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On the stability of the passive Ti-6Al-4V film of friction stir welds with stainless steel: effect of not native metal species

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Abstract

Mechanical and microstructural investigations of friction stir (FS) weldments using Ti-6Al-4V and stainless steel (SS) has been well described in literature; however, little is known about the electrochemical properties of the FS weldment in terms of the passive film stability of TiO_2 grown in oxidizing media. To clarify this issue, potentiodynamic polarization, cyclic voltammetry, and electrochemical impedance measurements were carried out in the FS weldment in an overlap configuration with an AISI 304 austenitic SS to analyze the effects of Fe and Cr contamination on the passive film stability of TiO_2 in concentrated (6.0 and 11.5 mol L^{-1}) HNO_3 solutions. Lower transpassive potentials were observed for samples in the stir zone (SZ) than those of the base metal (BM) due to Fe and Cr contamination. Anodic charges obtained during cyclic voltammetry using 6.0 mol L^{-1} HNO_3 showed that the grown passive film was completely dissolved and regrown after consecutive scans, except for the BM sample. Upon X-ray photoelectron spectroscopy (XPS) analyses a Al deficient layer was obtained for the latter condition, which confirm the stability of TiO_2 film. The increasing values of charge transfer resistance obtained through electrochemical impedance measurements at distinct potentials in the passive region also supported the stability of the TiO_2 film grown in 6.0 mol L^{-1} HNO_3 solution. The formation of a medium frequency inductive loop and low frequency constant phase element were are related to the dissolution of the oxide film and adsorption of NO_3 species into the formed passive film, respectively, as evidenced by XPS analyses.

Keywords: Solid-state welding; TiO_2 film stability;surface reconstruction; adsorption of electrolyte species; inductive loop

1. Introduction

The use of nuclear fuel to generate electric energy is one of the most controversial issues faced by our society due to the potential impact on the environment and human lives as already attested by accidents in Chernobyl (Russia), Three Mile Island (USA), and in Fukushima (Japan). Another concern of nuclear power plants is the safe and secure disposal the spent nuclear fuel, which requires special man-made structures that last over than 250,000 years [1]. In this sense, reprocessing of the spent nuclear fuel might be an option to reduce costs of mining and enriching uranium, thus decreasing the volume of waste generated in the fuel cycle and shortening the required time that the waste must remain isolated to less than 1,000 years [1].

The conventional method used to reprocess spent nuclear fuel is based on aqueous nitric acid solutions and is named PUREX (*Plutonium-Uranium Extraction*)[2]. In order to ensure the integrity and availability of nuclear fuel reprocessing plants and parts for uninterrupted operation, careful selection, fabrication, and operation of metallic components are of paramount importance to resist corrosion at high temperatures and acidic conditions. Austenitic and nitric acid grade stainless steels used to be the material of choice for fabrication of vessels, tanks, piping and equipment in reprocessing plants; however, high corrosion rates is usually reported for these alloys in acidic media [2]. As alternative, Ti and its alloys have been progressively used in reprocessing plants due to its lower corrosion rates related to TiO_2 passive film formation which is not prone to dissolution under oxidizing conditions, such as in contact with HNO_3 solution [3]. Consequently, fabrication of dissimilar joints between austenitic stainless steel and Ti is desired to avoid high production costs. One of the difficulties encountered in the production of such dissimilar joints is their welding due to a mismatch in the physical properties of austenitic stainless steel and Ti resulting in a limited solubility of Fe in the alpha phase of Ti and formation of brittle intermetallic phases in the Fe-Ti system, as well as the conceivable development of complex phases involving Ti, Fe, Cr and Ni [4]. Among the available welding processes, solid state welding (such as friction stir welding - FSW [5]) is the option as it avoids the formation of brittle secondary compounds [4] and porosity [6], commonly observed in fusion weldments.

Basically, the FSW process can join materials through plastic deformation and flow of plasticized material by plunging a rotating tool between two metallic parts, such as stainless steel, Al, Cu, Mg, Ti and their alloys [7]. The high energy input results in

distinct microstructural and morphological evolution along the weldment [5], which is composed of the stir zone (SZ), thermomechanical affected zone (TMAZ), and heat affected zone (HAZ). Each of these regions are affected by many processing parameters during welding, such as tool rotation speed and welding velocity [8]. Despite the large number of studies reporting the microstructural evolution and mechanical properties along friction stir weldments for different metallic alloys, only few papers [9-12] investigated the electrochemical behavior of weldments made of Ti and its alloys. Atapour et al. [10] compared the corrosion behavior of a Ti-6Al-4V alloy and the produced fusion zone after its welding using a gas tungsten arc welding (GTAW) and FSW processes. The fusion zone of the GTAW process led to high corrosion rates in 20% HCl due to the combination of coarse vanadium-rich β phase grains and fine acicular α phase (high α/β interfaces) grains with the low stability of the TiO_2 film grown in the presence of the V-rich β phase. The influence of element segregation, particularly Al and V, as well as the content of the α and β phases on the Ti-6Al-4V alloy is of fundamental importance due to the possible formation of galvanic pairs, as reported in another work of Atapour et al. [12]. In that work, different microstructures and volume fractions of α and β phases were produced and analyzed in NaCl and HCl media. Despite similar corrosion behavior during potentiodynamic polarizations among tested samples, immersion tests in 3.5 M HCl showed a more intense pitting attack in the β phase. As described in the work of Nasresfahani [11], corrosion attack in the SZ zone of a Ti-6Al-4V sample in 5% HCl increased due to formation of a galvanic pair between the sample and WC-Co impurities from the FSW tool. Clearly, more work is needed to investigate the electrochemical performance of similar and dissimilar FS weldments made of Ti and its alloys in reducing and oxidizing media to assess the stability of TiO_2 passive film, especially in the case of dissimilar weldments.

Therefore, the aim of this work was to investigate the morphological and structural evolutions as well as the electrochemical performance on the surface of a Ti-6Al-4V alloy welded by FSW in an overlap configuration with a AISI 304 stainless steel (SS) plate. Potentiodynamic polarization, cyclic voltammetry, and electrochemical impedance measurements were carried out in the FS weldment to analyze the effects of Fe and Cr contamination [13] on the electrochemical performance of the Ti-6Al-4V alloy and its passive film in concentrated HNO_3 solutions (6.0 and 11.5 mol L^{-1}) to simulate nuclear power plant reprocessing conditions. In addition, passive films grown under potentiostatic

conditions that exhibited an inductive loop during electrochemical impedance measurements were fully characterized using X-ray photoelectron spectroscopy.

2. Experimental

2.1 Chemicals

All chemicals, including H_2O_2 (29-31%, Synth), KOH (a.r., Synth), 2-propanol (a.r., JT Baker), HNO_3 (a.r., Qhemis) were used as received and without further purification. All solutions were prepared using deionized water (Millipore Milli-Q system, $\rho \geq 18.2$ MΩ cm).

2.2 Friction stir weldment samples and their analyses

The friction stir welding process were produced in an overlap configuration between the Ti-6Al-4V (1.6 mm thickness) on top of an AISI 304 austenitic stainless steel (304SS - 2.4 mm thickness) plate, the chemical composition of the plates, can be found in Tables SI-1 to SI-3 and in a previous work [13].

First, samples (50 × 10 mm) of the Ti-6Al-4V alloy were extracted by electroerosion from the base metal and weldment, as schematically shown in Fig SI-1. The base material (BM) is the region not affected by thermal gradients or mechanical deformation (*i.e.* Ti alloy), while the weldment region is composed of the stir zone (SZ: mechanical mixture of the material), thermomechanically affected zone, and heat affected zone (TMAZ-HAZ). As these two latter regions of the weldment are very thin and difficult to delimitate (see further discussion below), no electrochemical measurements were carried out in that region. All morphological, structural, and electrochemical measurements were carried out on the surface of the Ti-6Al-4V plate.

The morphological characterization of the extracted samples was carried out by optical (Olympus Infinity I, model BX41M) and field-emission scanning electron (FEI Inspect F50 - coupled with energy dispersive X ray spectroscopy: EDS) microscopes. Before these analyses, the samples were wet-sanded with 80, 320, 400, 600,and 1500 abrasive papers and 1μm alumina paste. Then, samples were rinsed with H_2O and cleaned for 30 min in an ultrasonic bath containing 2-propanol. Chemical etching (ASTM E407-07) to reveal grain contours were carried out by immersion of samples in a solution composed of H_2O_2 (10 mL), deionized H_2O (10 mL) and KOH (8 g) for 7 min, followed by H_2O rinse and ultrasonic cleaning using 2-propanol.

X-ray diffraction (XRD) analyses were carried out in the BM and SZ of the weldment using a model RU200B Rigaku Rotaflex diffractometer with a Cu source (Kα = 1.5418 Å) and from 5° to 80° at 1° min^{-1} to follow any structural change resulting from the welding process.

Vickers microhardness measurements (Future Test, model FM800) were performed perpendicular to the welded region (see illustration in Fig. SI-1a) and using a conventional Vickers indenter with 100 gf of load during an indent period of 15 s, according to the ASTM: E384-17 standard.

Electrochemical measurements (Metrohm Pgstat 20) were carried out in a conventional three electrode cell using a Pt foil as counter electrode, reversible hydrogen electrode (RHE: Pt/H$_2$/H$^+$ at 0.5 mol L^{-1} H$_2$SO$_4$) with a salt bridge as reference electrode, and BM or SZ samples as the working electrodes (0.25 cm^2 of exposed area). Before any test, these samples were wet sanded with 600 abrasive paper, rinsed with H$_2$O and 2-propanol, and left in ambient conditions to dry. All measurements were carried out at ambient conditions and using HNO$_3$ solutions (6.0 and 11.5 mol L^{-1}) as electrolytes. The electrochemical tests in the BM and SZ samples were: *i*) determination of the open circuit potential (E_{OC}) after 5 h immersion in the electrolytes, *ii*) linear polarization from -0.60 to 3.00 V *vs*. E_{OC} at 0.17 mV s^{-1} to comparatively analyze the passivity and its breakdown in each region, *iii*) cyclic voltammetry from 0.00 to 1.00 V vs. E_{OC} to analyze the electric charge required for the reconstruction of the passive films, and *iv*) electrochemical impedance from 5 kHz to 3 mHz with a perturbation amplitude of ±10 mV (RMS) to investigate processes in the interface after attainment of the E_{OC} and in the passive region.

After electrochemical impedance measurements, chemical surface analyses of the BM and SZ zones were performed by X-ray photoelectron spectroscopy (XPS) using a conventional XPS spectrometer (ScientaOmicron ESCA+) with a high-performance hemispheric analyzer (EAC2000) and monochromatic Al Kα (h v = 1486.6 eV) radiation as the excitation source. The operating pressure in the ultra-high vacuum chamber during the analysis was around 10^{-7} Pa. The XPS high-resolution spectra was recorded at constant pass energy of 20 eV with a 0.05 eV increment. The spectra were fitted without placing constraints with multiple Voigt profiles using the CasaXPS software.

3. Results and Discussion

3.1 Structural and morphological analyses

Fig. 1 shows the obtained X-ray diffractograms of the BM and SZ of the welded joint. Most of the diffraction peaks were ascribed to the Ti α-phase in the BM with slight amounts from the β-phase. After the FSW process, a clear decrease of the diffraction peaks of the α-phase (at 38º, 53º, 63º, and 71º) is accompanied by an increase of peaks of the β-phase in the SZ, particularly at 39º and 57º. This phase transition is related to the high temperatures generated in the SZ during the deformation process, which might be close to 1100 ºC according to the work of Fazel-Najafabadi *et al*. [14], but not measured in the present work. As the β-phase is more stable at higher temperatures and considering that the weldment produced was left to cool under ambient conditions, leading to high cooling rates, an increase of the metastable β-phase in the SZ is expected. As will be showed latter, contamination of the SZ by Fe from the underlying 304SS and the presence of V in the Ti alloy also led to stabilization of the β-phase at ambient conditions after the welding process. The observed small shifts of the diffraction peaks with respect to the standard samples might be due to the chemical composition and strain of the Ti alloy [15].

Fig. 2 shows some optical micrographs representative of the BM, TMAZ-HAZ, and SZ. The microstructural evolution along the weldment region can be seen in Fig SI-2. As can be observed in Fig. 2a, the BM exhibited equiaxed grains ascribed to the α-phase (10 to 20 μm in diameter)with the β-phase in the contours of the grains as reported elsewhere [16]. The TMAZ-HAZ region showed elongated grains with some refinement due to the plastic deformation process (Fig. 2b). Fig. 2c shows that the fast cooling rate led to the formation of needle-shaped and finely dispersed martensite (α') phase in the SZ, resulting from β to α' phase transformation as well as retained α phase (lamella). The presence of the latter phase might be an evidence of the uneven temperature distribution in the welded region which prevented a complete transformation of α to β phase [17] during heating promoted by the plastic deformation.

The Vickers microhardness 2D map along the top surface of the weld can be seen in Fig. 3. As can be noticed, low values of microhardness (~340 $HV_{0.1}$) were observed in the extremes of Fig. 3, ascribed to BM. The TMAZ-HAZ and mainly SZ present up to 30% higher values of microhardness due to *i*) grain refinement, *ii*) increased number of dislocations promoted by the plastic deformation within this region, and *iii*) contamination of the Ti alloy by Fe and/or Cr leading to the possible formation of intermetallic compounds [18-19]. Along the analyzed weldment of Fig. 3, slightly higher values of microhardness (~420 HV) can be observed at the advancing side. This might be related to the formation of higher amounts of the α' phase (see Fig. SI-3), *i.e.* the

temperature during welding might have exceeded the one for the β phase formation resulting in the conversion of the α' phase during cooling. The contamination of the SZ by elements coming from the 304SS plate could be another cause of the observed high values of microhardness in the advancing side, as shown by the EDS mapping of Fig. SI-3, due to formation of intermetallic compounds (*i.e.*, FeTi, Fe_2Ti, and Cr_2Ti). These intermetallics were reported in the work of Kurt et al. [20] during analysis of diffusion bonded interfaces of Ti-6Al-4V and AISI 316 L type austenitic SS. Moreover, there were some needle-shaped structures of the α' phase enriched by Fe and Cr in the advancing side with respect to the retreating side. As discussed in the work of Cho et al. [21], the relationship between translation and rotation speeds of the tool have a complex influence on the heating rate and strength distribution, which usually result in higher hardness in the advancing side of friction stir weld made with 304L SS.

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3.2 Electrochemical and morphological analyses

3.2.1 Open circuit potential, linear polarization, and cyclic voltammetry measurements

As described in section 2.2, all electrochemical assays were carried out in the BM and SZ of the friction stir weldment (see Fig. SI-4 for the exact positions), due to the small width of the TMAZ and HAZ regions (~200 μm) in comparison to the delimited area (0.25 cm^2 and Ø = 560 μm) for the electrochemical experiments.

Table 1 shows the obtained open circuit potentials (E_{OC}) after 5 h resting in HNO_3 solutions at 6.0 and 11.5 mol L^{-1}. Within the experimental errors, E_{OC} values are equal in BM and SZ regions for both HNO_3 concentration. In addition, the 0.2 V higher E_{OC} values observed for the more concentrated HNO_3 solution can be related to the thicker TiO_2 passive layer formed on the Ti alloy. The E_{OC} time evolution along the resting time can be seen in Fig. SI-5, showing a faster E_{OC} saturation (2 h) at higher HNO_3 concentration.

After the resting period, linear polarization measurements were carried out in the BM and SZ for distinct HNO_3 solutions, shown in Fig. 4. In all tested conditions, samples exhibited a passive behavior with a low current density from the E_{OC} until the onset of the transpassive potential (E_{TP}), which is characterized by a steady increase of the current density due to dissolution of the passive film. In this regard, the BM always exhibited higher E_{trans} with respect to the SZ independently of the HNO_3 solution, as showed in Table 1. That behavior suggests that the BM could be more resistant towards corrosion

in boiling HNO_3, which is the condition encountered in nuclear fuel reprocessing plants. In order to understand the superior corrosion susceptibility of the SZ, scanning electron micrographs and EDS analyses were carried out after linear polarization measurements in 6.0 mol L^{-1} HNO_3. As can be seen in Fig. SI-6, dissolution at specific points was noticed in the BM sample, which resemble grain boundaries. Compositional analyses performed by EDS (see Table SI-4) showed a slight decrease of the V content inside the corroded area that might be ascribed to the β-phase, commonly encountered in grain boundaries and usually enriched in V. For the SZ, three morphologies can be observed in Fig. SI-7: *i*) a smooth surface with a certain degree of corrosion (region 1), *ii*) small (characteristic of the α' phase) and large (α phase) needles (region 2), and *iii*) a highly corroded area (region 3). Considering the EDS analyses in Table SI-5, the smooth surface and its corroded area are enriched by Fe (3% mass) and Cr (1% mass) in comparison to the large needles, due to the mixture with the 304SS plate during weldment. As the passive film produced in the presence of those extraneous metals is unstable in highly acidic medium and at high potentials, corrosion took place preferentially in that region of the weldment. This latter process could be also intensified by the produced galvanic pair as the smooth surface is located between the less corroded needles. Another important effect of the Fe and Cr contamination in the Ti alloy is the decrease of the α to β phase transition temperature, so that the smooth region might be characteristic of the β phase [22]. A similar behavior was observed for samples of the BM and SZ after performing the linear polarization using 11.5 HNO_3. In the case of the BM, a more pronounced corrosion attack can be verified as showed in Fig. SI-8, which resembles grain boundaries due to the stronger oxidation medium. The low values of the V content reported in Table SI-6, in comparison to the assays carried out in 6.0 mol L^{-1} HNO_3, might be due to V leaching when BM samples were exposed to a high concentrated HNO_3 solution. For the samples of the SZ channel-like morphologies of the corrosive attack were observed due to contamination of the β-phase with Fe and Cr (see Table SI-7) from the 304SS plate (Fig. SI-9). One important characteristic showed in Table SI-7 was the detection of small amounts of W due to contamination of the welding tool.

The passive film stability of the BM and SZ samples grown in HNO_3 solutions was evaluated by cyclic voltammetry (CV) through measurement of the anodic charges after consecutive scans. As can be observed in Fig. 5a, the BM sample in 6.0 mol L^{-1} HNO_3 showed an almost expected behavior for valve metals, which is a low anodic charge during the second scan after a high anodic charge during the first scan (see Table 2 for

the exact measured values). That behavior is due to the thickening of the insulating TiO_2 film during first scan, which is the main constituent in the oxide film [23]. In addition, no significant corrosion attack was observed in the scanning electron micrographs made after the second scan as showed in Fig. SI-9a. On the other hand, cyclic voltammograms of the SZ showed almost identical profiles during the first and second scans (see the anodic charges in Table 2). Such behavior is due to the dissolution of the TiO_2 film grown in the first scan; thus, the passive film was completely reconstructed (*i.e.*, oxidation of the Ti alloy) during the second scan. Scanning electron micrographs of the SZ showed the presence of small regions of corrosion attack as well as the presence of needles characteristic of the α' phase (see Fig SI-9b). The passive film dissolution is probably due to its contamination by Fe and Cr, as discussed above, indicating its lack of stability in highly acidic solutions and at high potential conditions. When CV measurements were carried out in 11.5 mol L^{-1} HNO_3, the anodic charges of the first and second scans were very close to each other and higher than the ones shown at 6.0 mol L^{-1} HNO_3, as can be observed in the CV profiles of Fig. SI-10 and Table 2. That behavior was expected for the SZ sample due to its contamination by Fe and Cr, as discussed above. In the case of the BM sample, the produced passive film was also unstable in 11.5 mol L^{-1} HNO_3 solution, even without contamination by Fe and Cr. The possible leaching of Al or V, which are alloying elements might be one of the reasons for the film dissolution (see discussion below). Upon analysis of the scanning electron micrographs of Fig. SI-10, small corrosion attacks can be observed in the BM and SZ samples.

3.2.2 Electrochemical impedance (EI) measurements

In order to investigate how distinct concentrated HNO_3solutions could affect the electrochemical properties of the passive film as well as the role of Fe and Cr contamination, AC impedance measurements were carried out after 5 h resting at open circuit conditions. Fig. 6 shows the Nyquist and Bode plots for the BM and SZ of the FS weldment using 6.0 and 11.5 mol L^{-1} HNO_3 solution. Electrochemical parameters obtained by fitting the data (at least three repetitions) using an equivalent circuit (see inset of Fig. 6a) over the frequency spectrum are listed in Tables SI-8 to SI-11 of the supplementary content file. The electrochemical impedance profiles of Fig. 6 are characterized by a high frequency capacitive loop, a medium frequency inductive loop, and a low frequency pseudocapacitance, which is well known for valve metals in concentrated acid solutions. The interpretation and analysis of these type of spectra were

done by Bojinov et al. [24] using the surface charge approach (SCA) and taking into account the point-defect model proposed by Macdonald et al. [25-27]. The most controversial discussion in the interpretation of the equivalent circuit (see Fig. 6a) proposed (and used to fit the impedance spectra obtained in this work) is the meaning of the inductor and faradaic pseudocapacitance at low frequencies, which is commonly reported as C_0 (CPE_0 in this study - CPE: constant phase element). For the former, that behavior might be due to a positive surface charge resulting from migration of positive defects (represented by a resistance and pseudo-inductance, R_L and L, respectively, for the charge relaxation process) [24, 28] or to the surface concentration of intermediate species taking part in the dissolution of the oxide film [29], whereas the latter is associated to the film thickness adjustment with potential or incorporation of foreign species (e.g., F^- ions) [29]. The remaining elements used to fit the experimental EI data were ascribed to the solution resistance (R_S), electric double layer capacitance (represented by a CPE_{DL}), and resistance to charge transfer (R_{CT}). The latter parameter is of fundamental importance in corrosion science and was obtained by extrapolation of the capacitive semi-circle to $Z_{im} = 0$. For passive films over valve metals, the R_{CT} could be interpreted as the resistance towards migration of oxygen and metal vacancies. So, high R_{CT} values means a more protective and stable passive film with restriction to the motion of vacancies. As can be observed in Fig. 6, the BM showed higher values of R_{CT} than the SZ in both acidic media, which is due to the contamination of the SZ by Fe and Cr. The comparison between two different HNO_3 concentrations, higher R_{CT} values were found for the diluted medium. As discussed above regarding the cyclic voltammetry results, the required charge for reconstruction of the passive film was close to 100%, except for the BM at 6.0 mol L^{-1} HNO_3 which was the condition that exhibited the highest value of R_{CT}. Thus, two main factors seem to influence the observed electrochemical behavior: *i*) contamination of passive films by Fe and Cr in the SZ that leads to failure of the passive film, and *ii*) passive film stability in concentrated HNO_3. The latter accounts for the distinct behavior of the BM sample in 6.0 and 11.5 mol L^{-1} HNO_3 during the EI and cyclic voltammetry measurements. In order to investigate the film stability of the BM in the passive region for both HNO_3 concentration, EI measurements were also carried out after applying distinct potential intervals for 1 h in sequence, *i.e.*, from 1.0 V to 1.6 V*vs*. RHE for the 6 mol L^{-1} HNO_3 and from 1.2 V to 1.8 V *vs*. RHE for the 11.5 mol L^{-1} HNO_3 at a step potential of 0.2 V (see the corresponding passive region for each curve in Fig. 4), including for pure Ti (99.5%) to avoid the influence of alloying elements. Fig. SI-11 and

SI-12, in the supplementary material file, shows the corresponding Nyquist and Bode plot profiles. The R_{CT} values resulting from fitting of the experimental curves using the equivalent circuit (inset of Fig. 6a) are shown in Fig. 7. Clearly, as the applied potential in the passive region increases, the R_{CT} values for the BM in 6 mol L^{-1} HNO_3 and pure Ti in 6.0 and 11.5 mol L^{-1} HNO_3 increase one order of magnitude. That behavior clearly shows that the grown passive film is thickening and seems to be stable in those conditions. On the other hand, for the BM in 11.5 mol L^{-1} HNO_3 and SZ in both concentration values, the R_{CT} values decreased continuously. For the SZ samples, the observed R_{CT} values were expected as the passive film was contaminated with Fe and Cr; however, for the BM in 11.5 mol L^{-1} HNO_3, the decrease of the R_{CT} values is due to the dissolution of the grown passive film, which could be a consequence of film instability due to the alloying elements (Al and V), as suggested by the opposite effect exhibited by pure Ti.

To analyze the near surface composition and bonding structure, *ex situ* XPS analyses were carried out for samples of the BM and SZ after the chronoamperometric and EI measurements (Fig. SI-11 and SI-12). As can be seen in Table 3, the surface of the BM and SZ samples are mainly composed of TiO_2 (see the characteristic Ti 2p spectra of all samples analyzed in Fig. SI-13 as well as the XPS spectra of O 1s with the characteristic O-Metal bond at 530.2 eV in Fig SI-14), adventitious carbon (commonly found in *ex situ* measurements), and nitrogen due to adsorption/incorporation from the HNO_3 electrolyte. Fig. 8 shows the XPS spectra of N 1s for samples of the BM and SZ in 6.0 mol L^{-1} HNO_3 (see Fig. SI-15 for sample at 11.5 mol L^{-1} HNO_3) with two fitting components characteristic of the C-N (~400.0 eV) and NO_3 (401.8 eV) groups. That behavior confirms anion incorporation into the oxide film as the source for the low frequency pseudocapacitance (CPE_0 element in Fig. 6) formation, as described in the literature [29], during EI measurements carried out after chronoamperometric and open circuit assays (Fig. 6).

Another interesting point of Table 3 is that the only significant difference of the elemental composition refers to the low Al atomic percentage of the BM sample assayed in 6.0 mol L^{-1} HNO_3, contrasting with the result when the experiment was carried out with the same sample in 11.5 mol L^{-1} HNO_3. That behavior is consistent with the results cyclic voltammetry measurements (see Table 2) and also with the R_{CT} dependence in Fig. 7, showing that a thickening of the passive TiO_2 film (with dissolution of Al oxide) is occurring for the BM sample (as well as for the Ti samples in all conditions - see Fig. 7) in 6.0 mol L^{-1} HNO_3. On the other hand, for the remaining samples, a low film stability

due to the alloying elements, and for SZ traces of Fe (Table 3), results that film dissolution (source of the medium frequency inductive loop) might be taking place. Consequently, the Ti alloy is being constantly exposed to the electrolyte leading to formation of Ti and Al oxides and to a lower amount of V oxides. The deconvoluted XPS spectra of Al 2p and V 2p can be seen in Fig. SI-16 and SI-17.The contamination of SZ samples by the steel alloy was evidenced by a small noisy Fe $2p_{3/2}$ signals at 711 eV.

4. Conclusion

The FS weldment of the Ti-6Al-4V alloy over an AISI 304 stainless steel resulted in distinct morphologies, *i.e.* equiaxed, elongated, and needle shaped grains as well as crystalline structures from the base metal to the stir zone. The plastic deformation of the latter led to the formation of needle-shaped structures characteristic of the martensitic phase (α') as well as contamination of the produced weldment with Fe, Cr, and small amounts of W, which resulted in higher values of microhardness in the stir zone.

Linear polarization measurements of the stir zone showed that Fe contamination is deleterious to the produced passive film as a narrow passive range and lower overpotential for the onset of the transpassive potential were obtained. Cyclic voltammetry also confirmed that the produced passive films are unstable and are practically reconstructed after the first scan for all conditions analyzed, except for the base metal sample using 6.0 M HNO_3. In this particular condition, XPS analyses showed that the produced passive film might be mainly composed of TiO_2, similar to other conditions analyzed, but with a lower amount of Al. Comparative electrochemical impedance measurements among samples of the FS weldment and pure Ti indicate that the alloying elements are deleterious to the stability of the produced passive film, specially at 11.5 mol L^{-1} HNO_3.

Finally, results of electrochemical impedance measurements and *ex situ* XPS analyses allowed to confirm that the inductive loop formation and low frequency constant phase element were due to dissolution of the oxide film and adsorption of NO_3 species into the produced passive film, respectively.

Appendix A. Supplementary data
Supplementary data associated with this article can be found, in the online version, at:

Acknowledgments

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TABLES

Table 1 Experimental values for the open circuit potential (E_{OC}) after 5 h resting and transpassive potential (E_{TP}) in distinct acidic solutions for the base material (BM) and stir zone (SZ).

Region / [HNO_3] in mol L^{-1}	E_{OC} *vs.* H^+/H_2 (H_2SO_4 0.5 mol L^{-1}) / V	E_{trans} *vs.* H^+/H_2 (H_2SO_4 0.5 mol L^{-1}) / V
BM / 6.0	0.62 ± 0.05*	2.33 ±0.02
SZ / 6.0	0.59 ± 0.07*	2.05±0.02
BM / 11.5	0.840 ± 0.004*	2.35 ±0.05
SZ / 11.5	0.84 ± 0.01*	2.11 ±0.04

*The error values were calculated after 3 repetitions

Table 2 Anodic electric charge (Q_a) for the first and second scans during cyclic voltammetry measurements carried out in samples of the BM and SZ in distinct HNO_3 solutions.

Region / [HNO_3]	Cycle number	$Q_a^* $ / C	Percentage of reconstruction[**] / %
BM / 6.0 mol L^{-1}	1st	2.867×10^{-2}	59
	2nd	1.684×10^{-2}	
SZ / 6.0 mol L^{-1}	1st	4.282×10^{-2}	96
	2nd	4.134×10^{-2}	
BM / 11.5 mol L^{-1}	1st	1.354×10^{-1}	97
	2nd	1.309×10^{-1}	
SZ / 11.5 mol L^{-1}	1st	1.175×10^{-1}	97
	2nd	1.143×10^{-1}	

*values refer to only one measurement for each sample

**these values were obtained by the quotient between the anodic charge of the second and first scans.

Table 3 Quantification results obtained after fitting the XPS experimental data from samples* of the base metal (BM) and stir zone (SZ) using distinct HNO_3 solutions.

	BM / 6 M HNO_3		SZ / 6 M HNO_3		BM / 11.5 M HNO_3		SZ / 11.5 M HNO_3	
	Position / eV	At. %	Position / eV	At. %	Position / eV	At. %	Position / eV	At. %
C 1s	284.5	19.8	284.5	26.9	284.5	22.6	284.5	29.8
N 1s	400.0	1.1	399.5	1.2	400.0	1.0	400.0	1.0
O 1s	530.5	62.3	530.5	53.8	530.5	57.0	530.0	52.1
Al 2p	74.0	2.2	74.0	3.9	74.0	3.7	74.0	3.2
Ti 2p	459.0	14.4	458.5	14.1	459.0	15.0	458.5	13.4
V 2p	516.5	0.3	515.5	0.3	516.5	0.5	516.0	0.4
Fe 2p	711.0	-	711.0	0.2	711.0	-	711.0	0.1

*ex situ XPS measurements obtained after chronoamperometric and electrochemical impedance measurements - see text.

FIGURE CAPTIONS

Fig. 1 X-ray diffractograms of the **a)** base material and **b)** stir zone of a friction stir weldment. (■) Ti α - JCPDS 65-6231; (■) Ti β - JCPDS 65-5970.

Fig. 2 Optical micrographs obtained after chemical etching representative of the **a)** base material, **b)** thermomechanically affected zone and heat affected zone, and **c)** stir zone.

Fig. 3 2D mapping of the Vickers microhardness obtained along the friction stir weldment.

Fig. 4 Linear polarization curves of the base material (black line) and stir zone (red line) in HNO_3 solution at **a)** 6.0 mol L^{-1} and **b)** 11.5 mol L^{-1}. Conditions: 5 h resting before polarization at 24 ºC and using 0.17 mV s^{-1}.

Fig. 5 Cyclic voltammetries (0.17 mV s^{-1}) carried out using samples of the **a)** base material and **b)** stir zone in 6.0 mol L^{-1} HNO_3 solution at 24 ºC. Black and red lines refer to the first and second scans, respectively.

Fig. 6 Nyquist (**a** and **c**) and Bode (**b** and **d**) plots for the base material (BM) and stir zone (SZ) after electrochemical impedance measurements using HNO_3 solution at 6.0 mol L^{-1} (**a** and **b**) and 11.5 mol L^{-1} (**c** and **d**). The equivalent circuit used to fit (red lines) the experimental values are indicated in the inset of **a)**.

Fig. 7 Evolution of the charge transfer resistance (R_{CT}) as a function of applied potential (E) in the passive region of the base material, stir zone, and pure Ti using HNO_3 solution at 6.0 mol L^{-1} and 11.5 mol L^{-1}.

Fig. 8 XPS spectra of N 1s for samples of the **a)** base metal and **b)** stir zone after chronoamperometric (see details in the text) and electrochemical impedance measurements were carried out in 6.0 mol L^{-1} HNO_3.