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Improvement of corrosion resistance of AA2024-T3 using femtosecond laser peening without protective and confining medium

Uroš Trdan^{a*}, Tomokazu Sano^b, Damjan Klobčar^a, Yuji Sano^c, Janez Grum^a, Roman Šturm^a

^a Faculty of Mechanical Engineering, University of Ljubljana, Aškerčeva 6, 1000 Ljubljana, Slovenia

^b Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

^c Japan Science and Technology Agency, K's-gobancho, 7, Gobancho, Chiyoda-ku, Tokyo, 102-0076 Japan

*Corresponding author: Asist. Prof. Uroš Trdan, PhD.

Email: uros.trdan@fs.uni-lj.si

Tel.: +386 1 477 1432

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Abstract

This work reports for the first time the effect of femtosecond laser shock peening (fLSP) without a sacrificial overlay under atmospheric conditions (no confinement) on the corrosion behaviour of AA2024-T3. After fLSP and additional exposure to air a superhydrophobic state ($\theta = 160 \pm 4^\circ$) is achieved. Moreover, fLSPed corrosion-resistant surface contributes to increased polarization resistance, reduced corrosion current and lower anodic dissolution, with long-term stability in aggressive chloride solution. Furthermore, SEM/EDS

characterisation reveals reduction in pitting and complete eradication of intergranular corrosion (IGC) attack due to reduced metal/electrolyte contact area and homogeneous, refined microstructure which prevents chain-link IGC propagation.

Keywords:

A. Aluminium

B. Polarization

B. SEM

C. Intergranular corrosion

C. Pitting corrosion

1. Introduction

High-strength aluminium alloys are widely used in the transport and aerospace industries for various applications, e.g., fuselages, trailing edge panels, dorsal fins, etc., especially due to their good strength/weight and load capacity/weight ratios and their high mechanical properties [1,2]. However, AA2024-T3 remains one of the most studied aluminium alloys in the scientific corrosion literature due to its poor corrosion resistance in chloride-containing aqueous environments [3,4]. High corrosion susceptibility to localised corrosion, such as pitting and intergranular corrosion (IGC), originates from its complex heterogeneous microstructure with compositional variation, which leads to strong micro-galvanic coupling between various alloy phases [4-8].

Although Cu-rich particles, such as S-Al₂CuMg phase, θ -Al₂Cu phase, Guinier-Preston-Bagaryatsky (GPB) zones, S'' and S' phase, produced by the matrix precipitation during solute segregation and ageing processes, highly improves the strength of the alloy, at the same time drastically increase pitting and IGC susceptibility [9]. Since S-phase with the corrosion potential of -920 mV (in a 0.5 M NaCl solution) [10] is more active than the surrounding

54 matrix phase, severe dealloying by dissolution of Al and Mg may occur, resulting in the
55 formation of Cu-rich particle remnants, which then behave as the noble sites [12]. Although,
56 S-phases dealloy preferentially, also at the same time dealloying of the θ -phase, with
57 corrosion potential of -700 mV [10], occurs by selective dissolution of Al from the θ -phase
58 resulting in porous Cu-rich θ -phase remnants, comprised of randomly oriented metallic
59 copper particles and copper oxides with sizes of 10–50 nm [11].

60 Moreover, due to the microstructural complexity and various intermetallic phases in the
61 AA2024 alloy, corrosion is extremely stochastic, and there is still an open debate on the
62 precise role of specific intermetallic phases, which also depend on the temper condition
63 [4,13,14].

64 Since IGC attack can eventually lead to cracks and complete collapse of the structures, this
65 must be avoided in industry and can be achieved with various protective coatings [15-17],
66 corrosion inhibitors [18-20] or severe plastic deformation (SPD) methods to obtain a refined,
67 more homogeneous microstructure with higher grain boundary volume fractions and
68 redistributed Cu-rich precipitates [7,9,21]. However, one should note that microstructural
69 alteration by SPD can be complex and challenging since it is reflected in changes in grain
70 size, dislocation density, particle fragmentation, solute rearrangement and redistribution,
71 which all drastically affect corrosion activity [7].

72 Laser shock peening or laser peening (LSP/LP) is a rapidly emerging and competitive SPD
73 surface modification technique that generates laser-driven shock waves resulting in local
74 plastic deformation, which in turn improves material properties with considerably deeper
75 compressive residual stresses compared to traditional shot peening [22-24]. LSP using
76 nanosecond (ns) laser pulses, which can be applied with or without a protective/sacrificial
77 coating at the laser–matter interaction zone, depending on the characteristics of the different
78 laser sources, has already been recognised as an advanced and efficient surface treatment

79 technique to improve several aspects of the treated material, e.g., mechanical properties
80 [25,26], wear resistance [27,28], fatigue strength [29-32] and corrosion resistance [33-38].

81 Our previous studies [34][36] have already confirmed nanosecond LSP (ns-LSP) without
82 coating as an effective surface treatment to improve corrosion resistance of precipitation-
83 hardened AA6082-T651 alloy. Results have confirmed enhanced passivity, 7-times higher
84 polarization resistance R_p with lower double-layer capacitance C_{dl} , due to the high density of
85 dislocations and compressive residual stress [39] and a modified/thicker, more stable, passive
86 oxide film [36]. Krawiec et al. [40] also demonstrated a sharp increase in the charge transfer
87 and oxide film resistances at sites containing the matrix with AA2050-T8 alloy, due to the
88 development of compressive stresses during ns-LSP. Lu et al. [37] showed that massive ns-
89 LSP treatment can greatly improve resistance to stress corrosion cracking and electrochemical
90 properties in a 0.598 M NaCl solution, whereas higher pulse energy contributes to higher
91 corrosion resistance. Moreover, Karthik et al. [41] reported significantly improved corrosion
92 resistance after massive ns laser peening without coating with 19-times lower corrosion rate
93 and 5-times higher charge-transfer resistance R_{ct} compared to the untreated material.

94 Nonetheless, with all ns-LSP processes it is essential to cover the surface with a confining
95 transparent medium (water, glass) to suppress plasma expansion which in turn produces
96 sufficient shock-wave generation to deform the material plastically [23,30]. In contrast,
97 femtosecond LSP (fLSP) is opening new possibilities of direct laser irradiation under
98 atmospheric conditions without sacrificial overlay, which makes it a more economic and
99 cleaner technology, producing lower waste gas emissions. Although the energy of the fs pulse
100 is low, the extremely short pulse width reflects in extremely high intensity, sufficient to
101 produce intense shock waves even in air [42], producing metastable high-pressure phases
102 [43,44], dense dislocation configurations [45,46] and compressive residual stresses [24].
103 Moreover, despite intensive research efforts [47,48] devoted to fs laser texturing to obtain

multifunctional hierarchical superhydrophobic surfaces, the effect of fs LSP using high laser fluence in excess of 10 Jcm^{-2} to drive a strong shock wave propagating into the material, corrosion and superhydrophobic developments have never been reported.

Hence, the purpose of this work is to study how fLSP without protective and confining medium performed in air affects mechanical properties via nanoindentation and residual stress measurements, wettability and electrochemical properties of aeronautical AA2024-T3 alloy in a chloride environment. Corrosion was evaluated using potentiodynamic linear and cyclic polarization (CP) and electrochemical impedance spectroscopy (EIS), whereas the specific attention was focused on determining the long-term stability and durability of pre-corroded samples after longer immersion times. In addition, the effect of surface ablation and fs laser-driven shock waves on the intensity of pitting and IGC attack was examined using SEM/EDS analyses.

2. Material and methods

2.1. Material and femtosecond laser shock peening

In this study 15 mm discs were cut using an electric discharge machine from 3 mm thick plates of commercial aluminium alloy AA2024-T3. [Table 1](#) shows the chemical composition in wt.% of this aluminium alloy. The surface of the specimen to be irradiated by fLSP treatment was electropolished in 20% sulphuric acid/methanol electrolyte for 30 s to remove the work-strained layer.

[Fig. 1](#) illustrates schematically the experimental setup for femtosecond laser peening. The specimen of AA2024-T3 was mounted on an x-y stage as shown in [Fig. 1a](#). Femtosecond laser pulses (Spectra-Physics Inc., Spitfire) with a wavelength of 800 nm, a pulse width of 120 fs and pulse energy of 0.6 mJ were focused using a plano-convex lens with a focal length of 70 mm and irradiated normal to the electropolished surface of the specimen in air.

For the peening treatment, the aluminium specimen was moved in the x - and y -directions during laser irradiation as shown in Fig. 1b to be irradiated with a coverage C_v of 692% which is expressed by $C_v = \pi D^2 N_p / 4$ where D is the spot diameter of the laser pulse irradiated and N_p is the number of pulses per unit square.

2.2. Surface morphology, nanoindentation and residual stress measurements

Surface morphology of the femtosecond laser-peened aluminium alloy was observed using a Hitachi S-3000H scanning electron microscope (SEM). Measurement of surface roughness was performed using a Keyence VK-9700 laser microscope with a wavelength of 408 nm and a depth resolution of 0.05 μm .

The residual stress on the femtosecond laser-peened surface was estimated from the Al(311) diffraction peak of CrK α X-rays (2.2897 $\text{\AA}$) using a Young's modulus of 70.3 GPa and a Poisson's ratio of 0.345. Thin layers of the surface were successively removed by repeated step-wise electrolytic polishing using 10% HClO₄ solution at an applied voltage of 16 V to obtain the depth profile of the residual stress. The removed thickness was determined from the step difference between unremoved and removed areas measured using a laser microscope. The hardness of the cross-section was measured by an Elionix ENT-1100a nanoindentation system with the applied load of 1 mN. Before the nanoindentation measurements, the cross-section was polished by a JEOL SM-09010 using a 5 keV Ar-ion beam to remove the work-hardened layer.

2.3. Wettability and electrochemical measurements

The hydrophobicity, i.e. water repellency, of the samples was studied by a static contact angle (SCA) measurement, using the a goniometer of our own design, where a droplet of distilled water with a volume of 5 μL was delivered to the investigated surface [49,50]. The

measurements on base material (BM) and fLSPed samples were conducted after exposure to ambient conditions ($T = 23\text{ }^{\circ}\text{C}$, $RH = 35\%$) for one month, where prior to SCA measurements both samples were ultrasonically cleaned in distilled water and rinsed with ethanol.

Electrochemical measurements were carried out with a PAR Versastat-4 potentiostat/galvanostat/ZRA using a three-electrode corrosion cell under static conditions, with a saturated calomel electrode (SCE) as a reference and a graphite rod as a counter electrode. Immediately prior to each corrosion experiment, all specimens were cleaned and degreased in an ultrasonic bath of ethanol followed by deionised water for 3 min each, dried under a stream of warm air and embedded in a Teflon PAR holder as the working electrode (1 cm^2). The test medium was a naturally aerated ($T = 22 \pm 1\text{ }^{\circ}\text{C}$) 0.6 M NaCl solution, freshly prepared with deionised water before each experiment.

Afterwards, the samples were immersed in the solution and open circuit potential measurements ($E_{\text{ocp}} = f[t]$) were performed for 60 min in order to stabilise the surface, and corrosion potential E_{corr} , was determined at the end of the stabilisation process. Followed by OCP, linear polarization resistance (LPR) measurements were performed in the potential range $\pm 10\text{ mV}$ relative to E_{corr} using 0.1 mVs^{-1} potential scan rate. The EIS measurements were performed after the LPR measurements and prior to the cyclic polarization (CP) scans [51,52] at steady free corrosion potential (E_{corr}) by applying a sinusoidal 10 mV RMS perturbation signal at frequencies ranging from 50 kHz down to 100 mHz. Impedance data was experimentally determined by fitting, using an equivalent electrical circuit with ZsimpWin software.

CP scans were performed after the EIS measurements. CP was conducted in the anodic direction with a scan rate of 1 mV/s , starting at -150 mV vs. E_{corr} . The polarization direction was reversed at the switching potential E_{sw} at which the potential reached a limited threshold value of 1 mAcm^{-2} and progressed in the cathodic direction towards the starting potential. The

consistency of consecutive electrochemical measurements was ensured by repeating all experiments twice with different samples prepared by the same parameters in a freshly prepared electrolyte solution, and as a result a representative curve was selected.

To evaluate surface condition and corrosion morphology after the CP tests, each specimen was cleaned ultrasonically in alcohol, rinsed gently with deionised water, dried and stored in a desiccator. Samples for cross-section examination of the microstructure and intensity of IGC attack after CP were cut along the LT–ST plane using a diamond saw followed by hot mounting and polishing to a mirror finish (0.04 μm colloidal silica suspension) and etching with Keller's reagent. The surface condition, microstructure and chemical composition of the surface after CP were examined using a JEOL JSM-5610 SEM microscope equipped with EDS microanalysis hardware. Acceleration voltage during SEM experiments was kept constant at 20 kV.

In order to investigate long-term stability against corrosion and to obtain insights into the active-passive behaviour, the formation of corrosion products and the durability in aggressive chloride solution, additional electrochemical measurements were carried out on pre-corroded surfaces after CP and exposure to air under ambient conditions for six months. Here, EIS measurements (using the same configuration as described above) were performed after 24 h immersion at OCP. All electrochemical corrosion techniques were pre-tested to ensure the repeatability of the experiments.

3. Results and discussion

3.1. The effect of fLSP on surface morphology and mechanical properties

Fig. 2 shows the SEM images of the femtosecond laser-peened surface of the AA2024-T3 with multidirectional structures as a consequence of constant melting, ablation and deposition of the recast material during laser treatment. Nonetheless, droplets were not observed,

indicating that the femtosecond laser treatment creates a negligibly small molten layer. The surface roughness R_a is 1.2 μm , which is more than 2-times lower than that of a nanosecond laser-peened [53] as well as shot-peened surface [54], respectively.

Fig. 3 depicts the residual stress along the x -direction σ_x and y -direction σ_y , and hardness as a function of depth from the surface. The surface region within around 100 μm has a compressive residual stress for both x - and y -directions, of which maximum value is about 300 MPa at a depth of 6 μm , which is almost same as the 0.2% proof stress of AA2024-T3. The region within 6 μm from the surface with the most compressive residual stress corresponds to the most hardened region. The largest value of the hardness is almost twice that of the unpeened aluminium alloy with a hardness of 2.0 GPa, which indicates that local work-hardening or plastic deformation induces the compressive residual stress.

3.2. Electrochemical studies

3.2.1. Open circuit potential

The OCP curves ($E_{\text{ocp}} = f[t]$) of the femto laser-peened (fLSPed) and BM samples in a 0.6 M NaCl aqueous solution are depicted in Fig. 4. Potential-time transients indicate more anodic (positive) values of the fLSPed sample compared to the BM sample, with relatively stable potential values with lower fluctuations after approximately 30 min immersion in the test solution. The initial OCP values were $-640 \text{ mV}_{\text{SCE}}$ and $-665 \text{ mV}_{\text{SCE}}$ for fLSP and BM samples, respectively. Afterwards, a small gradual potential decrease with longer immersion time was observed, which after 1 h immersion achieved a potential of $-650 \text{ mV}_{\text{SCE}}$ and $-663 \text{ mV}_{\text{SCE}}$.

Similar results of small potential differences between LSPed and BM samples during 1h immersion was also confirmed in our previous research [34,36] in which nanosecond laser peening without coating had been applied. Nonetheless, despite small E_{corr} ennoblement, the

results confirmed improved corrosion resistance with smaller anodic dissolution and 12-times lower corrosion current compared to the untreated BM sample ($0.14 \pm 0.04 \mu\text{Acm}^{-2}$ vs. $1.76 \pm 0.34 \mu\text{Acm}^{-2}$) [36].

On the other hand, rest potential recording at a longer, 24 h, immersion time on pre-corroded samples after CP and exposure to air at ambient conditions for six months (inset in Fig. 4) showed a completely different situation. The fLSPed sample showed a more durable surface state, i.e. lower corrosion activity with 86 mV higher potential after 24 h immersion ($-638 \text{ mV}_{\text{SCE}}$ vs. $-724 \text{ mV}_{\text{SCE}}$). Although both samples showed a similar descending trend in the initial 4 h immersion, afterwards with the fLSPed sample the potential shifted in the anodic direction and held a stable value over a longer duration. Furthermore, two distinctive regions of potential ennoblement could be observed with fLSPed sample, i.e. the first from 4–10 h and the second from 12–24 h immersion, whereas with BM sample a constant potential drop was observed. Such results imply higher resistance of fLSPed surface, with increased long-term stability during longer immersion in the corrosive environment. If this holds true it will be either confirmed or rejected by the wettability measurements, LPR, CP and EIS tests in the following sections.

3.2.2. Linear polarization resistance

LPR measurements were conducted after 1 h immersion at open circuit in the potential range $\pm 10 \text{ mV}$ relative to E_{corr} using 0.1 mV/s scan rate. The values of polarization resistance R_p , determined from the slope of $E-i$ curves [$R_p = (dE/di)$] are given in Table 2.

LPR analysis showed much smaller electric current variation in the given potential range with the fLSP-treated sample, with 18-times higher polarization resistance R_p value for the fLSP sample than the BM sample, i.e. $34.83 \pm 4.51 \text{ k}\Omega\text{cm}^2$ vs. $1.92 \pm 0.23 \text{ k}\Omega\text{cm}^2$.

Furthermore, calculated values of protective efficiency ($P_{\text{EF}} = (R_p^{\text{fLSP}} - R_p^{\text{BM}}) / R_p^{\text{fLSP}} \times 100$)

indicate almost 95% higher resistance to corrosion in a 0.6 M NaCl solution after fLSP treatment as a consequence of surface ablation and generated shock waves [34,40].

3.2.3. Cyclic polarization and wettability measurements

In this section, electrochemical characteristics are analysed via CP curves to study active/passive behaviour and the propensity of material towards pitting corrosion [49,55]. CP curves of non-processed (BM) and fLSP AA2024-T3 samples with the insert of water droplets obtained during the wettability measurements (prior to corrosion experiments) are shown in Fig. 5.

The SCA measurements of the plain non-processed and non-polished Al surface indicate a hydrophilic state with $SCA = 89 \pm 5^\circ$, despite being exposed to ambient conditions for at least one month (or an even longer time, i.e. from the very production onward). On the other hand, the fLSPed sample exposed to ambient conditions for one month after laser treatment developed superhydrophobic properties in a Cassie-Baxter regime [56] with $SCA = 160 \pm 4^\circ$. However, it should be noted that immediately after laser treatment the entire surface was in a superhydrophilic [48,49,57], saturated state [58] of a Wenzel regime [59] with a contact angle $SCA = 0^\circ$, so was more susceptible to corrosion than the base, unprocessed sample [50]. Nonetheless, after a given time (depending on several mechanisms, which are still under debate [60] and not fully accepted to explain this behaviour [50]), superhydrophobicity within a nanostructured surface develops [48,50,61,62]. Therefore, in the scope of this research we will study how this transition to the superhydrophobic state of the fLSPed sample, which was achieved prior to immersion in electrolyte solution, influences the corrosion behaviour.

The various characteristic potentials, such as E_{corr} , E_{pit} and E_{rp} obtained from CP scans, are denoted in Fig. 5 and presented in Table 2, and their detailed description and definition are given in Ref. [50]. From the CP experimental results, a good correlation with the OCP and

LPR measurements can be seen, indicating that after fLSP treatment superior corrosion resistance is achieved. Nonetheless, by comparing E_{ocp} and E_{corr} an opposite tendency can be seen. This is most likely associated with the sequence itself (OCP $\rightarrow$ LPR $\rightarrow$ EIS $\rightarrow$ CP). However, with the fLSPed sample a smaller difference between E_{ocp} and E_{corr} compared to the BM sample was obtained (15 mV vs. 38 mV) indicating more stable condition, with lower corrosion activity during LPR and EIS measurements.

Moreover, despite lower E_{corr} of the fLSPed sample (-656 ± 12 mV_{SCE} vs. -627 ± 7 mV_{SCE}) and a typical active behaviour in the forward (anodic) scan, the BM sample showed a wider hysteresis loop and, consequently more negative E_{rp} and lower E_{sw} , indicating higher susceptibility to localised corrosion attack. Moreover, corrosion current density i_{corr} , obtained via the Tafel extrapolating method confirm an almost 4-times lower value after fLSP treatment (1.95 ± 0.28 μAcm^{-2} vs. 0.49 ± 0.07 μAcm^{-2}). A similar trend was observed for corrosion rate (20.2 ± 2.9 μmyear^{-1} vs. 5.1 ± 0.8 μmyear^{-1}) which was calculated according to Faraday's law [63] in accordance with ASTM G-59-97 standard [64] and by taking into account all the elements, their concentrations and valences that are being oxidised and contributing to corrosion [65].

To evaluate further the effect of fLSP treatment on the improvement against localised corrosion in a chloride-containing solution, ΔE trends [34,55] were determined and compared (Fig. 6). Results clearly demonstrate the beneficial effect of fLSP treatment towards improved corrosion resistance. Analysis confirm a lower degree of material anodic dissolution with 2.5-times larger $E_{sw} - E_{corr}$ value (148 ± 9 mV vs. 59 ± 6 mV) and improved, faster repassivation with smaller $E_{corr} - E_{rp}$ value (122 ± 10 mV vs. 160 ± 9 mV).

Moreover, to obtain information about general resistance against anodic dissolution in a Cl^- solution, the $\Delta E/\Delta i$ gradient was also considered; ΔE represents the difference between two potentials $|E_{sw} - E_{corr}|$ and Δi corresponds to difference between the current density of the

potentials [34]. A distinctive shift in $\Delta E/\Delta i$ gradient can be observed with the fLSP sample, with a more than 150% higher value compared to the BM sample.

Although during CP neither BM nor fLSPed samples showed the classical passive behaviour and that E_{corr} and E_{pit} were superimposed/coincided ($E_{\text{corr}}=E_{\text{pit}}$), all the above results clearly demonstrate the beneficial effect of fLSP treatment against corrosion. Increased corrosion resistance of the fLSPed specimen surface could be attributed to several possible effects produced during the fLSP process, e.g., extreme water repellency, a more stable and corrosion-resistant surface of lower capacitance, refined microstructure and generated compressive residual stresses in the surface layer.

Fig. 7 shows the surface condition of BM and fLSPed samples after polarization tests. Although, both samples confirm pitting attack, the untreated one shows inferior surface integrity with extensive, widespread localised corrosion attack in the form of surface-hemispherical and crystallographic pitting. In contrast, for the fLSPed sample, which was in a superhydrophobic state prior to corrosion testing, the pitting attack was almost eradicated and was mainly confined to few isolated regions (possible areas of non-homogeneity, i.e. fLSP-affected craters, etc.).

From the CP scans (Fig. 5) and SEM observations (Figs. 7 to 9) it seems that the developed superhydrophobicity with entrapped air reduces the fractional area of liquid–solid interface, as suggested by the Cassie-Baxter model [56], hence making the penetration of water molecules and halide ions to the surface more difficult [50,61]. EDS analysis of the top-surface regions (marked on Figs. 8a and 9a) confirmed much smaller incorporation of Cl in the corrosion product on the fLSPed surface, with almost 2-times lower average chloride content than with BM sample (0.56 wt.% vs. 1.11 wt.%). In addition, insets in Figs. 7a and c confirm thicker corrosion product with intensive cracks on the BM sample, which occurred due to dehydration after exposure to ambient conditions. In contrast, with the fLSPed sample fewer

cracks were detected, indicating improved conditions, since cracks presents free paths into the interior of the material, which could promote local acidification and intense material dissolution if the sample were again exposed to a corrosive environment.

Figs. 8 and 9 show SEM/BEI micrographs of BM and fLSPed sample surfaces after CP, along with the EDS analysis results, respectively. On the top surface of the BM sample extensive pitting and IGC attack (Fig. 8b) can be seen, whereas with fLSP the surface condition is greatly improved with reduced pitting and no sign of IGC attack. The IGC attack after CP (Figs. 8d and 9d) was additionally examined by metallographic cross-section observations in the LT–ST plane where the IGC was the most severe [7,9]. With the BM sample (Fig. 8d) several coarser, irregularly shaped Al-Cu-Fe-Mn and smaller S-phase (Al_2CuMg) particles can be seen with IGC penetration to a depth of approximately 30 μm from the surface. Although it is generally accepted that IGC in 2xxx alloys commence with the dissolution of S-phase (dealloying by dissolution of Al and Mg) on grain boundaries due to its active character and micro-galvanic coupling [7,9,12], beyond the pitting potential other effects prevail. Microstructural heterogeneity, active phases along grains, Cu-rich remnants, compositional variations between solute-depleted zone/matrix and solute-depleted zone/S-phase particles with strong galvanic coupling promote increase kinetics leading to ‘chain-link’ shaped IGC attack along the grain boundaries [5,7,11,14].

In contrast, the cross-sectional observations of the fLSPed sample (Fig. 9c and d) did not reveal any signs of IGC attack. Such improvement is associated with fLSP treatment, producing more homogeneous, refined microstructure on the top surface, with smaller amount and/or evenly distributed constituent particles within the Al matrix at the surface. Moreover, it should be noted that with precipitation-hardenable alloys, such as the AA2024 alloy, the size and distribution of the intermetallic precipitates depends on

the quenching and artificial ageing conditions. Thus, the continuous precipitation of intermetallics at grain boundaries can be reduced [34]. Hence, IGC attack can be reduced or prevented in both peak-aged and over-aged AA2024 samples due to dislocation pile-ups, which prevent the diffusion of super-saturated solutes into the grain boundaries and continuous S-phase precipitation [9].

Although the fLSPed sample had the same nominal composition and microstructure, local chemical composition and grain boundaries at the top surface were altered by SPD, high density dislocations [24] and sequential melting/rapid cooling and deposition of the recast material during fLSP treatment, which can contribute to higher charge-transfer resistance R_{ct} with reduced fractional area of the liquid–solid interface and corrosion activity. In addition, as can be seen in Fig.9c, the recast layer was negligibly small ($\sim 2 \mu\text{m}$), homogeneous and with no cracks. Recently, Brunner et al. [7] investigated the corrosion resistance of ultrafine-grained AA2024-T351 produced by severe deformation using multiple-pass equal-channel angular pressing (ECAP) in a 0.5 M NaCl solution. These same authors confirmed mixing and re-distribution of S-phase particles and solute-depleted zones along with significant breakup of second-phase particles after the ECAP process. In addition, results have confirmed that grain-refined and homogenised microstructure with newly formed grain boundaries is not susceptible to IGC attack.

Surface morphology of the BM sample (Fig. 8a) also indicate numerous regions with removed passive/oxide film, which presumably occurred during polarization. EDS analysis results inside this region (Fig 8c – area 3) depicted the highest amount of Al, with $\sim 91 \text{ wt.}\%$, and lowest oxygen content ($\sim 1 \text{ wt.}\%$). Although, the passive/oxide film on Al has very low solubility and electronic conductivity in neutral, noncomplex solutions [66], the oxide film is thinner on the areas with numerous intermetallic phases beneath it. Hence, oxygen reduction and solubility of the oxide film occur in such cathodic areas [67]. In contrast, the fLSPed

sample did not reveal this, indicating a more corrosion-resistant oxide film and a less active surface due to local surface melting, ablation and consecutive shock waves.

3.2.4. Electrochemical impedance spectroscopy

The corrosion resistance and durability in aggressive chloride solution was also examined by EIS studies after 1 h and 24 h immersion (pre-corroded sample after CP tests and exposure to air under ambient conditions for six months) in a 0.6 M NaCl solution at OCP. The EIS spectra are presented in Fig. 10, as Nyquist (a, c) and Bode plots (b, d). The Nyquist plot after 1 h immersion in 0.6 M NaCl in Fig. 10a confirms the conclusion, drawn from the wettability data, LPR and CP tests about the significant influence of fLSP towards a more efficient, corrosion resistant surface. It can be clearly seen from the Bode plot in Fig. 10b that much lower corrosion resistance is obtained with the untreated, BM AA2024-T3 sample, with a smaller diameter capacitance loop and lower, less stable and lower absolute impedance value $|Z|$ at low frequency range with smaller phase angle maxima across a wider frequency range compared to the fLSPed sample.

The EIS spectra after 24 h immersion (Fig. 10c and d) which were performed on pre-corroded samples (after CP + 6 months exposure at ambient conditions) indicate an increased diameter of the capacitance loop with the BM sample, and a new relaxation process at high frequency, which is most probably explained by a porous corrosion product layer and its thickening [19]. In contrast, the fLSPed sample showed similar behaviour regardless of the immersion time in the test solution, with improved long-term stability even when corrosion had been initiated. Moreover, Bode plots in Figs. 10b and d show more stable, higher absolute impedance $|Z|$ values with higher, more stable phase angle maxima across a wider frequency range.

For a more detailed analysis and a deeper discussion of corrosion behaviour, the EIS results were fitted using $(R_s[Q_f(R_f(Q_{dl}R_{ct}))])$ equivalent electrical circuit (EEC), which is presented as an inset in Fig. 10. Although the fitted line of EIS spectra in Fig. 10b show some deviations compared to the experimental data in the low/low-to-mid frequency ranges, the obtained fitting results are in good accordance with other studies in the recent corrosion literature [21,68,69]. The chosen EEC, along with the constant phase elements (Q -CPE), was used due to the best fitting and smallest error ($\chi = 2.29 \times 10^{-4}$ to 2.65×10^{-3}). The oxide film (C_f) and double-layer (C_{dl}) capacitances were calculated from the CPE (Q/n) and resistance R (of the specific group) by $C = (QR)^{1/n} / R$ [34,69]; a detailed description and definition of the specific circuit element are given in full in our recent work [51]. Extracted EIS data from the equivalent circuit are shown in Table 3.

EIS results after 1 h immersion indicated the presence of barrier-type oxide film on both, i.e. BM and fLSPed samples, with similar impedance-associated capacitive response in the Bode spectra. However, the fLSPed sample confirmed a 1.6-times smaller barrier-type oxide film capacitance C_f compared to the untreated sample ($7.39 \mu\text{Fcm}^{-2}$ vs. $11.8 \mu\text{Fcm}^{-2}$). Moreover, the double-layer capacitance C_{dl} decreased more than 30-times ($22 \mu\text{Fcm}^{-2}$ vs. $689 \mu\text{Fcm}^{-2}$), and charge-transfer resistance R_{ct} increased more than 5-times ($30.1 \text{ k}\Omega\text{cm}^2$ vs. $5.33 \text{ k}\Omega\text{cm}^2$) after fLSP treatment. These results suggest that the fLSP treatment in the presence of chlorides contributes to a partial blockage of the active areas, which offers a more corrosion-resistant surface.

EIS spectra obtained after 24 h immersion on pre-corroded samples also showed similar capacitive slopes for both samples. However, due to the presence of an additional element (porous corrosion product film) in the case of the BM sample C_f decreased 4-times, which is in accordance with results from Fig. 8 (EDS results of region 1 & 2). This is also confirmed by the film resistance R_f , which decreased for the BM sample from $4.74 \text{ k}\Omega\text{cm}^2$ to only

30.42 Ωcm^2 . In contrast, the R_f of the fLSPed sample increased sharply from 140 Ωcm^2 to 2.88 $\text{k}\Omega\text{cm}^2$, which indicates a more resistant oxide film compared to the BM sample.

Furthermore, by comparing the changes of the total resistance R_t ($R_t = R_f + R_{ct}$) and double-layer capacitance C_{dl} of BM and fLSPed samples after different immersion times, it can clearly be seen that with fLSP treatment the changes were much smaller than for the BM sample, indicating a durable, corrosion-resistant surface with reduced corrosion kinetics. Although the total resistance R_t of the BM sample increased with pre-corroded sample after longer immersion in the solution, R_t was still 1.8-times lower than for the fLSPed sample (14.7 $\text{k}\Omega\text{cm}^2$ vs. 26.3 $\text{k}\Omega\text{m}^2$); hence, the fLSPed surface can also inhibit the corrosion process on pre-corroded samples with longer immersion in chloride solution.

4. Conclusions

Femto second laser shock peening (fLSP) without a sacrificial overlay under atmospheric conditions with no confining medium was confirmed as an effective method to induce high compressive residual stress and increased hardness in the treated, top-surface layer. Moreover, a hierarchical superhydrophobic surface ($\text{SCA} = 160 \pm 4^\circ$) with almost negligible roughness increased and improved corrosion behaviour in a 0.6 M NaCl test solution.

OCP results during 1 h immersion confirmed potential ennoblement of the fLSPed sample, whereas during longer 24 h immersion time on pre-corroded samples after CP, reduced corrosion activity was also confirmed, with improved long-term stability of fLSPed surface, due to more resistant oxide film. LPR and CP results confirmed 18-times higher polarization resistance R_p (34.83 $\text{k}\Omega\text{cm}^2$ vs. 1.92 $\text{k}\Omega\text{cm}^2$) and 4-times lower corrosion current density i_{corr} (1.95 μAcm^{-2} vs. 0.49 μAcm^{-2}) for the fLSPed sample. Moreover, a lower degree of anodic dissolution, improved and faster repassivation, with more than 150% higher $\Delta E/\Delta i$ gradient

was confirmed for the fLSPed sample, indicating much lower anodic dissolution in aggressive Cl^- solution.

SEM/EDS analyses of the BM sample revealed extensive, widespread localised pitting and IGC attack. In contrast, for the fLSPed sample the pitting attack was confined to a few isolated regions, whereas the initiation of IGC was completely eradicated due to reduced fractional area of liquid–solid interface and a more homogeneous, refined microstructure with evenly distributed constituent particles, which prevented the ‘chain-link’ IGC effect. In addition, EIS results demonstrated good corrosion inhibitive properties of the fLSPed sample, similar to the LPR and CP results, with higher total resistance. Moreover, EIS results have shown similar behaviour of ‘fresh’ and pre-corroded fLSPed samples, with smaller variations of circuit parameters than the BM sample, indicating a durable surface with improved long-term stability against corrosion in a chloride environment.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study

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Electronic annex

Figure captions

Fig. 1. Schematic illustrations of (a) experimental setup for laser irradiation and (b) scan direction of laser pulses for the setup shown in (a).

Fig. 2. SEM images of the surface of AA2024-T3 sample after femtosecond laser peening.

Fig. 3. Residual stress and hardness through-depth distribution of the femtosecond laser-peened AA2024-T3 sample.

Fig. 4. Rest potential ($E_{ocp} = f[t]$) curves of BM and fLSP-treated AA2024-T3 sample (Inset: rest potential recordings at longer 24 h exposure time on pre-corroded samples after CP).

Fig. 5. Cyclic polarization (CP) curves in 0.6 M NaCl solution of BM and fLSPed AA2024-T3 samples (Inset: water droplet/contact angle measurement of BM and fLSPed samples prior to corrosion testing).

Fig. 6. Comparison of characteristic potentials $|E_{sw} - E_{corr}|$ and $|E_{corr} - E_{rp}|$ and anodic dissolution gradient ($\Delta E/\Delta i$) obtained from the CP tests in 0.6 M NaCl water solution.

Fig. 7. SEM/SEI observations of AA2024-T3 sample surface after CP measurements; (a,b) BM and (c,d) fLSPed sample.

Fig. 8. (a,b) SEM/BEI observations of BM surface after the CP, (c) EDS results corresponding to the specific regions and (d) metallographic cross-section (LT–ST plane) showing intergranular attack.

Fig. 9. (a) SEM/BEI observation of fLSPed surface after the CP, (b) EDS results of the specific regions, (c,d) metallographic cross-section (LT–ST plane) showing the top recast surface layer.

Fig. 10. EIS spectra presented as (a,c) Nyquist and (b,d) Bode plots after (a,b) 1 h and (c, d) 24 h immersion (pre-corroded samples after CP and exposure to ambient for six months).

Table captions

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702 [Table 2](#). Characteristic parameters obtained from electrochemical measurements of BM and
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705 [Table 3](#). Circuit parameters for AA2024-T3 samples obtained from simulation of EIS
706 measurements using EEC.

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Table 1. Chemical composition in wt.% of AA2024-T3 used in this study.

Cu	Mg	Mn	Fe	Si	Zn	Ti	Others	Al
4.4	1.4	0.55	0.05	0.02	0.02	0.01	0.01	Bal.

Table 2. Characteristic parameters obtained from electrochemical measurements of BM and fLSPed AA2024-T3 sample in a 0.6 M NaCl: R_p from LPR, and E_{corr} , E_{sw} , E_{tp} and i_{corr} from CP curves.

Parameter	Sample/Condition	
	BM	fLSPed
R_p [$\text{k}\Omega\text{cm}^2$]	1.92 ± 0.23	34.83 ± 4.51
E_{corr} [mV_{SCE}]	-627 ± 7	-656 ± 12
E_{sw} [mV_{SCE}]	-568 ± 5	-508 ± 6
E_{tp} [mV_{SCE}]	-787 ± 11	-778 ± 8
β_a [mV/dec]	20 ± 5	29 ± 3
β_c [mV/dec]	-409 ± 32	-146 ± 18
i_{corr} [$\mu\text{A}/\text{cm}^2$]	1.95 ± 0.28	0.49 ± 0.07
R_{corr} [$\mu\text{m}/\text{year}$]	20.2 ± 2.9	5.1 ± 0.8
SCA [$^\circ$]	$89 \pm 5^\circ$	$160 \pm 4^\circ$

Table 3. Circuit parameters for AA2024-T3 samples obtained from simulation of EIS measurements using EEC.

Parameter	Uncorroded samples after 1h immersion in 0.6 M NaCl		Pre-corroded samples (after CP) after 24h immersion in 0.6 M NaCl	
	BM	fLSPed	BM	fLSPed
R_s [Ωcm^2]	4.15	3.64	2.63	2.73
Q_f [$\text{Scm}^{-2} \text{s}^n$]	13.9×10^{-6}	7.39×10^{-6}	6.54×10^{-6}	13.2×10^{-6}
$n(Q_f)$ [/]	0.94	1	0.91	0.80
C_f [Fcm^{-2}]	11.8×10^{-6}	7.39×10^{-6}	2.67×10^{-6}	5.85×10^{-6}
R_f [Ωcm^2]	4.74×10^3	140	30.42	2.88×10^3
Q_{dl} [$\text{Scm}^{-2} \text{s}^n$]	68.9×10^{-5}	2.53×10^{-5}	1.99×10^{-5}	1.80×10^{-5}
$n(Q_{dl})$ [/]	1	0.67	0.76	0.82
C_{dl} [Fcm^{-2}]	68.9×10^{-5}	2.20×10^{-5}	1.34×10^{-5}	1.49×10^{-5}
R_{ct} [Ωcm^2]	0.53×10^4	3.01×10^4	1.47×10^4	2.34×10^4
R_t [Ωcm^2]	1.01×10^4	3.02×10^4	1.47×10^4	2.63×10^4