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## Abstract

The effect of dispersed carbon black nanoparticles in the electrolyte on the plasma electrolytic oxidation of aluminium under soft sparking regime is investigated. Increasing the concentration of particles reduces the breakdown voltage. It also makes the transition to soft sparking to occur earlier, which can favour a more homogeneous coating. However, it is shown that a too high concentration of particles can be detrimental to the coating morphology despite an apparent soft sparking regime characterized by a decrease in anodic voltage.

## 1. Introduction

Plasma electrolytic oxidation (PEO) has gained a growing interest over the last decades since it can advantageously replace anodizing and bring the processed parts new or at improved properties. Jaspard-Mecuson *et al.* [1] pointed out an interesting feature of PEO they named the "soft" regime. Indeed, when using an AC current to supply the processed parts, a transition from the conventional "arc" PEO to the "soft" PEO can occur depending on the processing parameters, especially the ratio of anodic to cathodic charge quantity $RCQ = Q_A/Q_C$ delivered to the system [1, 2]. Transition to soft sparking is often characterized by an anodic voltage drop [2, 3] as well as a decrease in acoustic emission [1, 3-4], and sometimes the discharge extinction [1]. It must be mentioned however, that

under certain conditions, all these phenomena do not necessarily occur at the transition to soft sparking and, conversely, that the transition to soft sparking can occur without any decrease in anodic voltage [5].

Over the years, some factors have been identified to promote the transition to soft sparking: a higher current density or current frequency [6], a lower *RCQ* [4], the thickness of a pre-existing oxide layer [3], and the ageing of the electrolyte [7].

Particle incorporation into the PEO layer has also been a concern over the last years to improve the performance of the coating for various applications. The review by Lu *et al.* [8] gives an extensive overview of the PEO processing with particle addition. Most papers however focus on the properties of the resulting coating, and only few of them report on the influence of the particles on the process itself [9, 10]. Particularly, there is quite no paper dealing with the effect of particle addition on the occurrence of soft sparking.

Thus, this work focuses on the influence of carbon black nanoparticles (CB) on the PEO process, especially on the transition to soft regime and on the structure and morphology of the resulting PEO coatings. Considering that carbon particles are electrically conductive, this work could be of interest to modify the electrical resistivity of the resulting PEO coating.

## 2. Materials and methods

PEO was carried out in a 2 L beaker with 1.7 L of electrolyte containing dispersed CB nanoparticles (Fig. 1). The electrolyte consisted of a base alkaline solution of potassium hydroxide ([KOH] = 17.8 $mmol \cdot L^{-1}$) and sodium silicate ([$Na_2SiO_3$] = 13.5 $mmol \cdot L^{-1}$) diluted in deionized water. The measured electrical conductivity and pH were 7.4 $mS \cdot cm^{-1}$ and 12.3, respectively. To prepare the electrolytes, CB nanoparticles (VULCAN® XC72) were dispersed in this base solution with concentration ranging from 0 to 12 $g \cdot L^{-1}$. Before PEO processing, these suspensions were sonicated

for 30 min. In the following, samples are referred to as CBx, where x stands for the CB concentration (in $g \cdot L^{-1}$) in the base electrolyte.

Water at 18 °C flowed in a copper coil, which ensured the stabilization of the electrolyte temperature at 40 °C during treatment. A magnetic stirrer served to homogenize the electrolyte and to prevent sedimentation of CB particles. Rectangular samples (50×32×5 $mm^3$) of 1050 aluminium alloy (> 99 wt% Al) served as working electrode. Two titanium plates (120×50×1 $mm^3$) placed 2 cm apart from each side of the sample served as counter electrodes.

A pulsed bipolar current generator (Ceratronic©) supplied the electrodes. The current waveform was specifically adjusted to achieve *RCQ* = 0.89 (Fig. 1b), which promotes soft sparking [1]. For all experiments, anodic and cathodic current amplitudes were set at $I_P$ = 15 A and $I_N$ = –9 A, respectively, the current frequency was set at 100 Hz, and the treatment duration at 60 min. Variations of the current and voltage during the process were recorded using an AD board (KPCI3100) and a 1 GHz oscilloscope (Agilent 8132B).

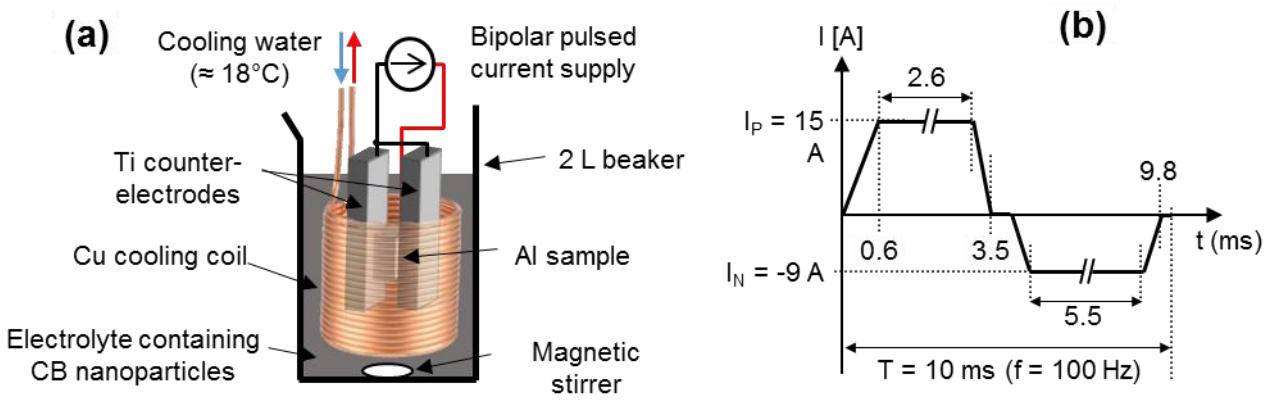


**Figure 1.** (a) Experimental set-up for PEO treatments with dispersed CB; (b) One period of the current waveform indicating the time at each change in the current rising/falling rate.

After PEO processing, samples were washed in an ultrasonic bath in ethanol and then dried in an oven at 100 °C before characterisation. Samples were observed by SEM (Quanta 650 FEG) working

in back-scattered electron mode (for cross section views) and secondary electron mode (for surface views). Prior to SEM examination, samples were coated with a 10 nm gold layer to avoid charging issues. SEM observations were made in the middle of the sample at 1 cm from the bottom of the samples.

## 3. Results and discussion

The evolution of the anodic voltage amplitude as a function of the processing time is plotted in figure 2a for different CB concentrations. Three main features can be noticed as the CB concentration varies. Firstly, the addition of particles reduces the breakdown voltage (inset in Fig. 2a) as reported in [9, 10]. Secondly, the higher the CB concentration in the electrolyte, the earlier the transition to soft sparking (Fig. 2a), and thirdly the amplitude of the voltage drop associated to the transition to soft regime increases with the CB concentration. It is also worth noting that the linear relationship between the time at transition to soft sparking and the CB concentration in the electrolyte (Fig. 2b) clearly evidences that there is a direct effect of the quantity of dispersed particles on the transition to the soft sparking regime. Up to now, the phenomena that sustain this effect are not clearly established. It could happen that the particles charge under the applied electric field, which would therefore affect the potential distribution at the electrolyte-coating interface, favouring the transition to soft regime.

As expected, a progressive decrease in acoustic emission of the process is also noticed for each treated sample. Except for high CB concentration (CB12), the time at which the process becomes almost silent corresponds to the transition to the soft sparking regime and the associated anodic voltage drop. Regarding the specific case CB12, the decrease in acoustic emission only occurred at ~ 45 min, that is 40 min after the sharp voltage drop observed at 6 min of process. This could mean that, despite the voltage drop, some discharges continue to ignite. Considering that the anodic voltage value stays around the breakdown voltage (see inset in Fig. 2) all along these 40 min, the acoustic emission could be associated to discharges igniting at some locations, thus creating large cavities

lined with a PEO layer as observed in Fig. 4 for CB12 sample. Consequently, the process may not pass to soft regime under these conditions of high concentration in CB particles.

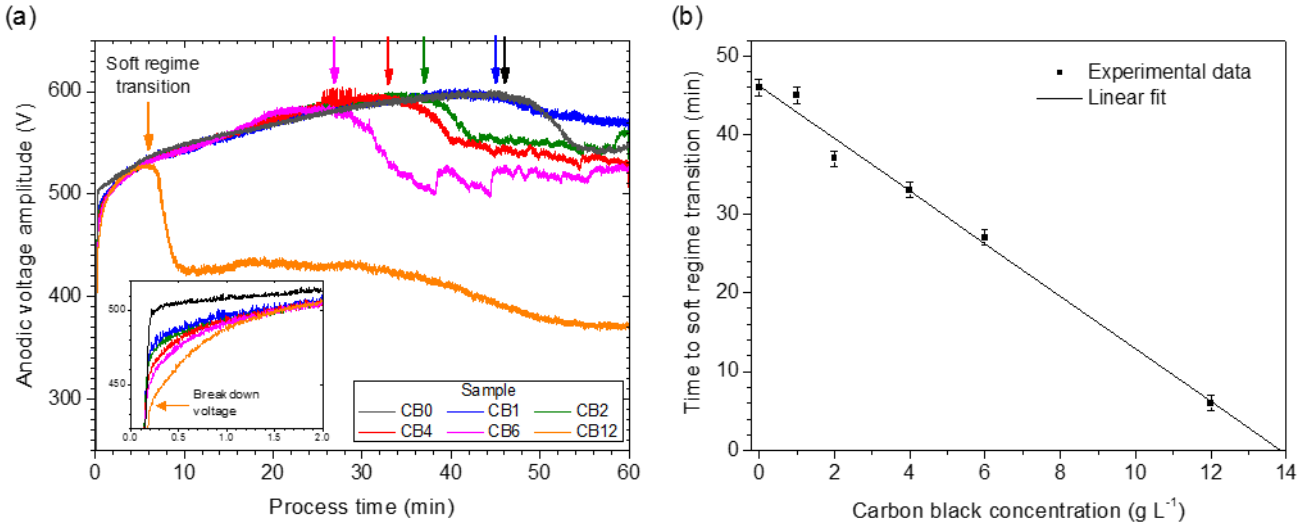


**Figure 2.** (a) Evolution of the anodic voltage amplitude as a function of the processing time for different CB concentrations. Inset is an enlarged view of the first two minutes of process. (b) Variations of the time to soft regime transition as a function of the CB concentrations.

Macroscopic views of the sample surface after treatment are shown in figure 3. The presence of CB in the electrolyte gives the samples a more or less dark grey colour as opposed to the very light grey (nearly white) aspect of sample processed without particle (CB0). This could indicate that carbon particles are indeed incorporated, at least on the top surface of the coating. An inhomogeneity can be observed between the centre and the edge of the samples, the edge being darker in case of a treatment with CB nanoparticles. Such an inhomogeneity is likely due to a stronger electric field at the edges (edge effect) [3, 6]. As the concentration in particles increases, the external aspect of the coatings becomes more homogeneous and darker, up to a concentration of 6 $g \cdot L^{-1}$ (CB6). For the highest CB concentration (CB12), the colour of the sample is clearer and cavities can be seen on the surface. Some areas still look like bare aluminium and some aggregates of carbon particles are observed on the upper part of the sample. These aggregates could form because of the high particle concentration, and be pushed upward and agglomerate at the top part of the sample because of strong bubbling.

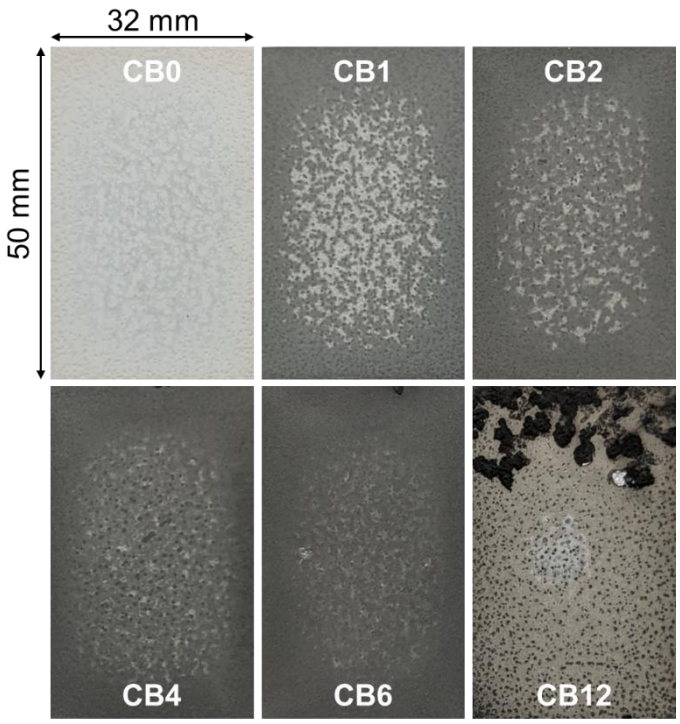


**Figure 3.** Visual aspects of the samples obtained after PEO treatment performed under soft regime conditions with different CB concentrations.

Top-most surface and cross-sectional SEM micrographs displayed in figure 4 show the morphology of the PEO coatings produced with various CB concentrations in the electrolyte. Without dispersed CB as well as for low concentrations (CB0 and CB2 in Fig. 4), two typical surface morphologies can be observed: the so-called “pancake”-like structure [11], and a “sponge”-like structure usually formed after establishment of the soft sparking regime. The cross section views confirm these two morphologies. In contrast, for sample CB6, only the “sponge”-like morphology is observed, thus forming a more homogeneous PEO coating due to a longer time under soft regime. As for CB12 sample, most of the surface is covered with a very thin oxide layer of about 3-5 µm in thickness with relatively large pores (up to 10 µm). In some places, large open spherical cavities (up to 50 µm in diameters) form open geodes-like structures with a porous oxide layer lining their internal walls.

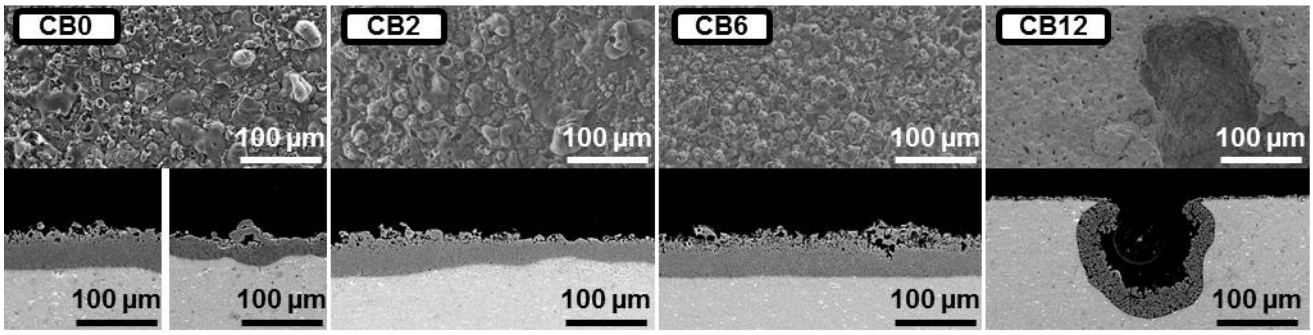


**Figure 4.** Top-surface and cross sectional SEM micrographs recorded at the centre of the samples treated with different CB concentrations.

## 4. Conclusion

The results presented in this study prove that adding CB nanoparticles in the electrolyte lowers the breakdown voltage and promotes a drop of the anodic voltage amplitude, which is usually associated with the transition to the soft sparking regime. However, this holds for reasonable CB concentrations (up to 6 $g \cdot L^{-1}$ presently). Indeed, for higher concentrations of particles, although a sharp anodic voltage drop is observed, the PEO process does not seem to enter the soft sparking regime, as indicated by the acoustic emission and pointed out by the morphology and microstructure of the resulting coatings. It can thus be concluded that, for PEO processing of aluminium, the transition to soft sparking regime, as indicated by an anodic voltage drop, is not necessarily the relevant criterion for dense and high quality PEO coatings.

## 5 Acknowledgements

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