the nature of the plasma. The optical emission spectroscopy allows to follow the arcs components evolution with time; particularly the aluminium and the electrolytes elements lines (H, OH, Na) (figure 5 and 6).

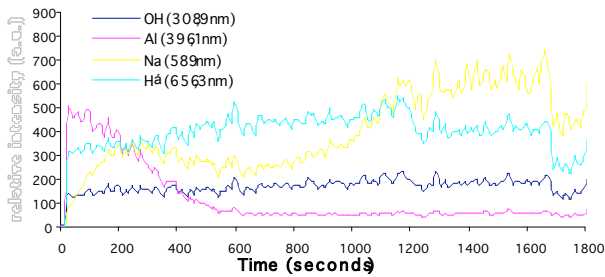


Figure 5: Time evolution of the plasmas species at 100 Hz according to the time of treatment for a 1050 alloy

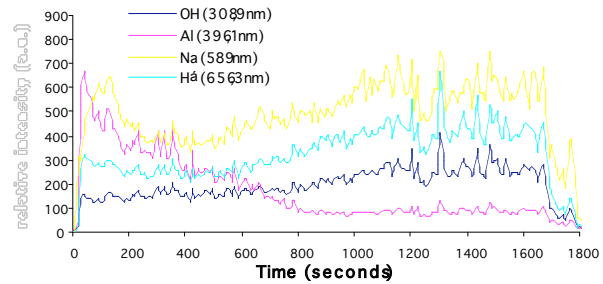


Figure 6: Time evolution of the plasmas species at 950 Hz according to the time of treatment for a 1050 alloy

We can see that the species contained in the bath (Na, OH, and H) exhibit similar trends over the treatment time; their emission intensity increases with time that is as the sparks evolve towards arcs. On the other hand, the intensity of the aluminium line increases strongly and rapidly at the early beginning of the treatment. Then, after 60 seconds (typical value depending on the operating conditions) this line intensity decreases progressively down to a constant value. It seems that after a thin oxide layer has grown through electrolytic oxidation, the sparks start to develop leading to the localized surface vaporization. Consequently, the density of vaporized aluminium increases as it is observed by OES. Pursuing the treatment, the oxide layer becomes thicker. Thus sparks change to micro-arcs and then arcs. Though these are stronger than sparks, they are less numerous and the vaporization of the aluminium is less efficient and the emission intensity of the Al line decreases. We also notice that the line intensities are greater at 950 Hz than at 100 Hz. This may be due to a competition between the repetition rate and the integration time of the optical detector. However, the observed changes in line intensities are not proportional to the change in operation frequency. This is significant of a modification in the process mechanisms with the current pulse repetition rate. Moreover, the difference in the variation of the characteristic rates of evolution rate of the species according to the frequency can indicate a variation in the growth rate.

Studying these temporal evolutions allows the understanding of the influence of different treatment parameters (current, frequency...) on the plasmas chemistry.

By changing the electrolyte components, the plasma composition changes too, and also the time evolution spectrum. For example, if the electrolytic solution consists of $\text{Na}_3\text{PO}_4 - \text{NaAlO}_2$, the time evolution of the specimen keeps the same shape. However, the Na emission is particularly greater because of Na_3PO_4 . The Al line seems to have a different evolution, we can explain it by two hypotheses:

- it could be the convolution of two phenomena (the evaporation of the aluminium like in the precedent case and the emission of aluminium, which is an electrolyte element, like H or Na).
- The evaporation of Al could be less important. Indeed, the conductivity of the electrolyte can play a role on this surface effect at the beginning of the process.

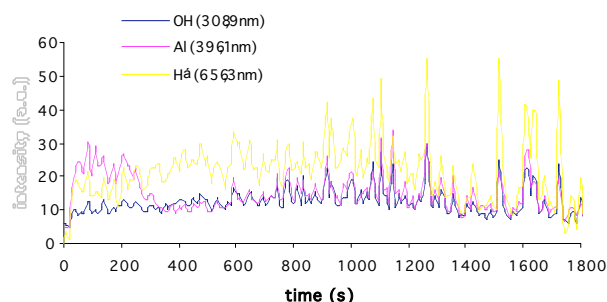


Figure 7: Time evolution of the plasmas species at 950 Hz according to the time of treatment for a 1050 alloy in an aluminate type bath

Other studies are currently in hand in order to answer to these questions and to better understand the mechanisms and the differences induced by changing electrical parameters or the electrolyte composition.

Conclusion

We present here a study of an electrolytic plasma oxidation process. The first results obtained by means of optical emission spectroscopy show the great influence of the process parameters on the arcs evolution. Further studies are on their way in order to get a better understanding of the ceramic layer growth mechanisms, particularly thanks to the coupling of plasmas and materials studies.

Références :

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