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1 **Enhanced properties of alumina coating produced by combining plasma**
2 **electrolytic oxidation and ultrasonic shot peening**

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7
8 **Abstract**

9 A short-duration ultrasonic shot peening (USP) is used as a post-treatment to plasma electrolytic
10 oxidation (PEO) coatings produced on a 2017 aluminium alloy under various sparking regimes (arc or
11 soft) and time durations. USP is detrimental on PEO layers produced for short durations and under the
12 arc regime because the typical pancake structure at the topmost surface is partially blasted. In contrast,
13 PEO layers grown under the soft regime not only keep their structural integrity after short duration
14 USP but also experienced a densification of their internal sublayer and a resurfacing of the sponge
15 structure at the external sublayer. Under the specific PEO soft regime, the proposed duplex surface
16 treatment makes the coating harder with a higher fracture toughness compared to the as-produced PEO
17 coating.

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21 **Keywords:** Aluminium; Plasma electrolytic oxidation (PEO); Ultrasonic shot peening (USP), Duplex
22 treatments.

1 **1. Introduction**

2 Plasma electrolytic oxidation (PEO) has gained a growing interest over the last decades since it can
3 advantageously replace anodizing to produce protective coatings on lightweight metals [1]. Growth of
4 the oxide layer takes place at high potentials resulting in the development of micro-discharges over the
5 processed surface. A proper management of the power supply is of crucial importance to control the
6 behaviour of these micro-discharges which, in turn, affects the properties of the PEO layers.
7 Specifically, PEO layers exhibit an intrinsic porosity as a consequence of oxygen entrapment in molten
8 alumina in the vicinity of these localized micro-discharges [2].

9 The use of a bipolar pulse current is known to improve significantly the final properties of the oxide
10 as well as to provide more flexibility in the control of the PEO process [3]. When applied on aluminium
11 alloys, Mécuson et al. [4] pointed out an interesting feature of PEO that they named the “soft” sparking
12 regime. Indeed, a transition from the conventional “arc” sparking regime towards a “soft” one can
13 occur depending on the processing parameters, especially when the anodic to cathodic charge quantity
14 ratio RCQ is slightly lower than 1. Transition to soft sparking is characterized by an anodic voltage
15 drop, which is also associated with a gradual disappearance of visible discharges as well as an increase
16 in the growth kinetic of the oxide layer.

17 Nevertheless, while progress has been achieved over the past years, PEO coatings still remain too
18 porous for various applications, including those for which wear resistance, corrosion resistance and
19 thermal protection are being sought. Surface machining post-treatments are usually applied to remove
20 the brittle and porous outer PEO sublayer [5] while post-sealing treatments are explored for plugging
21 pores of the inner sublayer [6].

22 However, there is quite no paper dealing with a surface treatment that could eliminate the
23 undesirable outer PEO sublayer, while reducing porosity of the inner sublayer. In particular, the use of
24 mechanical attrition by multidirectional shot peening techniques [7], such as ultrasonic shot peening

1 (USP) or surface mechanical attrition treatments (SMAT) applied on PEO coatings has never been
2 investigated. If pioneer works by Wen et al. [8, 9] already discussed the possibility to apply SMAT as
3 a pre-treatment of PEO to “activate” the surface and, thereby, increase the oxide thickness, the control
4 of porosity remains a problem. The main objective of the present study is to investigate short duration
5 of USP as a potential post-treatment, easier to implement at the industrial scale than machining or
6 chemical sealing, to improve the morphology and the mechanical properties (hardness and fracture
7 toughness) of PEO coatings.

8 **2. Materials and methods**

9 As presented in reference [4], PEO treatments were run in a solution of potassium hydroxide (17.8
10 mmol·L⁻¹) and sodium silicate (13.5 mmol·L⁻¹) diluted in deionized water. An Al2017 grade
11 aluminium alloy was used as substrate. Samples had a rectangular shape of 40×40×10 mm³. A pulsed
12 bipolar current generator supplied the electrodes. The current waveform was specifically adjusted to
13 achieve RCQ = 3, which corresponds to the arc sparking regime, or RCQ = 0.89, which promotes the
14 soft sparking. The anodic current amplitude and frequency were set at 30 A and 500 Hz, respectively.
15 Samples were PEO processed for 5 and 35 min for both RCQ conditions.

16 An optimized multidirectional peening (5 s duration) was then performed on one side of each PEO
17 sample by using ultrasonic shot peening apparatus (Sonats). Treatments were carried out at room
18 temperature with 2 mm diameter steel shots using a sonotrode vibrating amplitude of 40 µm and a
19 frequency of 20 kHz.

20 Top views and cross-sections of the coatings were examined by SEM at the centre of the samples.
21 The coating thickness was determined as an average value of 10 measures taken on cross-section over
22 10 different positions. Porosity was estimated from image analysis of the cross-sectional SEM
23 micrographs using ImageJ[®] software. The average mean surface roughness Ra of the samples was
24 assessed from surface topography measurements using confocal laser optical profilometry. Indentation

1 tests were carried out at the centre of the cross-section of the coatings using a Vickers micro-indenter
2 at a load of 1.961 N. Hardness was determined as the average value of 5 measurements.

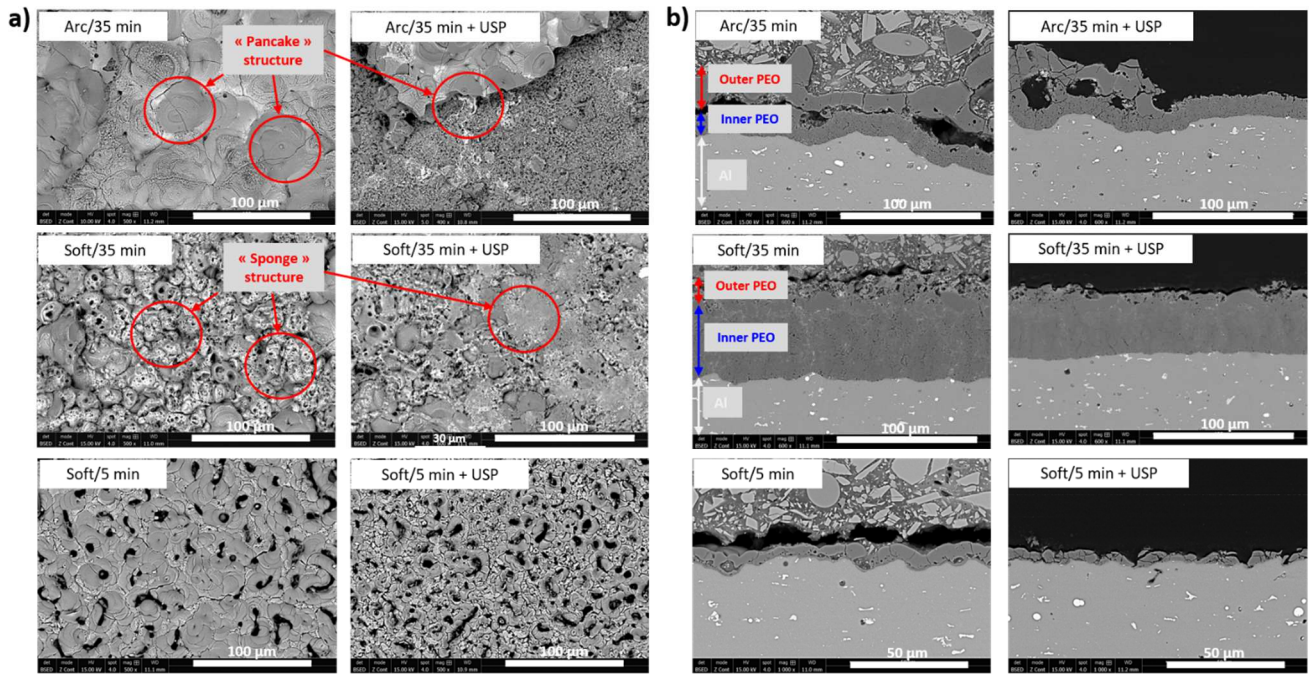
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4 **3. Results and discussion**

5 Top-most surface and cross-sectional SEM micrographs displayed in Fig. 1 show the morphology
6 of the PEO oxide coatings obtained before and after USP. PEO coatings can usually be divided into a
7 compact inner sublayer and a more porous outer sublayer [4]. Before USP, depending on the PEO
8 processing conditions, two typical surface morphologies can be observed through the outer sublayer:
9 the so-called pancake-like structure produced during the arc sparking regime, and a sponge-like
10 structure usually formed during the soft regime [10]. After USP, sections of the pancake-like structure
11 were partially removed letting the inner sublayer underneath appear. It results in a rougher surface. In
12 contrast, for the sample processed within the soft regime condition, the sponge-like structure is finely
13 pressed forming a more homogenous PEO coating, and also making the surface smoother.
14 Interestingly, in this specific condition, the overall PEO coating is thicker before than after USP. For
15 shorter PEO processing duration, oxide layer is thinner and USP post-treatment results in a slight
16 decrease in thickness and in a fissuring of the pancake-like structure as well.

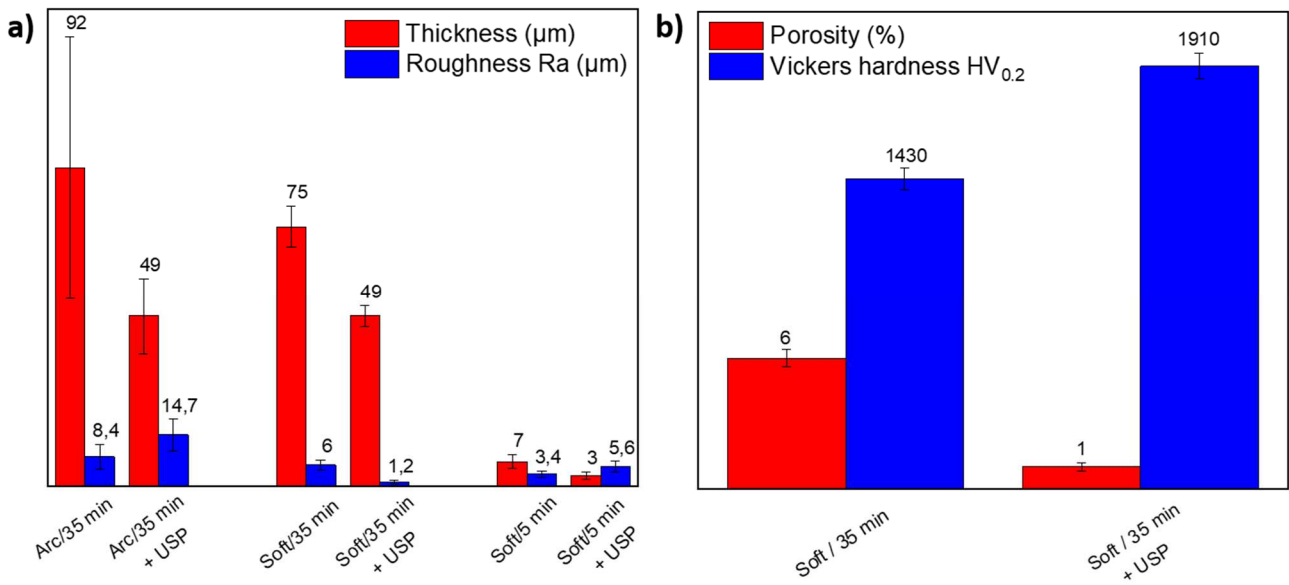
17 At higher magnification, top-surface SEM micrographs in Fig. 3 show that the porous sponge-like
18 structure formed at the top-most surface within the soft regime is pressed down making the surface
19 flatter. This is confirmed in Fig. 3 with the surface topography which evidences that the rough sponge-
20 like structure becomes smoother after USP. The measured roughness parameter Ra is $6.0 \pm 0.4 \mu\text{m}$
21 before USP and decreases to $1.2 \pm 0.1 \mu\text{m}$ after USP (Fig. 2a).

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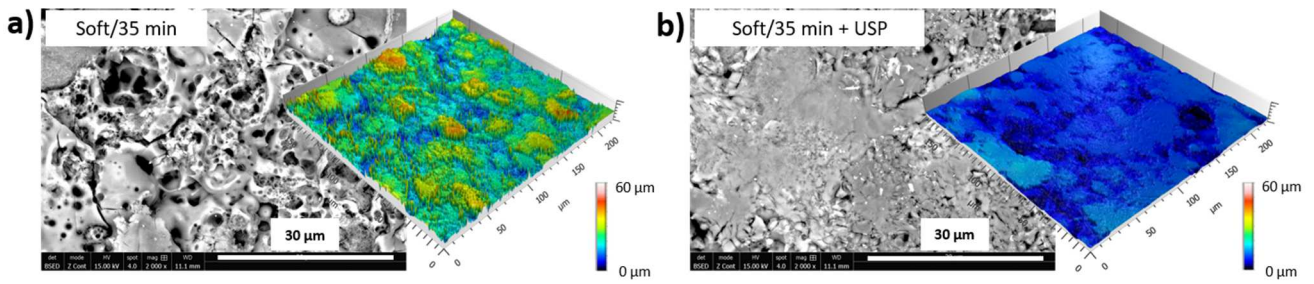
2 **Fig. 1.** (a) Top-surface and (b) cross sectional SEM micrographs of the PEO processed samples before
 3 and after USP.



4

5 **Fig. 2.** (a) Thickness and roughness, and (b) porosity and Vickers micro-hardness measured on the
 6 produced PEO coatings before and after USP.

7



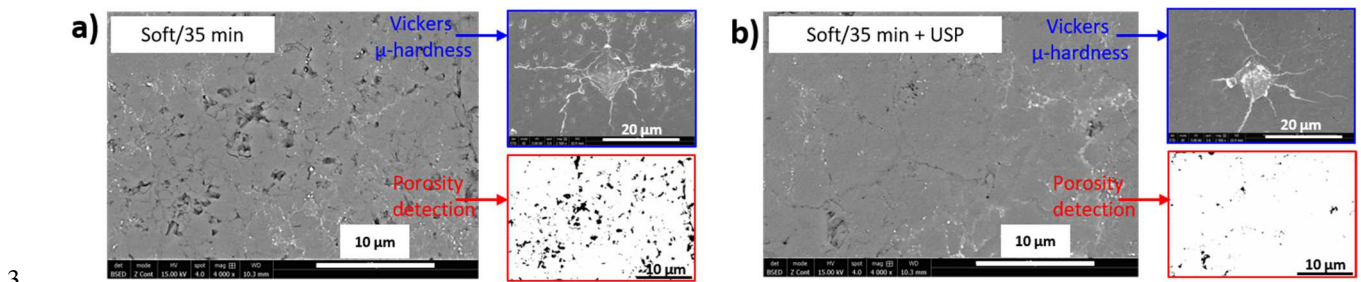
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2 **Fig. 3.** Top-surface SEM micrographs and the associated surface topography recorded on the sample
 3 PEO processed for 35 min under the soft sparking regime (a) before and (b) after USP.

4 Fig. 4 shows more specifically the inner sublayer of the PEO coating elaborated for 35 min under
 5 the soft regime, before and after USP. High magnification cross-sectional SEM micrographs evidence
 6 a reduction in the porosity of the PEO coating after USP. Image analysis performed on these SEM
 7 micrographs confirmed a significant densification of the inner PEO sublayer after short-duration
 8 USP. The estimated porosity for these two samples is about $6 \pm 0.5 \%$ before USP, while it drops to
 9 about $1 \pm 0.2 \%$ after USP (Fig. 2b). Thus, the densification of the inner sublayer combined with the
 10 top-most surface resurfacing explain the observed decrease in the thickness of the overall PEO coating
 11 after USP (Fig. 1b and 2a). It therefore appears that short-duration USP performed on a thick and dense
 12 PEO oxide layer grown under soft sparking conditions has a beneficial effect on the coating
 13 morphology.

14 Fig. 4 also shows the SEM micrographs of the Vickers micro-indentations carried out on the cross-
 15 section of the PEO coatings formed for 35 min in the soft sparking conditions before and after USP.
 16 Size of the indentation appears larger before than after USP. It suggests an increase in the coating
 17 hardness when a short-duration USP post-treatment is particularly applied on PEO coatings formed
 18 within the specific soft sparking regime. The Vickers micro-hardness of the as-grown PEO coating is
 19 of about $1430 \pm 50 \text{ HV}_{0.2}$ which is usual for layers produced in soft regime conditions [11], while it
 20 increases to about $1910 \pm 50 \text{ HV}_{0.2}$ after USP (Fig. 2b). This can be explained by the reduction in the

1 internal porosity making the coating more compact and therefore more resistant to the penetration of
2 the Vickers micro-indenter.



3
4 **Fig. 4.** Cross-sectional SEM micrographs and the associated Vickers indentations and image analysis
5 of the porosity recorded on the sample PEO processed for 35 min under the soft sparking regime (a)
6 before and (b) after USP.

7 Vickers micro-hardness technique is also used to determine the fracture resistance behaviour of
8 brittle materials from the branch cracks formed around the indented areas in the sample, the fracture
9 toughness being inversely proportional to the average crack length [12]. Fig. 4 shows that USP
10 treatment results in shorter length cracks around the indentation compared to the as-oxidized PEO
11 coating under the soft sparking conditions, suggesting therefore a higher fracture toughness. This result
12 can also be explained by the more compact morphology of the PEO oxide layer produced after USP
13 which in turn prevents more efficiently crack propagation and reduces the brittle behaviour of PEO
14 alumina coatings.

15 **4. Conclusion**

16 A short duration (5 s) of multidirectional peening done by USP was applied on PEO coatings produced
17 under various sparking regimes (arc or soft) and time durations (5 or 35 min). The results show that,
18 for short duration PEO treatments, the PEO coatings are too thin to resist the damaging effects resulting
19 of the inherent sputtering of the subsequent USP treatment. Similarly, the PEO coating grown under
20 the arc sparking regime is partially sputtered by subsequent shot peening resulting in an irregular
21 surface with an heterogenous thickness. However, the PEO coating produced under the specific soft

1 sparking regime keeps its structural integrity after USP while, also experiencing both a significant
2 densification as well as a resurfacing of the porous top-surface. Under these conditions, USP was
3 proved to have a beneficial effect on the PEO coating that finally exhibited improved mechanical
4 properties. Finally, based on the present work, further studies should be devoted to a finer
5 microstructural characterization of the processed coatings, and to get a better understanding of the
6 mechanisms involved during USP of alumina PEO coatings.

7 **5 Acknowledgements**

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