**A direct measurement of the activation potential of stainless steels in nitric acid**

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**abstract**

The activation potential that characterizes the passive-active transition of stainless steels has been measured for the first time directly in nitric acid. The measurement of the activation potential is not possible by classical electrochemical means in nitric acid due to an intense reduction current at very cathodic potentials masking the anodic dissolution current. Therefore, atomic emission spectroelectrochemistry (AESEC) was used to record simultaneously the overall current and the dissolution rates of the individual alloying elements of stainless steels. This methodology has been used to quantify the influence of several parameters on the activation potential: nitric acid concentration, temperature, and the addition of silicon in the steel composition.

*Introduction*

Nitric acid, HNO3, is a widely-used electrolyte in nuclear reprocessing plants for spent nuclear fuel (1, 2). In addition to its acidic properties, HNO3 is a strong oxidizing agent and therefore material choice for industrial devices must respect strict specifications. Austenitic stainless steels (SS) are frequently chosen because of their good corrosion resistance in concentrated nitric acid (1).

The cathodic and anodic reactions of stainless steel in concentrated nitric acid have been the object of numerous investigations (3-7). Cathodic processes involved in austenitic SS corrosion in concentrated nitric acid have been investigated since the beginning of the 20th century (6, 8-11). A large number of equilibria in solution and thus possible species that can be reduced at the interface have been ascertained. Among these equilibria, nitrous acid, HNO2, is formed by the oxidation of water to oxygen. At high concentration, nitric acid reduction is an indirect reduction process in which NO3- does not directly act as the electron provider at the interface. Rather, the oxidizing agent has been shown to be N(III) species such as such as nitrous acid, or the nitrosonium ion, NO+. These species reduce into the N(II) oxidation state following several possible mechanisms (eq. 1 to 3 as an example) happening at high potentials comprised between 0.65 and 1.15 V vs. NHE (7-9).

At lower potentials, ammoniac formation, NH3, is expected to happen at platinum interfaces (eq. 4). Dihydrogen formation will then dominate for potentials lower than 0.05 V vs. NHE.

The anodic reactions of stainless steel in the active state have proven difficult to investigate due to the fact that stainless steel is spontaneously passive in concentrated nitric acid; and when polarized to the active potential domain, the high cathodic current completely masks the anodic current. Under certain applications however, the presence of impurities can drive the potential of the nitric acid into the active domain. Therefore, it is of considerable interest to explore the passive layer stability on the edge of the active dissolution. When the electrode potential becomes increasingly cathodic and approaches the active state, the oxides making up the passive film become thinner, less protective, and the dissolution rate of the steel increases. In general, the thickness of the passive film is determined by a steady state between film growth and film dissolution. To a first approximation, the rate of film growth will decrease with decreasing potential, while film dissolution is less dependent on potential and more a function of electrolyte pH. Although the oxidation rate of the stainless steel should, in theory, decrease with decreasing potential, the rate of elemental dissolution will increase due to the decreased thickness of the passive film. The potential below which the dissolution rate becomes measurable is referred to as the “activation potential”, Ea.

Many studies of the “activation potential” have been made on various materials including pure iron (12, 13), iron-chromium alloys (14, 15) and more complex alloys involving nickel and other elements (16, 17). They lead to an establishment of a linear dependence between the activation potential and the logarithm of the proton activity. These measurements have mostly been performed in sulfuric acid, either based on linear sweep voltammetry (14, 15, 18) because hydrogen reduction occurs at low potential and there is a sufficiently wide electrochemical window to measure the active dissolution at low potentials. Frankenthal *et al.* (18) showed that an accurate measurement of Ea was possible within a few millivolts. However, in nitric acid, no cathodic loop behavior (defined as a small potential range where the total current becomes negative in the active domain of the steel) can be observed because the overall current is strongly negative. Such a method is not appropriate for concentrated nitric acid due to the high cathodic current in the active potential domain. Measurements of Ea can also be based on the spontaneous activation behavior of stainless steels in sulfuric acid (15, 17). After a passivation polarization of the sample in sulfuric acid, the potential at which passivity decays spontaneously to an active potential on shutting off this anodic polarization has been also called the “Flade potential” (16, 19). Once again, this method cannot be applied to nitric acid because the sample is spontaneously passive. It must also be noticed that using a voltammetric linear scan may have an impact on the mechanism of passivity breakdown in the case of chromium rich passive layers (18). King and Uhlig (15) highlighted that linear scan measurements doubled the slope Ea=f(pH) and that this difference could be related to differing chemical equilibria accompanying the breakdown of passivity.

In several references, samples were passivated in nitric acid and their activation potential was then studied in sulfuric acid (13, 20). According to these authors, stainless steel passivated in HNO3 and in H2SO4 show a very similar behavior. However, they were not able to perform the *in-situ* measurement since below the corrosion potential, the contribution of the anodic dissolution (active and passive) of the sample to the overall electrochemical current is completely masked by the cathodic reduction of nitrate. A few attempts have been made at measuring the activation potential by gravimetry in a discontinuous way to measure this anodic dissolution rate below the corrosion potential. The material was polarized at low potentials where the reduction reaction is intense, and the weight loss recorded after several hours of polarization (3, 21). However, they did not show the dependence of the activation potential on pH or temperature. Such a method also raises the issue of the solution chemical equilibria over the measurement time. It requires a massive electrode that releases a high quantity of metallic ions, while at the same time the counter electrode, in the same reactor, can highly disturb gas equilibria in the environment.

In this work, a novel method of measuring the activation potential of stainless steel in HNO3 is presented using atomic emission spectroelectrochemisty (AESEC). In this way, the anodic dissolution of the stainless steel was measured directly despite a cathodic current which is orders of magnitude larger. The variation of the activation potential was measured as a function of nitric acid concentration, temperature and silicon concentration of the steel and interpreted in terms of oxide stability. Previous work concerning the application of AESEC to stainless steel was essentially limited to the case of sulfuric acid, H2SO4. Briefly, the electrochemical kinetics of dissolution in the active state were investigated in the earliest AESEC publication (22). Additional studies concerned the formation of residual Cu rich films during active dissolution (23, 24) and the quantification of passive film growth kinetics during active passive transitions (25). An earlier work on passive film quantification was published in which AESEC was coupled with a quartz crystal microbalance (26). Finally, an investigation of the secondary peaks in the polarization curve of ferritic stainless steels in H2SO4 has been published (23).

*2. Experimental*

*2.1. Materials*

Silicon rich stainless steel and 304L stainless steel were used in this work for AESEC measurements. The specimens were cut into squares of 200 x 200 x 1 mm. The elemental analysis of the steel was performed by glow discharge optical emission spectroscopy (GD-OES) using a GD-Profiler™ from Horiba-Jobin Yvon. From the signals given by the GD-OES, the bulk of the sample was clearly reached from 10 to 150 µm depth and the composition of the steel was averaged over two craters on different samples. This analysis is given in Table 1. Si-rich and 304L SS are very similar stainless steels in composition, except for silicon and nickel. Relative ratios between major elements Fe, Cr and Ni are comparable. Prior to any use, the specimens were cleaned with ethanol and acetone in an ultrasonic bath, then polished to a mirror finish with 0.03 µm diamond paste. Polishing ensures good sealing in the AESEC flow cell and allows possible ex-situ surface analysis of the sample if required. All samples were then passivated for 24 h in nitric acid at the desired concentration and at room temperature in separate beakers. The passive film was then analyzed by X-ray photoelectron spectroscopy prior to AESEC measurements.

Table 1.

*2.2. Electrolytes*

Deionized water (18.2 MΩ cm) was prepared with a MilliporeTM system and used for all the reagents. Nitric acid 68% (Sigma Aldrich) was used to prepare the solutions. pH of each solution was verified using a Mettler-Toledo DL55™ titrator and NaOH 1 mol dm-3 reagent (Sigma Aldrich). All glassware was protected with a paraffin film to avoid any hazardous contamination. The electrolyte flow rate was approximately 2.8 dm3 min-1 measured to within 1% error for each experiment.

The experiments were performed at a temperature from 28 to 80°C (301 to 353 K) using a recirculating water system connected to a thermocryostat (LAUDA) constant temperature bath. Water from the bath was circulated through a hollow copper block connected to the rear of the working electrode so that the electrode was heated directly. The electrolyte reservoir was also heated in the constant temperature bath. Electrical isolation between the block and the sample was designed to prevent both current leakage and ensure heat transfer.

*2.3. Electrochemical measurements*

The AESEC flow cell has been described in detail in previous publications (22, 27). It consists of a three-electrode cell with the stainless steel specimen as the working electrode (Si-rich SS or 304L SS), a small platinum grid as a counter electrode, a mecury-mercurous sulfate reference electrode (MSE, E=+0.65 V vs. SHE in saturated K2SO4). The flow cell consists of a small volume working electrode compartment (approximately 0.2 cm3) with electrolyte input at the bottom and output at the top. The flow rate was measured accurately (2% precision) for each experiment and nominally 3 cm3 min-1. The reference and counter electrodes were in a separate compartment separated from the working electrode by a porous membrane to allow passage of electrical current but avoid bulk mixing of the two solutions. A Gamry Reference 600TM potentiostat functioning in the potentiodynamic linear polarization mode was used to measure electrochemical current density je with a 0.2 mV s-1 sweep rate. The analog outputs of the potentiostat were fed into the A/D converter and the data acquisition software of the inductively coupled plasma atomic emission spectrometer (ICP‐AES) so that the atomic emission intensity data and the electrochemical data were on exactly the same time scale.

*2.4. Atomic emission spectroelectrochemistry*

The experimental set-up including data acquisition has been described in detail in Ogle *et al.* (22, 24). Briefly, the working electrode releases ions into the electrolyte in the flow cell. The electrolyte is then continuously feed into the plasma of the ICP-AES were the emission intensities of the different ions are measured simultaneously. These emission intensities are converted into concentration using standard ICP-AES calibration techniques. Electrolyte transport is done using a peristaltic pump and the input to the plasma uses a concentric glass nebulizer and a cyclonic spray chamber. The ICP-AES used in this work was an Ultima 2CTM from HoribaJobin-Yvon consisting of a 40.68 MHz inductively coupled Ar plasma, operating at 1 kW and interfaced to independent polychromator and monochromator optical modules. The polychromator used a 50 cm focal length Paschen Runge with an array of photomultiplier tube detectors at given wavelengths allowing the measurement of up to 50 preselected elements simultaneously. Emission wavelengths were chosen for maximum sensitivity and low interferences. The monochromator (1 m focal length) using Czerny–Turner configuration is dedicated for high spectral resolution of a single element. In the present work, the monochromator was used to monitor the Cr signal. Wavelengths used for each element and corresponding detection limits are given in Table 2.

Table 2.

*2.5. AESEC data treatment*

For each element M, instantaneous dissolution rate νM and current jM are calculated from the instantaneous elemental concentration CM:

 (2)

 (3)

Where f is the flow rate of the electrolyte, A the surface area, F the Faraday constant, zM the oxidation state of the element M and MM its molar weight. Total dissolution current jΣ can be defined as the sum of major elements dissolution currents:

 (4)

And jΣ will be compared to electrical current je\* which is obtained by convoluting the electrical current measured by the potentiostat, je, using an experimental transfer function h(t), where h(t) represents the distribution of residence times in the flow cell (27). Complex physical processes contribute to the broadening of h(t). These processes include diffusion from the surface into the flowing electrolyte stream, mixing in the channel flow cell, spreading out during the laminar flow in the capillaries between the cell and the spectrometer, and the complicated nebulization system itself. Despite this complexity, an empirical function was simulated in the form of a log-normal distribution after an experimental measurement (24). A short pulse (10 mV during 0.5 s) was applied to a copper electrode in a 2 mol dm-3 deaerated HCl electrolyte under the same hydraulic conditions (length of tube, flow rate) as in the present experiments (24). This convolution treatment is necessary to compare electrochemical current with elementary equivalent currents that are estimated from the elementary concentration transients in solution. The convolution integral is:

 (5)

The detection limits, were calculated as following:

 (6)

where σblank is standard deviation of the background and α the sensitivity factorcalculated from the calibration curves of each element at their specific wavelength.

*2.6. X-ray photoelectron spectroscopy (XPS)*

XPS analyses were carried out with a Thermofisher Escalab 250 XI™ spectrometer using a monochromatic X-ray Al Kα source. The instrument was calibrated in energy with the silver Fermi level (0 eV) and the 3d5/2 core level of metallic silver (368.3 eV). The C-1s signal was used to correct a possible charge effect: the CC/CH contribution of C-1s spectra was fixed at 285.0 eV. The analysis zone consisted of a 900 µm diameter spot. The data processing was performed using the commercially available Avantage™ software. Main parameters used to decompose XPS spectra are presented in Table 3.

Table 3.

*3. Results and discussion*

*3.1 Anodic dissolution below the corrosion potential*

The AESEC method permits a direct measurement of the anodic dissolution of metals on an element by element basis even when the anodic current cannot be detected in the electrical current. A typical example of this for the Si-rich stainless steel in HNO3 is given in Fig. 1. In 4 mol dm-3 HNO3 at28°C, the open circuit potential was 0.19 ± 0.01 V vs. MSE, corresponding to the passive state of the steel. A cathodic AESEC linear polarization curve was performed beginning at the open circuit potential where the steel is still passive. As no significant dissolution rate is measured between the open circuit potential and -0.70 V vs. MSE, only a -0.70 V to -0.90 V vs. MSE. range of potential is recorded. Ammonia, NH3 can be expected to be produced below 0.05 V vs. NHE (-0.60V vs. MSE) (7) but in the same region the proton reduction reaction should also take place and dominate (7). As the potential decreases in the cathodic direction, |je\*| becomes increases; approaching -34 mA cm-2 at -0.9 V vs. MSE reflecting the reduction of H+ to H2. Supporting the idea that the proton reduction is the major reaction, two Tafel slopes of -40 mV and -120 mV per decade can be read on |je\*| in Fig 2 that are usually assimilated respectively to Volmer-Herovsky or Volmer-Tafel proton reduction mechanisms on metals in acidic environment (28).

Fig. 1

Fig. 1 gives as a function of potential je\* and the elemental dissolution currents of the alloying elements (jM, where M = Fe, Cr, Ni, Si, Mn). Like the cathodic current, the elemental dissolution currents, jM, also increase monotonically as the potential decreases below -0.7 V vs. MSE. Expressed as equivalent faradaic currents, their sum jΣ is also shown by way of comparison to je\*. Their systematic increase clearly demonstrates the loss of passivity as potential becomes increasingly cathodic. Note however that at the final point, -0.9 V vs. MSE, jΣ is only 2.4 mA cm-2 which is a quite small value as compared to the -34 mA cm-2 of je\*. This demonstrates the capacity of the AESEC technique to quantitatively detect very low anodic dissolution rates under circumstances when the electrochemical interface is dominated by the cathodic reaction. The activation transient of the stainless steel is not visible in the conventional polarization curve of je\* vs. E.

The operative definition of the activation potential Ea used in this work is shown in Fig 2. The logarithm of |jΣ| and |jMn| are plotted as a function of potential. As Mn is the alloying element with the lowest detection limit and is completely soluble in the HNO3 electrolytes used here, it is a logical candidate for the determination of Ea. The detection limit, expressed in A cm-2, is 1.5 ∙10-7 A cm-2 and is shown on Fig 2 (lower dashed line). As passive dissolution of the sample was not detectable by AESEC, being below the detection limit, Ea for this work is defined as the first potential where jMn rises to five times the detection limit (upper dashed line), in this case 7.5 ∙10-7 A cm-2. This measurement is actually coherent with any similar measurement on all of the elemental signals and enables to determine Ea with a precision of ± 10 mV.

Fig 3

Anodic dissolution was demonstrated to be congruent by the results of Fig. 3.

Chromium, nickel, silicon and manganese dissolution rates in µg s-1 cm-2 are divided by the mass ratio of the chemical composition of the steel given in Table 1. Mass ratios can be converted to faradaic ratios XM/XFe under the hypothesis of oxidation states of Fe(ìi), Ni(II), Cr(III) and Si(IV) (33). This leads to an accurate superposition of all the dissolution currents on jFe. Represented as a function of jFe, each signal reveals the general non-selective behavior of the active dissolution. It can be noticed that Mn presents a rigorously non-selective behavior to Fe, which supports the choice of Mn as the reference element for Ea determination. The non-selective behavior for all jM supports the conclusion that the active dissolution has been reached. One could expect a depletion or excess of chromium if an oxide was either forming or dissolving at the surface of the sample. A zoom of the low current values (inset to Fig. 3) does not confirm this expectation. However transient dissolution rate analysis should be more appropriate to measure any chromium relative enrichment. Such experiments were performed by Ogle *et al.* (25)in sulfuric acid using active-passive cycles.

*3.2. Activation potential depending on log(aH+)*

Previous measurements of the activation potential demonstrated a proportional relationship between Ea and the pH in sulfuric acid for several materials from pure iron to various types of iron-based alloys (12, 14, 16, 19, 29). AESEC measurements of Ea for the Si-rich SS in different concentrations of nitric acid enabled assessment of this relationship. Measurements of the activation potential of the Si-rich SS are shown in Fig. 4 for CHNO3 = 2, 4 and 6 mol dm-3.

Fig 4

Due to their method of measurement, most of studies cited before were not able to measure Ea for high proton activities. As AESEC is able to work with concentrated electrolyte, Ea of the Si-rich SS was possible with the identical precision even for concentrations up to 6 mol dm-3.

Each nitric acid concentration is associated to a certain proton activity which is calculated after Fallet et al.’s (30) work upon stoichiometric activity coefficient of the proton in 28°C binary HNO3-H2O solutions. This calculation takes into account the incomplete dissociation of the nitric acid in such solution. The following activities are given in Table 4.

Table 4.

Fig 5

The total cathodic current je\* increases with pH. This is not surprising since the proton reduction reaction is expected to dominate below -0.65 V vs. MSE. If the cathodic reaction is enhanced by the activity of the proton, it can also be accelerated by the passivity breakdown of the working electrode. The activation potential increases with the activity of the proton aH+ as shown in Fig. 4 with a slope of 0.12 V ± 0.03 V (Fig. 5.). According to Rocha *et al.’s* measurements (14) on various iron-chromium alloys at room temperature in the case of linear sweep voltammetry measurement, the activation potential of such alloys in sulfuric acid followed the equation (5) :

 (6)

With the *n* value of 0.5 measured in the same work, corresponding to an alloy that contains more than 15 wt.% in chromium, the activation potential curve should display a slope of 0.116. The results presented on Fig. 5 seem to be very similar to what was found in other electrolytes. Therefore, it is seen that the Ea of stainless steel in very concentrated nitric acid is comparable to sulfuric acid in terms of proton activity dependence.

The free enthalpy of formation may be accessed from the y-intercept. Rocha *et al.* (14) defined this y-intercept as the standard activation potential E°a and measured -0.26 V vs. SCE which is higher than -0.87 vs. MSE found in the present work (of about 200 mV). Uhlig *et al.* (15, 29) showed that a standard formation free enthalpy ΔrG° of the oxide can be obtained from the value of E°a and that it helps to assess the alloy’s affinity to oxygen in the electrolyte. The calculation is based on the equation of oxide formation as follow:

 (7)

where M is the metallic element considered. Such affinity might also depend strongly on the chemical composition and microstructure of the passive layer that is studied. These considerations lead to the idea that the oxide formation kinetics could be related to a specific oxide layer. Therefore the value of E°a could be explained by a different passive layer that is preferentially formed in the three different concentrations. XPS quantifications were performed for passive layers formed at Si-rich SS surface in the three nitric acid concentrations at 28°C and in sulfuric acid 2 mol dm-3 at 28°C. The results ascertained in Table 5 present relative concentrations in iron, chromium and silicon oxides regarding levels Fe-2p3/2, Cr-2p3/2 and Si-2p.

Table 5.

The differences between nitric and sulfuric electrolytes are not considered as significant and the results also demonstrate a reproducible passive layer composition in all nitric electrolytes. The oxide film’s nature and thickness (relatively evaluated by ratio of oxide and metallic peaks’ areas) does not seem to be sensitive to concentration or nature of the electrolyte. It is very likely that the solubilities of all species in the oxide layer increase with the proton activity. The impact of nitrates could play a role in this phenomenon. For example, in the case of the possible reduction reaction described by equation 4, occurring simultaneously with hydrogen reduction, the adsorbed radical leads to the formation of adsorbed NH3. Such a reaction could require a certain surface that could impact the total rate of electron exchange, leading to a slower dissolution of the material.

*3.3. Activation potential depending on temperature*

The proportional relationship between Ea and pH has been assimilated to a Nernst type equation by several authors (15, 20). It can then be expected that Ea also depends linearly on temperature. AESEC measurements of the Ea of Si-rich SS were performed in 4 mol dm-3 nitric acid at different temperatures. Fig. 6 displays the total dissolution rates obtained for the temperatures of 28°C, 40°C, 60°C and 80°C (respectively 301 K, 313 K, 333 K and 353 K).

Fig. 6.

Ea is comprised between -0.75 and -0.60 V vs. MSE in these conditions. The higher the temperature, the higher the dissolution rate measured at a given potential, resulting in a shift of Ea to higher potential. With increasing temperature, je\* also increases. This may be considered as a consequence of temperature elevation under the hypothesis of hydrogen reduction whose reaction rate follows the Butler-Volmer equation.

Fig. 7.

When the Ea values extracted from Fig. 6 are plotted as a function of temperature, a proportionality factor of 0.0027 ± 0.0004 is observed (Fig. 7). For a better legibility of the calculation, temperatures have been converted from degrees Celsius to Kelvin. Under the hypothesis of a Nernst type evolution of Ea vs. T the slope of the curve of Fig. 7 will depend on several parameters such as ionic activities of the elements in the alloy and the number of electrons exchanged. These parameters cannot be determined easily. Nevertheless, the linear dependence between Ea and temperature is for the first time demonstrated through the present work.

*3.4. Activation potential depending on the silicon content in the alloy*

The silicon enrichment of 18Cr-10Ni type SS has been shown to provide a homogeneous corrosion morphology in very oxidizing electrolytes (10, 31). In the present work, XPS measurements of the Si-rich SS confirmed the large presence of silicon in the passive layer which is also higher than in its bulk composition (Table 4). As compared to the 304L stainless steel, which is a 18Cr-10Ni type SS with 0.34 wt. % of silicon in its composition (Table 1), Si-rich SS presents a chemically different oxide layer. The chromine (Cr2O3) rich 304L SS’s passive layer was quantified by XPS measurements displayed in Table 6.

Table 6.

The oxide peaks energies measured for silicon suggest that the alloy is oxidized into some mixed iron-chromium silicates whose chemistry is not easy to determine. Similar conclusions can be found in Robin *et al.* (32). The activation potential of such different passive layer may provide interesting information about their respective properties in nitric acid, for example their affinity to oxygen.

The activation potentials of the 304L SS was measured by AESEC and compared in the same conditions as the Si-rich SS.

Fig. 8.

Fig.8 shows the total dissolution currents measured for the 304L SS during the activation of the sample as compared to the Si-rich SS’s in a 4 mol dm-3 HNO3 at 28°C. The reduction reaction increases shortly after the break of passivity occurs, as observed in Fig. 6. Considering that the interface reactivity is deeply modified by the break of passivity, one can expect an increase of the reduction kinetics regardless of the reduced species.

 A gap of about 200 mV appears between the activation potentials of both materials. The passive layer that contains more Cr presents the lowest activation potential in this medium. This supports the representation of the active dissolution as the result of a competition between oxide formation at metal/oxide interface and oxide dissolution at oxide/electrolyte interface, rather than the reducing of Cr(III) to Cr(II). Indeed, if the active dissolution was the only consequence of chromium reducing, the gap of activation between these two very similar alloys would not have been expected. As discussed in Section 3.2, and given the XPS results on the nature of the silicon-rich passive layer, the oxidation equation (eq. 7) on which ΔrG° calculation is based would be subject to certain modifications, and the oxide formation kinetics would better be impacted. It seems that silicon lowers ΔrG° which pushes the equilibrium of the equation 7 in the direction of the reduction. Silicon may lower the affinity of the alloy to oxygen and slower the kinetics of oxide formation. However, chromium reducing cannot be undoubtedly discarded as the steady state potential of the couple Cr(III)/Cr(II) is -0.41 V vs. NHE (33) which corresponds to -1.06 vs. MSE and this could be almost consistent with the activation potential of the 304L SS. A contribution of chromium reducing and affinity to oxygen impact by silicon is very likely to be responsible of this impact of Ea.

*4. Conclusions*

* The AESEC technique was used for the first time to sweep potential back to the value that enables the active break of passivity of stainless steels and analyze the dissolution rates of each major alloying element.
* The activation potential of the passive layer in a given environment gives information on the alloy’s affinity to oxygen and thus the stability of the oxides formed.
* A linear dependence between the activation potential and the logarithm of the proton activity was found, similarly to what has been found in the literature in other electrolytes. Slope of this linear dependence was found to be very coherent with sulfuric acid, although the standard activation potential was shifted to lower values. This shift might be explained by several parameters including the nature of the electrolyte (impact of NO3-).
* It was confirmed by XPS measurements that the initial passive layer is similar for all conditions in terms of thickness, structure and chemistry, enhancing the hypothesis of both an increase of the oxide solubility with the proton activity and an impact of the nitrates on the oxygen interaction with the alloy.
* For the first time, the linear dependence between Ea and temperature was demonstrated by an in-situ measurement for a wide range of temperatures from ambient to 80°C. The general tendency of this evolution would be in good agreement with a Nernst-type equation. However, determination of all parameters would require further investigations of activities of the alloyed elements.
* It was shown that silicon in the stainless steel increases the value of the activation potential. The passive layer displays a higher activation potential as it contains less chromium and more silicon.

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TABLES

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| --- | --- | --- | --- | --- | --- | --- |
|   | Fe | Cr | Ni | Si | Mn | Add. |
| Si-rich SS | 59.8 | 18.8 | 15.1 | 3.5 | 2.0 | 0.8 |
| 304L SS | 70.3 | 17.8 | 9.5 | 0.3 | 1.5 | 0.6 |

Table 1. Mass composition of Si-rich and 304L SS determined by GD-OES profiles performed on samples and averaged between 50 µm 150 µm depth expressed in wt.%

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Fe | Cr | Ni | Si | Mn |
| Wavelength / nm | 259.940 | 283.563 | 231.604 | 251.611 | 257.610 |
| Atomic weight / g mol-1 | 55.8 | 51.9 | 58.7 | 28.1 | 54.9 |
| Detection limit C3σ / µg dm-3 | 12.1 | 7.3 | 27.3 | 30 | 1.0 |

Table 2. Wavelengths used for each major element of the two stainless steels, corresponding atomic weights and detection limits associated (averaged over 10 experiments)

|  |  |  |  |
| --- | --- | --- | --- |
|  | [ Fe Ox ] / at.% | [ Cr Ox ] / at.% | [ Si Ox ] / at.% |
| Fe - 2p3/2 | Fe - 2p3/2 | Cr - 2p3/2 | Cr - 2p3/2 | Cr - 2p3/2 | Si - 2p | Si - 2p |
| Binding energy / eV | 709.69 | 712.07 | 576.26 | 577.32 | 578.99 | 102.05 | 102.65 |
| FWHM / eV | 2.36 | 2.93 | 1.08 | 1.92 | 1.71 | 1.36 | 1.32 |

Table 3. Parameters used for the deconvolution of XPS spectra (Avantage software) Binding energies and full width at half maximum (FWHM)

|  |  |  |  |
| --- | --- | --- | --- |
| CHNO3 / mol dm-3 | 2 | 4 | 6 |
| aH+ | 2.0 | 6.3 | 12.8 |

Table 4. Activity of proton for each nitric acid concentration CHNO3 = 2 mol dm-3; 4 mol dm-3; 6 mol dm-3 at 28°C calculated after Fallet *et.al.* (30)

|  |  |  |  |
| --- | --- | --- | --- |
|  | [ Fe Ox ] / at.% | [ Cr Ox ] / at.% | [ Si Ox ] / at.% |
| Nitric acid (aH+ = 2.0) | 21 | 49 | 30 |
| Nitric acid (aH+ = 6.3) | 19 | 54 | 27 |
| Nitric acid (aH+ = 12.8) | 22 | 44 | 34 |
| Sulfuric acid ([H+] = 4 mol dm-3) | 27 | 44 | 29 |

Table 5. XPS quantification in at. % of three passive layers compositions spontaneously established in nitric acid [HNO3] = 2 mol dm-3; 4 mol dm-3; 6 mol dm-3 (associated to their respective activity of the proton) and in sulfuric acid [H+] = 4 mol dm-3 at 28°C

|  |  |  |  |
| --- | --- | --- | --- |
|  | [ Fe Ox ] / at.% | [ Cr Ox ] / at.% | [ Si Ox ] / at.% |
| Si-rich SS | 19 | 54 | 27 |
| 304L SS | 40 | 60 | 0 |

Table 6. XPS quantification of two passive layers compositions spontaneously established on Si-rich and 304L stainless steels in nitric acid 4 mol dm-3 at 28°C expressed in at. %

FIGURES CAPTIONS

Fig 1

Elemental dissolution currents jM, total dissolution current jΣ and external current je\* as a function of potential for Si-rich SS in CHNO3 = 4 mol dm-3 28°C, cathodic direction, sweep rate: V = 0.2 mV s-1 (black : jΣ; red : jFe ; blue : jCr ; purple : jNi ; green : jSi ; orange : jMn ; red curve on the secondary y-axis : je\*)

Fig 2.

Log ( | je\* | ) (red), log ( | jΣ | ) (black), and log ( | jMn | ) (orange) as a function of potential during linear sweep voltammetry of Si-rich SS in CHNO3 = 4 mol dm-3 28°C, cathodic direction, sweep rate: V = 0.2 mV s-1. Dashed lines represents the jMn detection limit (lower line) and five times its value (upper line) given as a criterium for Ea. The inset on top represents the linear representation of jMn as a function of potential and jMn detection limit.

Fig 3.

Elemental dissolution currents jM multiplied by their faradaic ratios on Fe for Si-rich SS in CHNO3 = 4 mol dm-3 28°C as a function of iron dissolution current jFe over linear sweep voltammetry (cathodic direction, sweep rate V= 0.2 mV s-1)

Fig 4.

je\* (A) and corresponding jΣ (B) over linear sweep voltammetry (cathodic direction, sweep rate: V=0.2 mV s-1) of Si-rich SS performed in CHNO3 = 2 mol dm-3 (aH+ = 2.0); 4 mol dm-3 (aH+ = 6.3); 6 mol dm-3 (aH+ = 12.8) at 28 °C

Fig 5.

Activation potential of Si-rich SS as a function of the logarithm of the proton activity in nitric acid CHNO3 = 2 mol dm-3 (aH+ = 2.0); 4 mol dm-3 (aH+ = 6.3); 6 mol dm-3 (aH+ = 12.8) at 28°C

Fig 6.

je\* (A) and corresponding jΣ (B) over linear sweep voltammetry (cathodic direction, sweep rate V = 0.2 mV s-1) of the Si-rich SS in nitric acid solution CHNO3 = 4 mol dm-3 at T= 28 °C, 40 °C, 60 °C and 80 °C

Fig 7.

Activation potential of the Si-rich SS as a function of the temperature in nitric acid solutions CHNO3 = 4 mol dm-3 at T= 28 °C, 40 °C, 60 °C and 80 °C

Fig 8.

 je\* (A) and corresponding jΣ (B) over linear sweep voltammetry (cathodic direction, sweep rate V = 0.2 mV s-1) of Si-rich SS (red) and 304L SS (blue) in nitric acid solution CHNO3 = 4 mol dm-3 at T = 28°C