

Research Article

Galvanic and asymmetry effects on the local electrochemical behavior of the 2098-T351 alloy welded by friction stir welding



Mariana X. Milagre^{a,*}, Uyime Donatus^a, Naga V. Mogili^b, Rejane Maria P. Silva^a,
Bárbara Victória G. de Viveiros^a, Victor F. Pereira^b, Renato A. Antunes^c,
Caruline S.C. Machado^a, João Victor S. Araujo^a, Isolda Costa^a

^a Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN, Av. Prof. Lineu Prestes, 2242, São Paulo, Brazil

^b Laboratório Nacional de Nanotecnologia, LNNano/CNPEN, Rua Giuseppe Máximo Scolfaro, 10.000, Polo II de Alta Tecnologia de Campinas, Brazil

^c Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas, UFABC, Av. dos Estados 5001, Santo André, Brazil

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ABSTRACT

Scanning electrochemical microscopy (SECM) and scanning vibrating electrode technique (SVET) were used to investigate the electrochemical behaviour of the top surface of the 2098-T351 alloy welded by friction stir welding (FSW). The SVET technique was efficient in identifying the cathodic and anodic weld regions. The welding joint (WJ), which comprises the thermomechanically affected zone (TMAZ) and the stir zone (SZ), was cathodic relative to the heated affected zone (HAZ) and the base metal (BM). The reactivities of the welding joint at the advancing side (AS) and the retreating side (RS) were analyzed and compared using SECM technique in the competition mode by monitoring the dissolved oxygen as a redox mediator in 0.005 mol L⁻¹ NaCl solution. The RS was more electrochemically active than the AS, and these results were correlated with the microstructural features of the welded alloy.

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1. Introduction

Friction stir welding (FSW) was developed in the 90s' as an alternative to conventional methods for welding alloys of low weldability. This process is characterized by the joining of materials without melting. The heat is generated from the friction caused by the relative movement of the tool against the material to be welded. The traverse and rotational movements of the tool create an asymmetric joint, since the velocities of two symmetrical points on the advancing side (AS) and retreating side (RS) are different. Since the heat transfer and material flow on both sides of the weld are dissimilar, the two sides of the joint present different microstructural features. The material transport occurs from the RS to the AS. In the AS, the directions of tool rotation and traverse motion are the same, whereas in the RS they are in opposite directions [1–4]. Due to the different thermal cycles and the deformation experienced during the process, different welding zones are generated. In the stir zone (SZ), the high temperatures reached during the FSW process cause dynamic recrystallization to occur. This zone is characterized

by equiaxed grain shapes and phase dissolution. In the thermomechanically affected zone (TMAZ), the grains are deformed due to the tool movement and the high temperatures reached, and dissolution of strengthening phases occurs [4,5]. In the heat-affected zone (HAZ), however, the temperatures reached are not sufficient for the total dissolution of strengthening phases. Thus, this zone is characterized by partial phase dissolution and coarsening. The shapes and sizes of the grains are the same as those of the base metal (BM).

Some authors have reported differences in the corrosion resistance of the AS and the RS. According to Deng et al. [6], the AS is the most susceptible to stress corrosion cracking (SCC). Dudzik [7], in his study of a welded 7020 Al-alloy, reported that for the FSW parameters used, the AS presented higher corrosion resistance than the RS. Most recently, Queiroz et al. [8] showed that the FSW process caused unequal distribution and clustering of the coarse intermetallic particles across the welding zones of a similar 2024-T3 welding joint. They also observed that these clusters were more abundant in the TMAZ of the RS, resulting in high localized corrosion susceptibility of this zone. However, reports on the asymmetry effects of the FSW process on the corrosion behaviour of Al-Cu-Li alloys are still scarce.

* Corresponding author.

E-mail address: marianamilagre@yahoo.com.br (M.X. Milagre).

The Al-Cu-Li alloys are advanced materials designed for the aircraft industry. The addition of Li in these materials increases the mechanical resistance of the alloy and reduces its density. Therefore the application of these materials in aircraft structures is of interest in terms of the reduction of fuel consumption [9–12]. The corrosion behaviour of the Al-Cu-Li alloys has been reported [13–18]. Machado et al. [15] correlated different types of localized corrosion in the friction stir welding (FSW) zones of the 2198-T8 alloy with the variation in microstructure when the alloy is subjected to corrosion test in a hydrogen peroxide-chloride environment. The corrosion modes were correlated with T1 phase distribution along the weldment. According to the authors, galvanic coupling effects were pronounced since the SZ was not attacked when tested in the coupled state but it was strongly attacked when exposed separately. Corral et al. [18] showed that the 2195 FSW zone and BM behaved similarly, having nearly the same currents and corrosion potentials. In a recent study, Donatus et al. [13] correlated the corrosion resistance, anodic hydrogen evolution and microhardness, that is related to T1 phase content, in the friction stir weldment of 2198-T851 alloy. In this case, the results revealed that the BM is the region most susceptible to corrosion, unlike other 3rd generation Al-Cu-Li alloys where the welding regions are the most vulnerable to corrosion. Moreover, a strong correlation between microhardness, corrosion resistance and anodic hydrogen evolution during dissolution was also observed by the authors, since they are all dependent on the volume fraction of T1 phase across the friction stir weldment of the alloy. Finally, Ma et al. [19] showed that friction stir welding parameters, such as rotation speed and the welding speed, affect the Al-Cu-Li alloy 2198 microstructure. Consequently, the corrosion behavior can be modified by welding. Due to the complex microstructure of Al-Cu-Li

alloys and the effects of the welding parameters, each FSW process is unique.

The 2098-T351 is a 3rd generation Al-Cu-Li alloy, which was developed as a substitute for the conventional 2XXX series alloys [20–23]. This type of alloy present different types of phases, which has been reported in several other studies [4,24,25]. Salem and Lyons [24] and De et al. [25] identified the presence of β' (Al_3Zr), δ' (Al_3Li) and T1 (Al_2CuLi) phases in this kind of alloys. More recently, in one of our previous works, the phases present in the 2098-T351 alloy welded by FSW were identified [4]. Besides the T1, δ' and β' phases, the Ω (Al_2Cu) and θ' (Al_2Cu), were also identified in the BM. However, the morphology and amount of these phases were modified by the FSW process. The T1 phase content was reduced in the welding zones. This phase was also coarser and smaller in these zones than in the BM. The δ' content increased in the welding zones and GP-zones were found in these regions. On the other hand, the θ' content was significant only in the BM. All these modifications can affect the corrosion behaviour of the welded alloy in relation to the BM. Limited reports about the corrosion behaviour of the 2098 Al-Cu-Li alloy were found in the literature [23,26,27]. Moreover, investigations related to the effects of FSW on the corrosion susceptibility of the 2098 Al-Cu-Li alloy are scarce.

There are a few reports on the use of local electrochemical techniques for the electrochemical characterization of Al-Cu-Li alloys [23,27,28]. Al-Cu-Li alloys are highly susceptible to localized corrosion [13,29,30]. This is characterized by non-uniform current densities and variations in the distribution of electrochemically active species [28]. In this regard, scanning probe techniques are suitable for this kind of study [31–33], particularly in the study of welded Al-alloys. Bertonecello et al. [34] used the scanning vibrating electrode technique (SVET) to study the corrosion behaviour

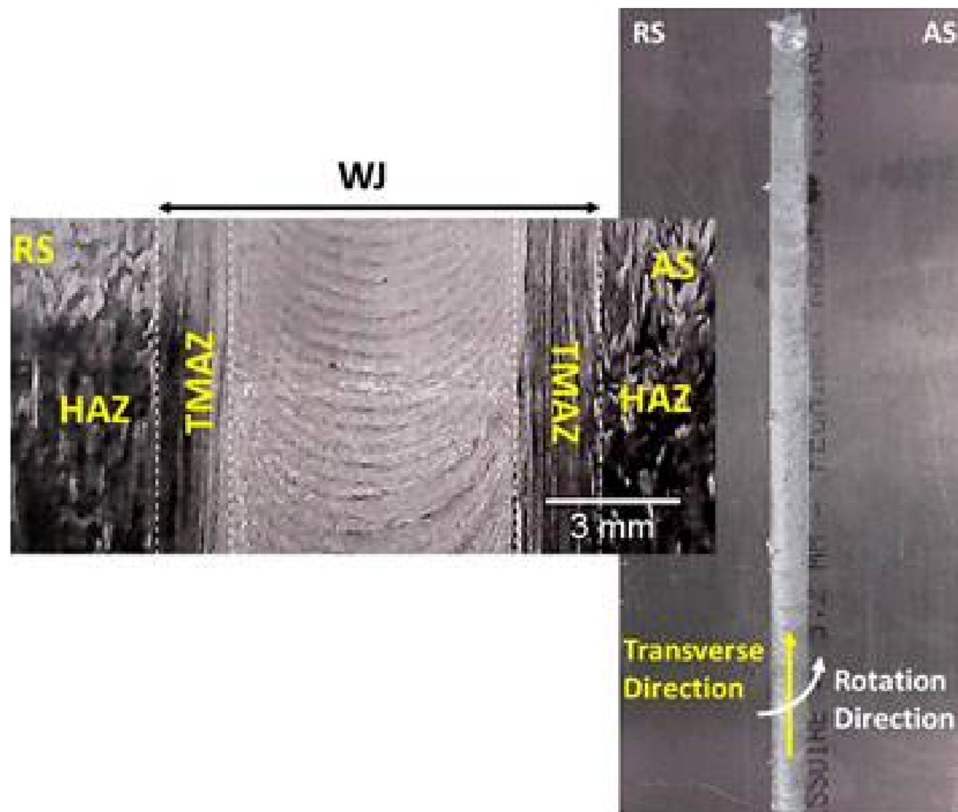


Fig. 1. Optical macrographs of the surface of the friction stir weldment of the 2098-T351 alloy showing the welding zones at the retreating side (RS) and advancing side (AS) of the weldment. TMAZ is the thermomechanical affected zone, HAZ is the heated affected zone and WJ is the welding joint which corresponds to the stir zone (SZ) and the TMAZ.

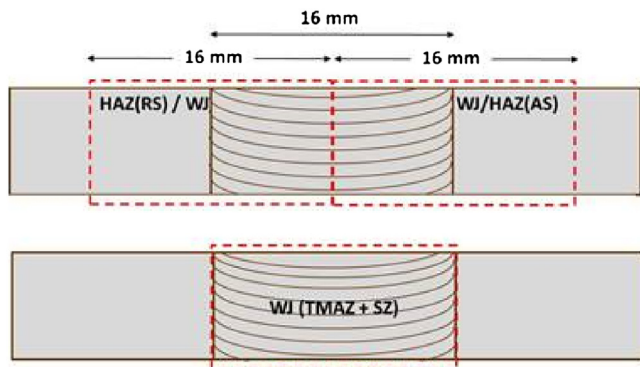


Fig. 2. Schematic diagram of the 2098-T351 alloy welded by FSW showing the regions (red rectangles) analyzed by SVET.

of friction stir lap weld of 7050/AA2024 alloys. Using this technique, the authors showed galvanic coupling effects resulting from the joining of the two alloys. Galvanic coupling effects were also found by De Abreu et al. [35] in their study of dissimilar alloys of 2024 and 7475 alloys welded by FSW using local electrochemical impedance spectroscopy (LEIS). Donatus et al. [13] also used SVET

measurements to establish a correlation between corrosion resistance, anodic hydrogen evolution and T1 phase for the 2198-T851 welded alloy.

Scanning electrochemical microscopy (SECM) is a powerful technique for the investigation of localized corrosion processes [36,37]. The technique presents the advantages of obtaining *in-situ* topographic and electrochemical reactivity information on the surfaces exposed to aqueous solutions [31]. However, this technique has been rarely used for the study of the electrochemical activities of different zones affected by welding [38]. One of the few works is that of Sidane et al. [38] who used SECM and LEIS to investigate the local electrochemical behaviour of the interface in the welded zones of the dissimilar 2050-T8 and 7449-T79 alloys welded by FSW. According to the authors, SECM was useful for evaluating the electrochemical kinetics of the passive layer in the different zones of the welded alloy.

In this work, the galvanic and asymmetry effects of the FSW process on the microstructure of the 2098-T351 was investigated and correlated with the electrochemical behaviour of each side of the welded joint using conventional and local electrochemical techniques in a chloride solution. To our knowledge, the effects of asymmetry generated by the FSW process on the corrosion resistance of Al-Cu-Li alloys have not yet been reported.

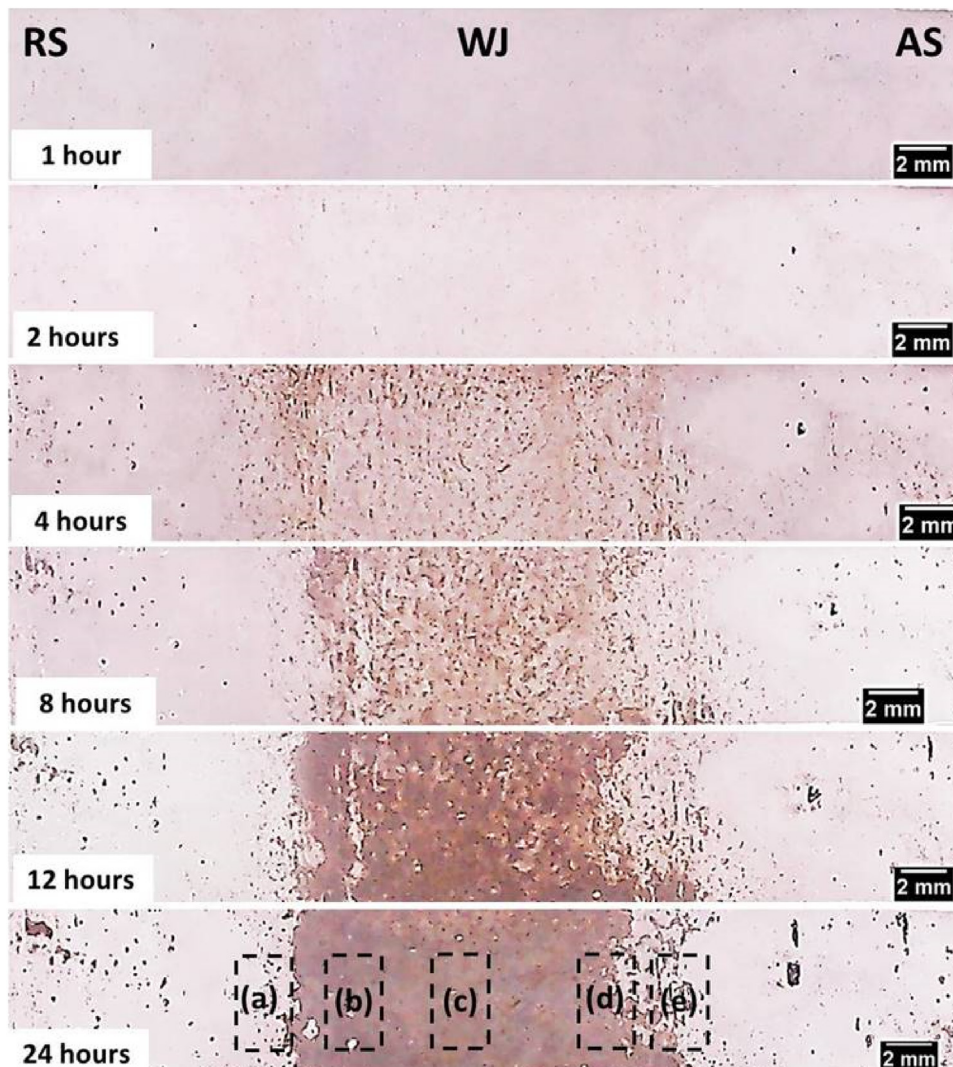


Fig. 3. Optical images of the surface of the 2098-T351 alloy welded by FSW after various immersion times in 0.005 mol L⁻¹ NaCl solution.

2. Materials and methods

2.1. Material

3 mm thick plates of the 2098-T351 alloy (3.4 wt% Cu, 1 wt% Li, 0.3 wt% Mg, 0.3 wt% Ag, 0.4 wt% Zr, 0.04 wt% Fe, 0.05 wt% Si, 0.02 wt% Zn, 0.003 wt% Mn) were used in this work. The FSW process was performed using a rotation speed of 700 rpm, a transverse speed of 300 mm/min and a load in the range of 8–15 kN. An H13 steel tool with a 16 mm diameter shoulder and an adjustable pin, 3.2 mm in length in accordance with the plate thickness, was used. More details about the welding procedure are provided in our previous work [4]. All tests in this work were carried out on the top surface of the weldment. Fig. 1 shows the welded plate and the dimensions of the welding zones.

2.2. Microstructural characterization

Samples of the welded 2098-T351 were ground and polished using silicon carbide papers (#800, #1200 and #4000 grit sizes) and diamond pastes (3 μm and 1 μm). Optical microscopy was used to characterize the top surface of the weldment after etching the samples in a solution composed of 2% HF and 25% HNO_3 . Scanning electron microscopy (SEM) images were acquired using a Hitachi TM 3000 microscope with an incident beam of 15 kV. Samples were prepared for transmission electron microscopy (TEM) by using discs of 3.0 mm which were punched from mechanically polished samples and electropolished at 20 V in a solution of nitric acid (30%) in methanol. TEM samples were prepared using TenuPol electropolishing equipment. TEM imaging was carried out in JEOL 2100 microscope operating at 200 kV. Microhardness measurements were used to correlate the microstructural modifications on both sides of the weldment with the electrochemical results using a Knoop/Vickers Tukon 1202 Wilson Hardness tester. Microhardness measurements were obtained at the surface of the sample in steps of 0.2 mm using a load of 200 gf for 10 s. Images of the corroded samples were also obtained using a 3D profilometer ZYGO's ZeGageTM.

2.3. Immersion test

The surfaces of the prepared samples were immersed in naturally aerated 0.005 mol L^{-1} NaCl solution. The samples were removed, rinsed and dried after different times of immersion for surface observation at selected intervals until 24 h. The immersion tests were carried out at room temperature ($22 \pm 2^\circ\text{C}$). The exposed surfaces of the samples were observed by SEM and optical microscopy.

2.4. Gel visualization test

The anodic and cathodic zones in the weldment were evaluated using a gel visualization test. The gel was prepared by adding 3 g of agar-agar and 7 mL of universal indicator to 100 mL of a boiling 0.7 mol L^{-1} NaCl solution [35,39]. The surfaces exposed to the gel were sequentially polished up to 1 μm . The other regions of the samples' surface were protected using varnish coating. Subsequently, the gel was poured on the polished surfaces and the surfaces were monitored for 4 h.

2.5. Surface characterization

The chemical composition of the surfaces of the samples was analyzed by X-ray photoelectron spectroscopy (XPS) using a ThermoFisher Scientific spectrometer, model K-alpha⁺. The beam was produced by a monochromatic AlK_{α} radiation source. The spot size

was 400 μm and the analysis chamber pressure was approximately 10^{-7} Pa. Survey XPS spectra of the welded samples were obtained from the welding joint (WJ), before and after immersion in 0.005 mol L^{-1} NaCl solution for 24 h.

2.6. Open circuit potential measurements

The open-circuit potential of the samples was monitored as a function of time using $\text{Ag}/\text{AgCl}_{\text{KCl(sat)}}$ as a reference electrode. The exposed surface of the working electrode was 0.25 cm^2 , and the electrolyte was 0.005 mol L^{-1} NaCl solution. The welding zones were individually masked using beeswax and the delimitation of the zones isolatedly tested was based on the microstructural characterization. Open circuit potentials were measured every 2 for 24 h.

2.7. Scanning vibrating electrode technique (SVET)

An Applicable ElectronicsTM SVET machine with Automated Scanning Electrode Technique (ASET) software was employed for the scanning vibrating electrode technique (SVET) tests. The probe used was a 15 μm diameter Pt-Ir probe with a vibrating amplitude of 19 μm . It was placed at (100 ± 3) μm above the surface. The welded samples of the 2098-T351 alloy were used as the working electrode and they were embedded in epoxy resin for the measurement procedure. The configuration of the samples for the measurements is shown in Fig. 2. The electrolyte used for the SVET tests was 0.005 mol L^{-1} NaCl solution, and the test duration was 24 h. SVET maps were obtained for every 2 h. More details about the SVET experiment are provided in previous work [28].

2.8. Scanning electrochemical microscopy (SECM)

Scanning electrochemical microscope produced by Sensolytics GmbH Bochum, Germany was used in a three-electrode configuration. The tip was a 25 μm Pt disk. Pt was used as the auxiliary-electrode and an $\text{Ag}/\text{AgCl}/\text{KCl}_{\text{(sat)}}$ electrode as the reference electrode.

The calibration of the microelectrode, prior to the SECM measurements, was carried out by cyclic voltammetry (CV) in 0.1 mol L^{-1} KCl solution with 0.005 mol L^{-1} $\text{K}_4[\text{Fe}(\text{CN})_6]$. A sigmoidal shaped CV was obtained [40]. CV data provides the steady-state diffusion-controlled limiting current (i_{lim}). The tip potential during calibration was set at +0.40 V Ag/AgCl to perform the oxidation of ferrocyanide to ferricyanide ions at the tip, Eq. (1):



The redox species through which the tip–substrate interaction is mediated can diffuse in or out of the tip/substrate gap. If there is a diffusion of redox active species between the tip and substrate, it can impact both spatial and temporal resolution. So the tip/substrate separation distance should be minimized without an occurrence of contact between the tip and analysed surface [41]. The limiting current (i_{lim}) is a function of the microelectrode radius (a), the concentration of the species (C), and its diffusion coefficient (D), as shown by Eq. (2):

$$i_{\text{lim}} = 4nFDCa \quad (2)$$

In order to find the optimal tip working distance, z-approach curves were obtained using the competition mode. In this mode, the approach-curves obtained by oxygen reduction showed a reduction in current when the tip approaches the surface since the sample is consuming oxygen. The approach-curves provided information on the distance at which it was possible to observe the electrochemical response of the surface. In this study, it was 20 μm above the surface.

The experiments were performed in 0.005 mol L^{-1} NaCl solution at room temperature and at the OCP of the sample. The competition mode of the SECM was used, and the reduction of oxygen in the surface of the 2098-T351 alloy weldment was studied. In this mode, the molecular oxygen content is monitored from its electro-reduction at the tip at -0.70 V Ag/AgCl , Eq. (3), in aerated neutral and alkaline electrolytes. More details about this SECM operation mode are provided in the literature [32,33,42].



3. Results and discussion

3.1. Galvanic coupling effects

Monitoring of the welded samples of the 2098-T351 alloy immersed in 0.005 mol L^{-1} NaCl solution showed different evolution of corrosion features on the various welding zones, as shown in Fig. 3. The differences between the welding joint (WJ), the HAZ and the BM were easily identified. Severe localized corrosion (SLC) was observed in the HAZ and the BM; whereas, in the WJ, the corrosion attack was mainly associated with the micrometric particles which resulted in trenching and cavities. Although the develop-

ment of SLC started immediately after immersion, differences in corrosion features between the zones only became more evident between 2 h and 4 h of the test. On the HAZ and the BM, corrosion products deposition was localized, as indicated in Fig. 4(a) and (e). On another hand, deposition of corrosion products was evenly distributed on the surface of the WJ and it increased with time, as evident in Fig. 4(b–d). This behaviour is due to the galvanic coupling between the HAZ and the WJ.

The WJ (TMAZ and SZ) was cathodic relative to the BM and the HAZ and the dark colour observed in the WJ could be related to the alkalization of the environment in contact with this region which resulted in the chemical attack of the oxide film. The local pH increase of solutions in contact with Al alloys has been previously reported and associated with the micrometric particles which act as local cathodes relative to the matrix [43,44]. Fig. 5 shows EDX maps of the micrometric particles in the 2098-T351 alloy. These are majorly composed of Al-Cu-Fe or Al-Cu, thus cathodic in relation to the matrix [28]. Moreover, as previously reported, the tool movement breaks down the micrometric particles increasing the surface area of the cathodic region on the WJ joint. Fig. 6 shows the differences between the distribution of the micrometric particles in the BM and the WJ. In the BM, the micrometric particles are aligned with the deformation direction, while in the WJ, the

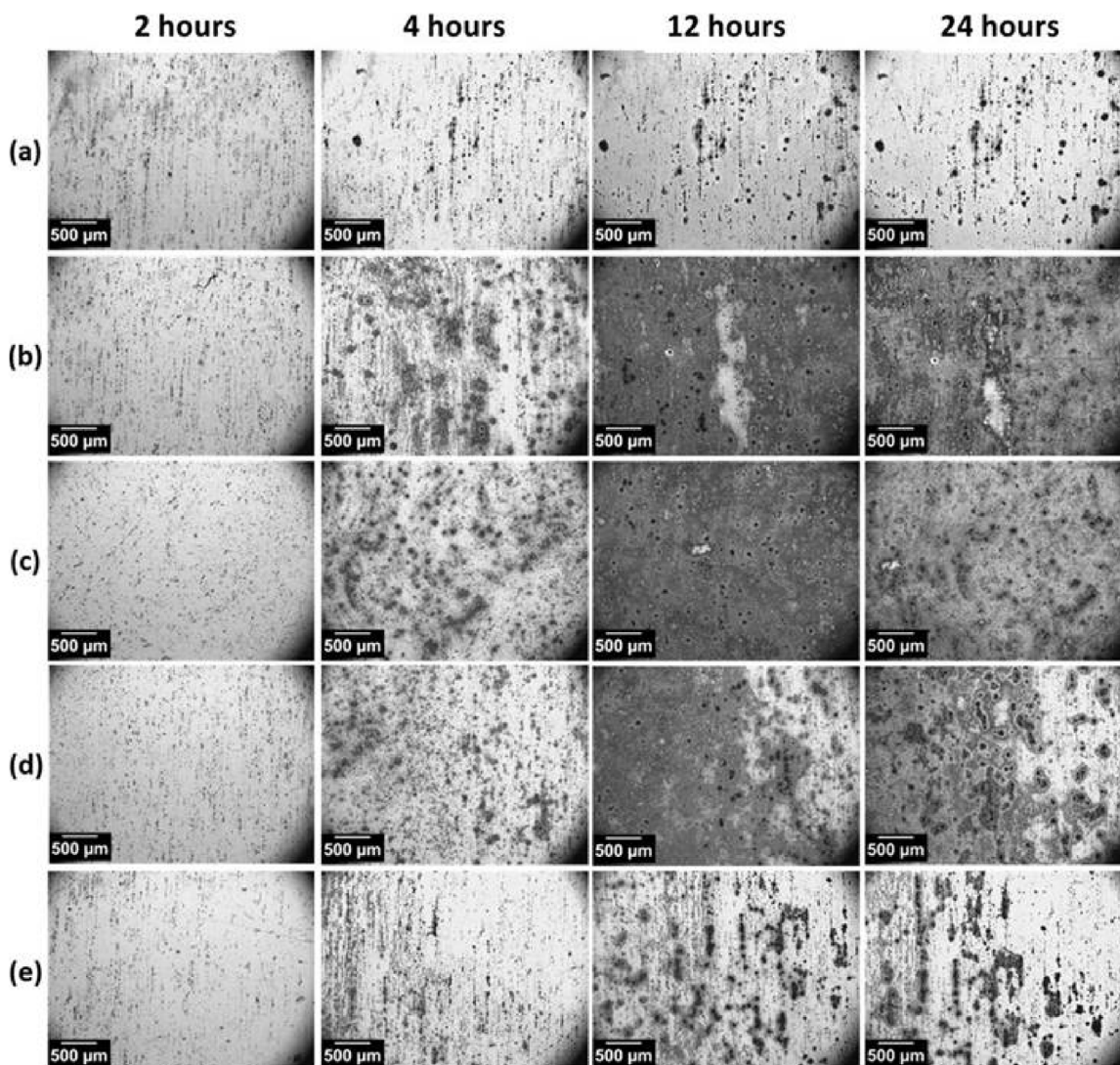


Fig. 4. Optical images in high magnification of the squared regions in Fig. 3 of the 2098-T351 alloy welded by FSW after various immersion times in 0.005 mol L^{-1} NaCl solution.

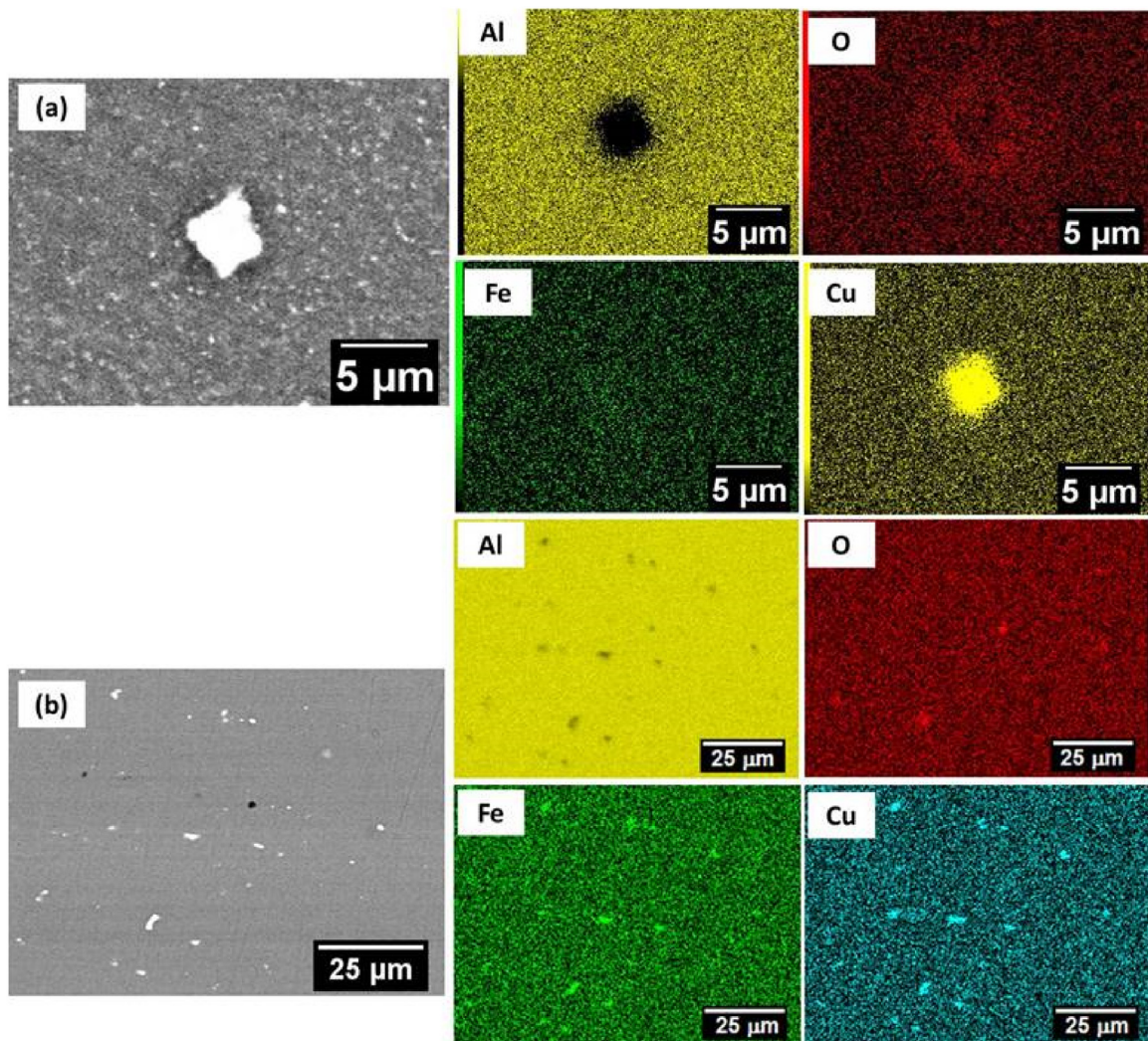


Fig. 5. EDX analysis of the (a) Cu-rich and (b) Cu, Fe-rich micrometric particles in the 2098-T351 alloy.

micrometric particles are broken and randomly distributed. In our previous work [4], modifications in the distribution and morphology of the nano-sized particles were observed. Fig. 7 shows TEM images from the different welding zones. As observed, T1 (Al_2CuLi) and δ' (Al_3Li) phases are dominant in the BM and HAZ, whereas the T1 particles are rare in the WJ where the δ' (Al_3Li) and Ω (Al_2Cu) are present. Li containing phases are anodic in relation to the Al-matrix [13,15,28,45–47]. In the HAZ and BM, the large number of T1 and δ' phases explain their anodic behaviour in relation to the adjacent zones. The temperatures reached in the HAZ during the welding process ($<380^\circ\text{C}$) were lower in relation to those reached in the WJ ($600\text{--}300^\circ\text{C}$) [4]. The high temperatures reached during the welding process, in addition to the mechanical effects of the welding tool, promote the modifications in the microstructure of the 2098-T351 alloy. T1 phase dissolution and the enrichment of the matrix in Li and Cu favour potential differences between the HAZ/BM and the WJ. The T1 phase is responsible for SLC sites in the Al-Cu-Li alloys [23,28,47]. Finally, the anodic currents associated with these sites are larger in relation to that related to trenching. Recently, Araujo et al. [48] showed how thermomechanical treatment affects the corrosion resistance of the 2198 Al-Cu-Li alloy and how the density of T1 phase lead to increased anodic currents associated with the corrosion process. Thus, it is believed that the decrease in the amount of the T1 phase in the WJ is responsible for the macro-galvanic coupling between the BM/HAZ and the WJ.

Agar gel test has been employed effectively in the study of galvanic coupling in welded Al alloys [35,39]. This test is efficient in the identification of anodic and cathodic regions in welded samples by pH modifications due to the change in colour to green (alkaline) at the cathodic sites, and to red (acidic) at the anodic regions. In this study, Fig. 8 shows the results obtained with the agar-gel test when the weldment was analyzed in different coupling configurations. From Fig. 8(a), when the HAZ and the WJ zones are galvanically coupled, the agar gel in contact with the WJ shows an increase in pH due to the preferential occurrence of cathodic reactions on this zone. However, as shown in Fig. 8(b), when the WJ is analyzed separately, no significant differences between the TMAZ and SZ are observed.

In neutral aerated solution, the main cathodic process is the oxygen reduction reaction according to Eq. (3) [35], which lead to a local alkalization, whereas at the anodic areas, the main reaction is shown by Eq. (4):



Also, a global electron exchange, related to cation hydrolysis, can be represented by Eq. (5):



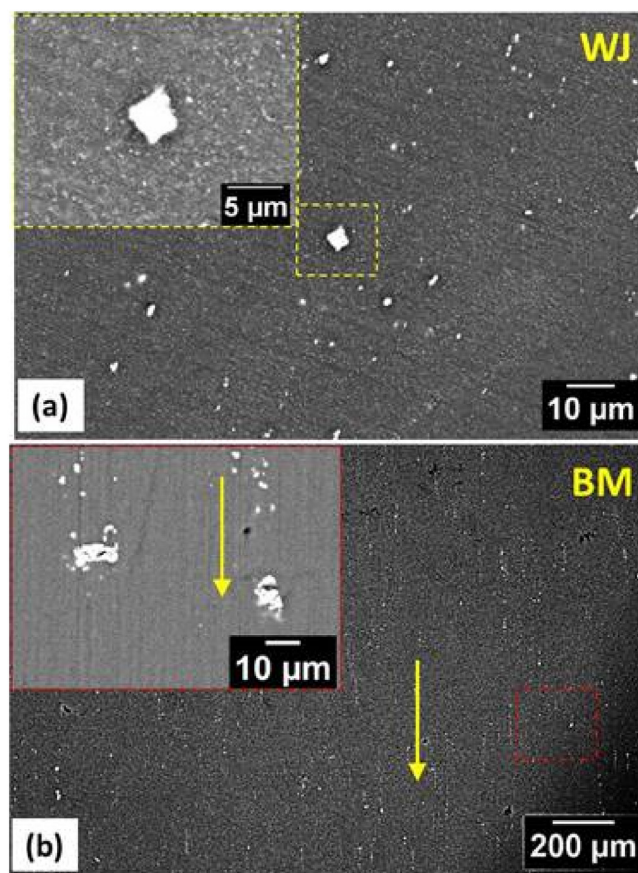


Fig. 6. SEM micrographs showing the distribution and sizes of the micrometric particles in the (a) welding joint and (b) base metal of the 2098-T351 alloy.

This promotes acidification of the region. As can be inferred from Figs. 3 and 4, metal dissolution and oxygen reduction occur initially in all zones of the weldment. However, as the corrosion proceeds, the cathodic reactions became predominant in the WJ, and this was shown by the green colour in the agar gel in this zone. On the other hand, an orange colour developed in the agar gel above the HAZ and BM due to acidification resulting from the hydrolysis reactions related to metal dissolution. The orange areas were mainly associated with SL. In these sites, metal dissolution and hydrolysis occurred producing H^+ , and, consequently, a decrease in local pH. On the other hand, in the WJ, production of hydroxyl ions simulates the behaviour of aluminium alloys in alkaline solutions [43,44,49–52]. The increase in pH leads to increased solubility of the aluminium oxide film and exposure of the bare metal which is oxidized, making the mechanism of Al dissolution in alkaline environment complex due to the competition with hydrogen recombination, as shown by Eqs. (6–8) [51].



According to Koroleva et al. [44], the alkalization process involves the chemical dissolution of the naturally formed alumina film over the surface of an aluminium alloy. Also, the cations of Al^{3+} generated by oxidation at the alloy/alumina film interface migrate across the residual alumina film and get ejected into the solution. Furthermore, matrix oxidation results in the ejection of cations of alloying elements into the solution, for example, Cu^{2+} , Ag^+ , which

can redeposit at the cathodic sites providing further sites for the continuity of the process.

Fig. 9 shows XPS results obtained for the polished and corroded samples of the 2098-T351 alloy after 24 h of immersion in 0.005 mol L^{-1} NaCl solution. The film of the corrosion products was enriched in Ag and Cu, as observed when the spectra of the corroded sample are compared with that of the polished sample. The higher Mg content in the polished sample in relation to the corroded one is related to the high activity of this element, which is rapidly dissolved during the attack of the matrix. Peaks of Mg1s with binding energies around 1303.9 eV are due to magnesium oxide [53]. The insolubility of Mg at high pH has been reported [51]. Binding energies between 932.2 eV and 953.2 eV indicate the presence of Cu-rich remnant particles in the alloy [54], Cu [55,56] and Cu oxide redeposition [57]. The Ag peaks are related to the presence of Ag oxide (374 eV) and metallic Ag^0 (368 eV) [58]. All these modifications in phase distribution contribute to potential differences between the WJ and the HAZ or the BM. Redeposition of elements on the cathodic sites in alkaline environments has been reported [59]. Ag and Cu deposition on the WJ accelerates the corrosion process at the anodic regions. Comparison of the tested welded samples with the BM, as presented in Fig. 8(a, b) and (c), respectively, shows that while cathodic and anodic regions were observed on the welded samples from the first minutes of the test, a longer period of time was required to observe the anodic and cathodic areas on the BM. Thus, the welding process promotes electrochemical activity and, consequently, pH modifications over the electrode surface. Enlarged cathodic area related to the WJ increased the aggressiveness of the attack.

The potential differences between the welding zones and the BM were confirmed by OCP measurements, as shown in Fig. 10.

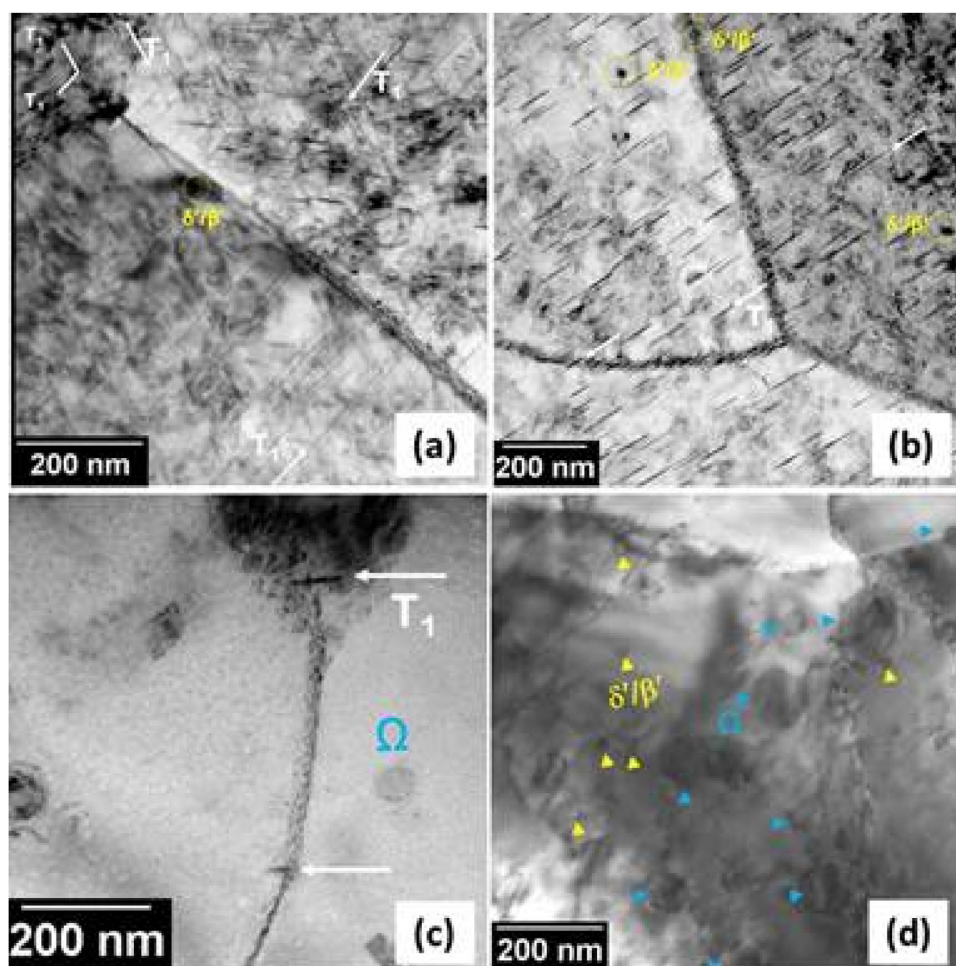


Fig. 7. TEM bright-field images showing nano-sized phases distributions in the (a) base metal (BM), (b) heated affected zone (HAZ) and (c, d) welding joint (WJ).

Monitoring of the OCP with the time of immersion in 0.005 mol L^{-1} NaCl solution showed higher potentials for the WJ in relation to the HAZ and BM during the 24 h of immersion. According to Keddam et al. [60], OCP variations are related to changes in the surface oxide. The variation in the OCP values depends on the volume of second phases. The increase in the population of the cathodic particles due to tool movement, as revealed in Fig. 6, and the decrease in the anodic ones, in the WJ, led to an increased rate of aluminium matrix dissolution. The decrease in OCP in the first hours of immersion might be related to oxide film dissolution. The subsequent increase in OCP could be due to Cu and Ag enrichment at the surface, as revealed by XPS measurements and, also, to corrosion product deposition at the exposed surface. Furthermore, the OCP measurements showed that the zones of the weldment with lower potentials are the interfaces between the HAZ and WJ in the RS and AS. In these regions, the galvanic coupling is efficient since a region of higher amounts of T1 (anodic HAZ) was exposed to the electrolyte with a region of lower amounts of T1 phase (WJ).

One major criticism of the agar-gel test is related to the hindrance to free movement of ions in the gel environment. In order to further investigate the sites where the corrosion phenomena predominate, SVET tests were performed and the SVET maps obtained after 2 h and 24 h of immersion in 0.005 mol L^{-1} NaCl solution are shown in Figs. 11 and 12, respectively. The welding zones were analyzed in different arrangements, as illustrated in Fig. 2. The results agreed with those of the other tests and showed that the WJ is cathodic in relation to the BM and the HAZ. The anodic sites in the WJ presented lower current densities when compared with

the anodic sites on the HAZ of both the AS and RS. This behaviour is related to the phase dissolution, which decreases the effect of SLC on the anodic current densities and also to the increase in the cathodic areas due to the fragmentation of the micrometric particles promoted by the tool movement. This results could be related to the results obtained by Araujo et al. [48]. The authors compared the corrosion behaviour of the 2198 alloy with different thermomechanical treatments. The SVET maps showed that the higher anodic currents were promoted by the SLC observed on the T851 and T8 alloys, which presented a high density of the T1 phase due to the artificial ageing. For the T3 condition, the current densities obtained by SVET showed lower anodic currents, since natural ageing does not promote the precipitation of the T1 phase (which is associated with SLC in this alloy) in large amounts. This makes trenching the main corrosion process, and the associated current densities of this process are far lower compared with those of the SLC process. Similarly, in the welding joint of the welded 2098-T351, where the T1 phase density is lower, the main anodic process is related to trenching. Thus, the anodic currents associated with the WJ are lower in comparison with those of the BM and HAZ, which presents SLC sites. Also, the predominance of cathodic activities in the WJ became evident for longer periods of immersion, as shown in Fig. 12. The activities on the WJ decreased with time. A uniform current density distribution was observed in the WJ, as shown in Fig. 12(b), and the current densities related to this region were ten times lower than those resulting from the galvanic coupling between the WJ and the HAZ, where SLC sites (red arrows) were seen both on the AS and RS, as presented in Fig. 12(a) and (c). The reduction in the electro-

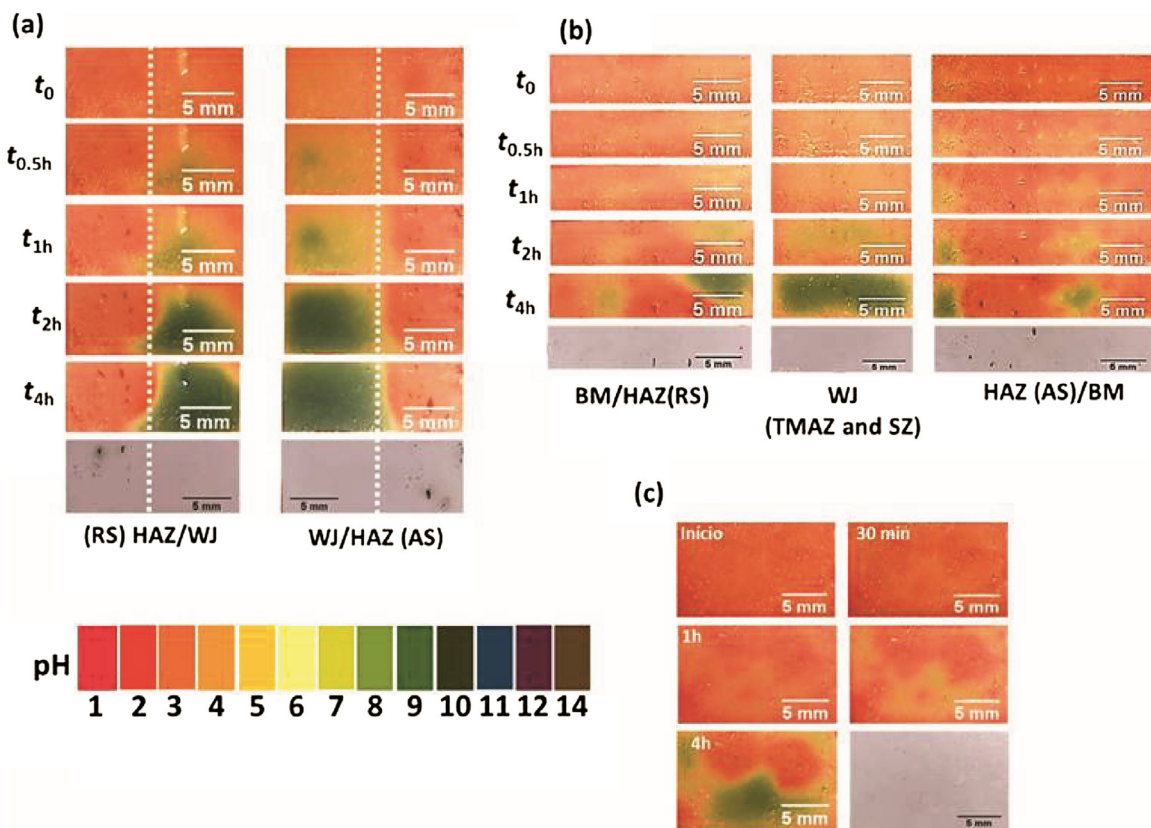


Fig. 8. Agar visualization test for different configurations of the 2098-T351 alloy welded by FSW: (a) galvanic coupling between the welding joint and the heat-affected zone (WJ/HAZ) for both the retreating (RS) and advancing (AS) sides; (b) three differently separated regions of the weldment comprising the base metal and HAZ (BM/HAZ) and the thermomechanical affected zone and stir zone (TMAZ/SZ) or WJ.

chemical activity of the WJ, as observed in Fig. 12(d–f), is related to the growth of the oxide film on this zone, which can act as a barrier for the continuity of the process.

The SVET maps showed that the highest anodic currents were related to SLC. At these sites, the corrosion process is autocatalytic. The pH decreases inside the pit at the SLC site leading to corrosion attack propagating deep into the exposed materials. However, when the adjacent zones are coupled, the WJ is not susceptible to SLC, and the attack in this region is mainly related to the trenching around the micrometric particles. Therefore, galvanic coupling affects the penetration of corrosion in the different welding zones. Fig. 13 compares the depths of corrosion penetration for the WJ and HAZ, in the AS and the RS, after 24 h test. The depth of attack in the SLC sites, as revealed in Fig. 13(a) and (c), is usually deeper than on the sites of attack associated with the micrometric particles, as shown in Fig. 13(b); consequently, anodic currents associated with the trenching process are lower.

3.2. Asymmetry effects

According to the SVET maps shown in Fig. 11, after 2 h of immersion, the proportion of anodic areas was larger in the HAZ (RS) compared to the HAZ (AS). The WJ also developed a larger number of anodic sites when coupled with the HAZ (RS) compared to HAZ (AS). This result shows that the asymmetry of the welding process affects the electrochemical behaviour of the welded alloy, mainly in the first hours of immersion. Higher temperatures were reached in the AS than in the RS leading to a reduction in T1 phase content at the AS. In a previous work [4], variations in the contents of the nano-sized phases were shown when the TMAZ/HAZ interfaces in the AS and RS were compared. Differential scanning calorime-

try (DSC) and microhardness results, in addition to TEM images, showed a reduction in T1 phase at the TMAZ/HAZ (AS) interface. These variations are related to the thermomechanical process during welding. The material flow is asymmetric and this behaviour, in addition to the temperature reached in the welding zones, modifies the nano-phase distribution, as revealed in Fig. 7, and the extension of the welding zones in the AS and RS, as shown in Fig. 1. In addition, the drag of the micrometric particles from the RS and their deposition at the AS favour the cathodic behaviour in this side, as indicated by the agar-test result in Fig. 8. The lower temperatures reached in the HAZ and TMAZ of the RS reduced the effect of T1 phase dissolution, and, as a consequence, more SLC sites were observed in these regions in comparison with the AS. In the TMAZ of the AS, the temperatures were the highest. This occurs because, in this region, the tangential rotation speed of the tool and the process direction are the same. Thus, the AS region is kept heated for longer periods than the RS, favouring T1 phase dissolution. The higher currents associated with the SLC compared to trenching explains the higher activity of the RS which showed more anodic activity than the AS.

The effects of the asymmetry of the FSW process on the electrochemical response of the welded 2098-T351 sample were easily identified by the SECM technique, as revealed in Fig. 14. The results obtained in the competition mode showed the electrochemical behaviour at the HAZ/WJ interface. In this mode, the oxygen present in the solution acts as a redox mediator. The differences in oxygen reduction currents seen in the SECM maps, as evident in Fig. 14(a) and (b), are related to the depletion of oxygen. On surfaces of high electrochemical activity, the currents related to oxygen availability at the tip are lower since it is consumed at the cathodic sites. As observed in Fig. 14(a) and (b), for the RS, the oxygen reduction currents at the tip increase from the HAZ to the HAZ/WJ boundary and

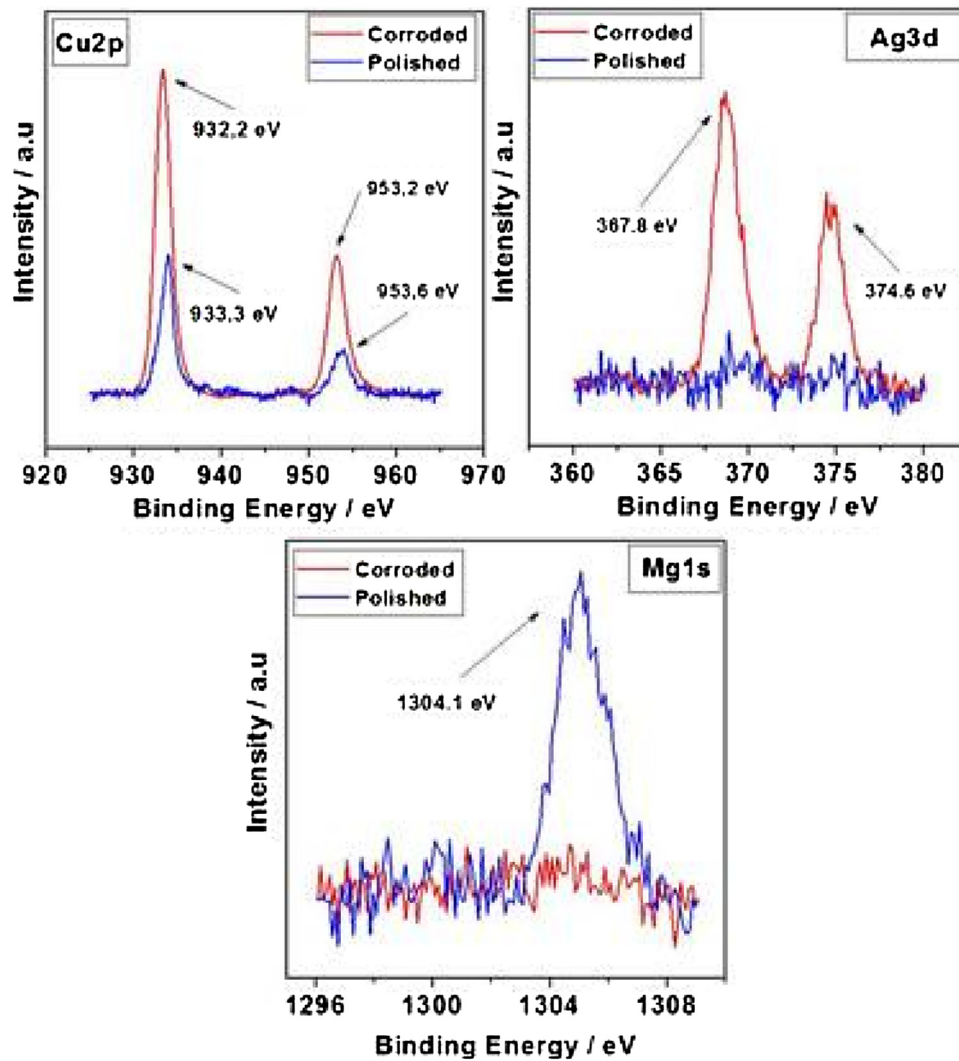


Fig. 9. High-resolution XPS spectra obtained in the welding joint (WJ) of the 2098-T351 alloy welded by FSW prior to (polished) and after (corroded) 24 h immersion in 0.005 mol L^{-1} NaCl solution.

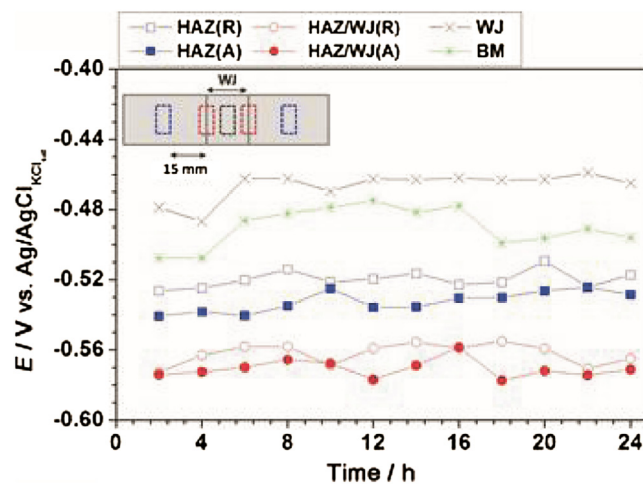


Fig. 10. Open circuit potential (OCP) measurements as a function of time of immersion in 0.005 mol L^{-1} NaCl solution for the different welding zones. Measurements were obtained every 2 h for 24 h.

decrease in the WJ region. However, in the AS, the areas corresponding to high current densities at the tip extended over larger areas. This behaviour is in agreement with the immersion test results

presented earlier in Fig. 3. As observed from the test, while the cathodically protected area in the AS is not well defined, in the RS, a narrow and well defined protected area is observed in the HAZ/WJ

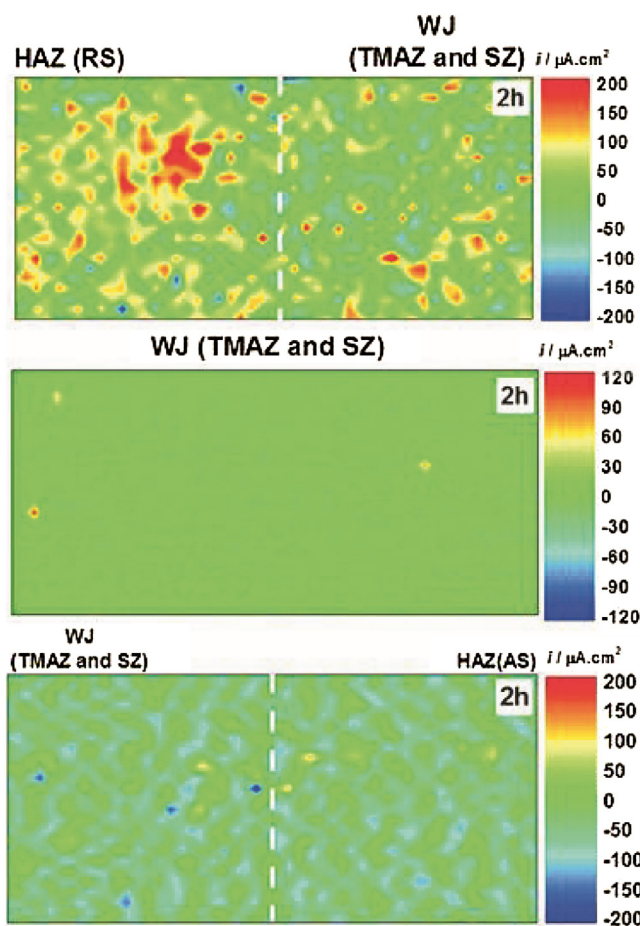


Fig. 11. SVET maps of the welded 2098-T351 alloy after 2 h of immersion in 0.005 mol L⁻¹ NaCl solution.

boundary for long periods of the test. Fig. 14(c) shows a welded sample immersed in 0.005 mol L⁻¹ NaCl after 8 h of immersion. The features observed in the SECM maps were compared with the samples immersed for longer periods and the microstructural features showed a good correlation with the SECM results, as revealed in Fig. 14(d) and (e). The contrast observed between the grains at the HAZ/WJ transition region can provide an indication of the activity variation across the weldment. While a narrow and non-attacked region is observed in the RS, the shape of the grains in the AS is not well-defined. Since the grains reactivity is related to T1 phase content, the regions with higher oxygen currents can be related with the HAZ/WJ boundaries of comparatively lower amounts of T1 phase.

The material flow in the FSW process is complex since it depends on various parameters such as tool design, shoulder characteristics, welding parameters (rotational speeds, transverse and direction of rotation) inclination angle, welded material properties, type of contact between the tool/matrix interface, etc. [61]. Some studies show that portions of the material on the top surface do not penetrate in the wake of the shoulder, stacking in the shoulder interface at the RS as the process progresses [62]. These interfaces between the matrix and the shoulder are regions of microstructural and deformation level variations which, according to the results of SECM, showed influence on the electrochemical response of the 2098-T351 alloy. This flow pattern effect modifies the grain morphology, the concentration of micrometric particles and favours the precipitation/dissolution of nano-sized phases. All these modifications alter the electrochemical response on both sides.

Finally, a relationship between the electrochemical behaviour and the mechanical properties of the 2098-T351 welded by FSW can be established from the SECM results. The line-scan results obtained in competition mode and the microhardness profile are compared in Fig. 15. Since the main strengthening phase in Al-Cu-Li alloys is the anodic T1 phase, it can be seen that as the microhardness decreases, the oxygen reduction reaction current at the tip increases. The SECM result showed that the highest electrochemical activity occurred at regions of the weldment where T1 phase can be observed, whereas the protected areas are related to the regions with lower amounts of T1 phase. In the boundary of the HAZ/WJ (which comprise the TMAZ zone) of the RS and AS, the microhardness values are lower when compared with the other zones. Nonetheless, it was observed that the lowest values of microhardness were observed in the HAZ/WJ boundary of the AS, that was the side which presented more oxygen availability.

In summary, scanning electrochemical techniques, SVET and SECM were useful in the study of the corrosion behaviour of the welded Al-Cu-Li alloy. The correlation between the modifications of the microstructural features and the electrochemical reactivity of each zone was established. SVET technique showed that the zones with high amounts of T1 particles, such as the HAZ and BM, are anodic in relation to the WJ, where T1 phase is rare. Furthermore, the localized electrochemical techniques showed that the electrochemical activity at the RS is higher than in the AS, where the amount of T1 phase is lower. According to the SECM results, the corrosion protected areas are related to the HAZ/WJ (TMAZ domain) region where the T1 phase content reaches the lowest values.

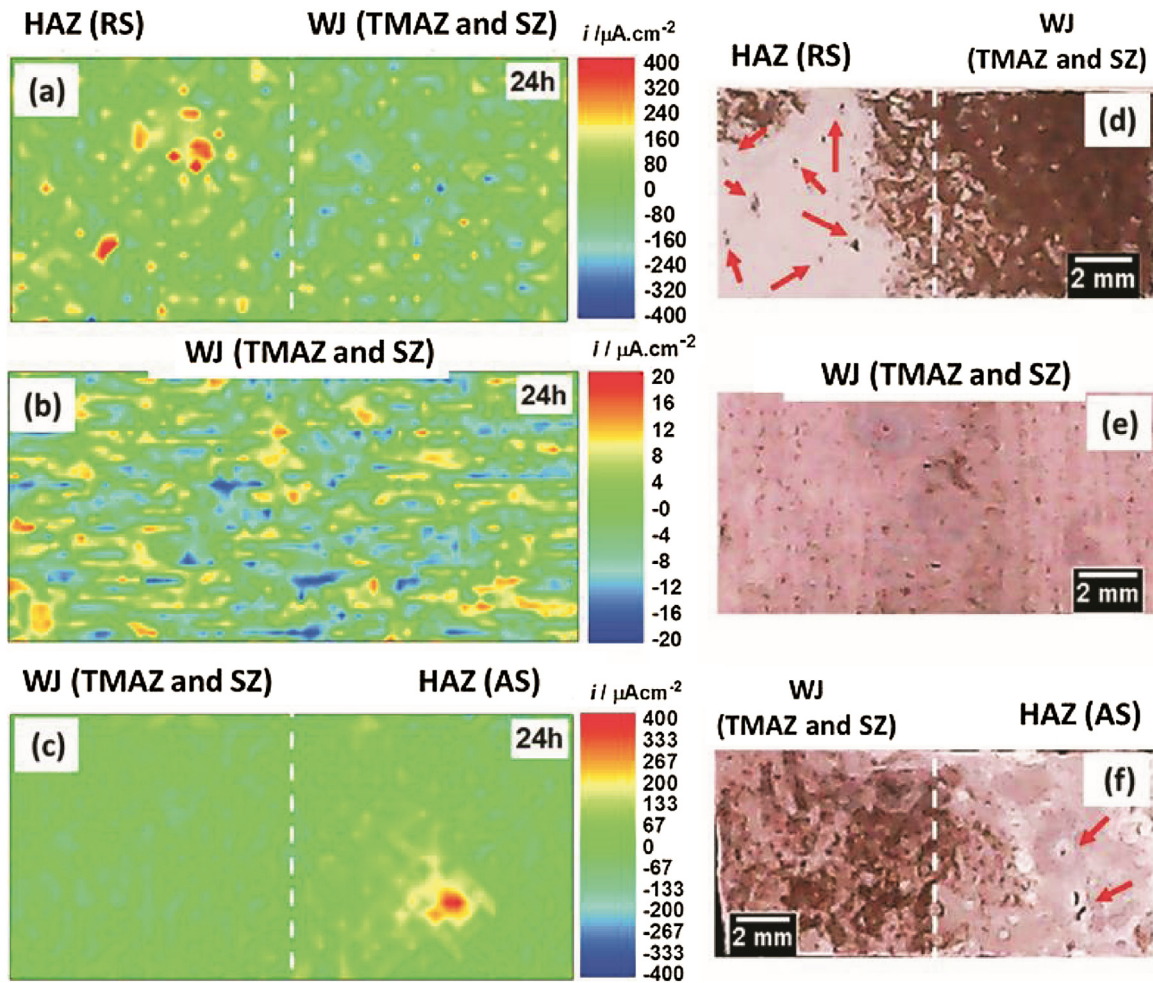


Fig. 12. SVET maps (a–c) and in situ optical images (d–f) of the 2098-T351 alloy welded by FSW after 24 h immersion in 0.005 mol L⁻¹ NaCl solution.

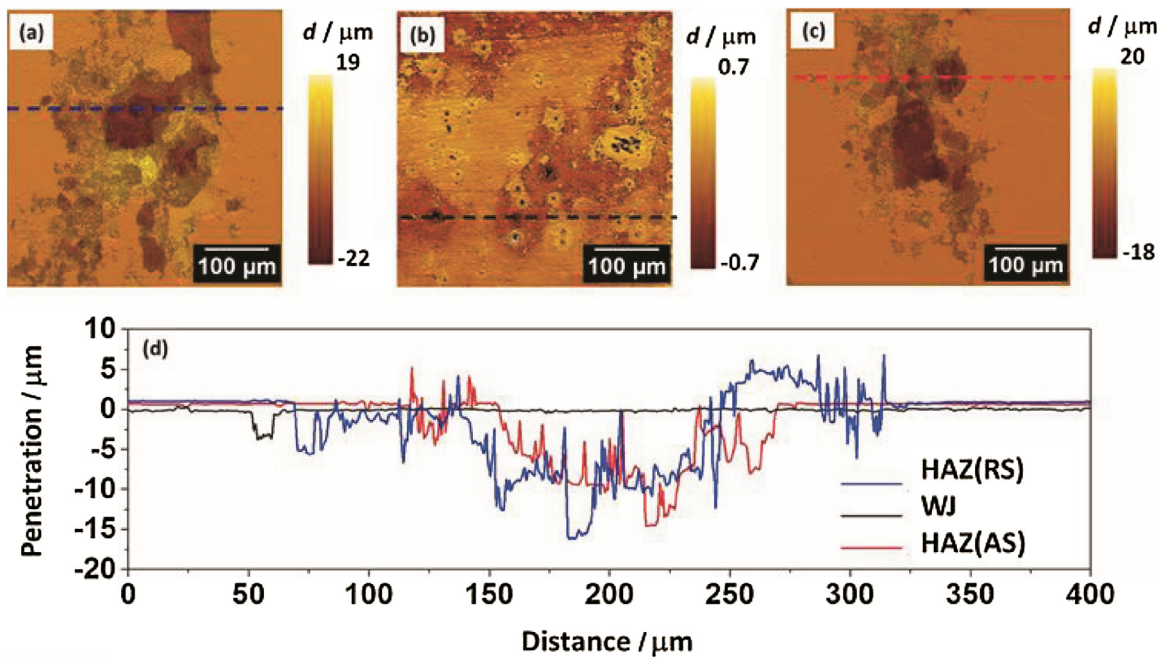


Fig. 13. Optical profilometry images of the corroded surfaces of the welding zones of the 2098-T351 alloy after 24 h of immersion in 0.005 mol L⁻¹ NaCl solution: (a) HAZ (RS); (b) WJ; (c) HAZ(AS); (d) depth penetration profile relative to dashed lines in (a–c).

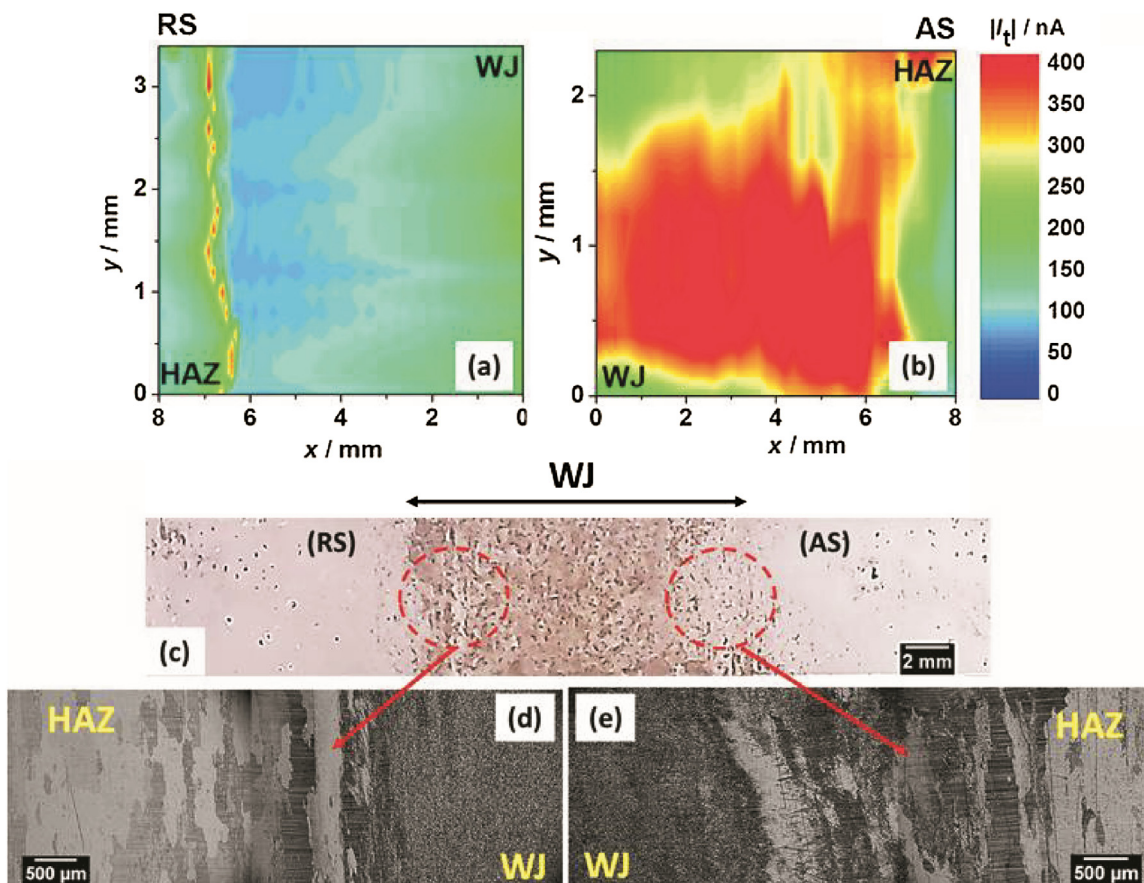


Fig. 14. SECM maps corresponding to the TMAZ/HAZ boundary in the (a) RS and (b) AS of the welding joint in 0.005 mol L⁻¹ NaCl solution; (c) welded 2098-T351 alloy after 8 h of immersion in 0.005 mol L⁻¹ NaCl solution; welding zones features in the (d) RS and (e) AS, revealed after etching (2% HF and 25% HNO₃).

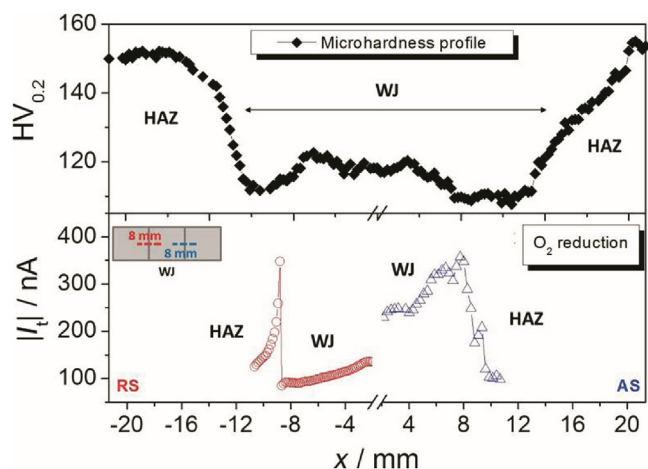


Fig. 15. Plots correlating the microhardness across the top surface of the weld with the SECM line scan plot along the welding joint.

4. Conclusion

The electrochemical characterization of the 2198-T351 alloy showed that the base metal (BM) and the heat-affected zone (HAZ) were anodic in relation to the welding joint (WJ) which comprises the thermomechanically affected zone (TMAZ) and the stir zone (SZ). Microstructural modifications due to the asymmetric effects induced by the friction stir welding (FSW) process led to differences in the corrosion behaviour of the weld zones. The largest difference was observed at the interfaces between the HAZ and

the WJ (TMAZ and SZ), independent of whether it is the advancing side (AS) or retreating side (RS). The SVET and SECM (in the competition mode) techniques were very sensitive to identifying the differences between the electrochemical behaviour of AS and RS. The electrochemical activities related to the RS were higher than those of the AS when the welding zones were galvanically coupled. Finally, the results showed good agreement with different microstructural features observed in each welding zone.

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