Effect of Mechanical Stress on the Properties of Steel Surfaces: Scanning Kelvin Probe and Local Electrochemical Impedance Study

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The influence of mechanical stress on the electrochemical properties of ferritic steel SAE 1008 and austenitic stainless steel 301LN was studied using Scanning Kelvin Probe and Localized Electrochemical Impedance Spectroscopy (LEIS) techniques. The probe-working electrode Volta potential difference was mapped in situ under load. It was found that the influence of elastic deformation on the potential was small. Plastic deformation decreased the potential of steel by 150–300 mV, whereas the relaxation of the load from the plastic domain increased the Volta potential. However, some locations, which can contain residual stress, remained at low potential. The pre-strained surfaces were characterized by X-ray Photo Electronic Spectroscopy and by Atomic Force Microscopy. Distribution of the capacitance across strained and strain-free surfaces was studied by LEIS in boric/borate electrolyte. The plastic stress increases the capacitance and decreases the ability of the steels to passivate the surface indicating that emerging of pile-ups of dislocations create defective oxide films.

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Abstract

Stress corrosion cracking (SCC) is a well-known complex corrosion process caused by the combination of stress and corrosion, which can lead to wear, cracking or fatigue failures. In many cases, the residual stress from plastic deformation or wear accelerates the corrosion rate. In the classic film rupture model, tensile stress breaks the passive film creating anodic locations at the bottom of the crack, which propagates through an activation/passivation process. This model was developed from the “slip dissolution-film rupture model” pointing out the importance of formation of dislocations and metal dissolution through dislocation slip lines. The slip dissolution-film rupture model of crack advance was discussed in details previously. This model can predict the crack growth rate for the stainless steels, nickel alloys, and low-alloy steels in high temperature water.

The effect of the yielding on the rate of dissolution of many metals was found to be much pronounced in comparison with the influence of elastic deformation. The dissolution rate showed a marked rise at the beginning of the plastic region that is asymptotic with increasing strain. Similar effects of plastic deformation on the anodic current during dissolution were also found for stainless steels. To explain this mechanical-electrochemical effect, both the increase of dissolution rate at slip edges and dislocations, and the increase of surface roughness from plastic deformation were pointed out. On the other hand, the selective slip dissolution can be ascribed to the local excess of Gibb potential, thus contradicting earlier works. Has shown that both enthalpy and entropy of activation were not significantly altered by cold work, which means that the free energy of activation for anodic reaction should remain almost constant. A calorimetric study showed that residual energy from cold work was less than 7 calories per gram without any significant impact on Gibbs potential during the deformation.

Interestingly, Sahal et al., and Saito and Kuniya reported that elastic (hydrostatic) stress can modify the chemical potential of the dissolving species, and accordingly the energy of activation of the metal dissolution. The dissolution rate in acidic electrolyte was found to be proportional to the dissolution density created by plastic strain. As a result, surface roughness associated with emergence of slip bands promoted the dissolution process in relation with the electronic state of the surface. The activation energy of the dissolution process can be influenced by long-range internal stresses due to the heterogeneous distribution of dislocations, evolution of kink density and emergence of the lines of the dislocations, whereas plasticity and formation of dislocations or kinks can modify the solid configurational energy. Thus, the activation energy to transfer metallic ions in the electrolyte is decreased by dislocations.

In addition, the properties of the surface oxide film can be modified by plastic strain. A less protective passive film was created by cold working, which was attributed to the presence of defects such as dislocation pile-ups. A study of austenitic stainless steel showed that cold work and plastic deformation lead to the formation of dislocations and α-martensite that decreased the ability of the steel to passivation. Martensite was formed in deformed areas, where slip planes intercepted the passive film and a large number of dislocations may be concentrated.

Electrochemical Impedance Spectroscopy (EIS) and Mott-Schottky analysis were shown to be efficient to analyze the semiconducting properties of passive film on stainless steels (316L and 304) under mechanical stress. The conductivity and capacitance of the oxide film increased when an elastic or a plastic stress was applied. This effect was explained by an increase of the concentration of donors and acceptors compared to a stress-free state. Under these conditions, the formation of oxygen vacancies according to the point defect model was proposed to explain the sensitivity of stainless steel to localized corrosion such as pitting corrosion and stress corrosion cracking.

Thus, the stress can decrease the activation energy of anodic dissolution, which was found during the active dissolution of steel. Moreover, in previous studies, the use of scanning Kelvin probe (SKP) showed that plastic tensile and compressive strain decreased the electrochemical (Volta) potential of stainless steel by 200–300 mV. The measurements were performed in air, thus minimizing the influence of adsorption of ions or the hydrogenation on the potential. The strain-induced drop of the electrochemical potential was explained by the formation of dislocations that broke the oxide film. However, plastic deformation transforms austenite to martensite phase that can also influence the potential. Thus, it was important to continue the study and to compare the effect of the stress on the potential of ferritic and austenitic steels. Determination of the potential in the locations containing the residual stress due to previous plastic deformation is also a point of interest. In this work, two complementary local probe techniques with similar level of spatial resolution were used for the characterization of carbon and austenitic steels. SKP was used to measure the electrochemical potential of the surfaces with stress, whereas

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local electrochemical impedance spectroscopy (LEIS) was used to characterize the passive films in stressed conditions and the ability of these areas to repassivation. The role of the applied stress on the stability of passive oxide film and the reactivity of the stainless steel surface in aqueous electrolyte was studied using local electrochemical techniques in a preliminary investigation.\textsuperscript{21}

**Experimental**

**Material and specimens.**—In this study, carbon steel SAE 1008 and austenitic stainless steel 301 LN (EN 1.4318) were used. The nominal compositions of the two steels are given in Table I. The materials were machined to obtain samples compatible with the local probe techniques used. The sketch of the shape of the samples is shown in Figure 1. The tensile samples contained a gauge section (called “notch” hereafter) working as stress concentrator within the specimen. The thickness of the 301 LN steel plate was 1 mm and the “gauge section” was milled down to 0.1–0.2 mm. The reference material was a carbon steel (“Q Panel”, SAE 1008, ISO specification 3574, CR1-type) with a thickness of 0.8 mm and a hardness (on Rockwell B) of 50–65 Hb. The 301 LN was investigated in the tempered and rolled condition meaning that substantial work hardening and strain-induced martensitic phase were present.\textsuperscript{20} The mechanical properties were determined by tensile testing on a flat specimen with a testing speed of 0.0067 s\textsuperscript{−1} (see Table II).

Unless otherwise specified, the steel surface for SKP and LEIS measurements was grinded using silicon carbide paper down to SiC #1000, degreased in ethanol, rinsed in deionized water and stored in dry air. A constant load cell equipped with load sensor was used to apply tensile load in the range of 200–650 MPa.\textsuperscript{20}

**Scanning kelvin probe.**—SKP is often used for measuring the Volta potential difference with respect to any reference electrode or the electron work function (\(\text{ewf}\)) with respect to the zero level in vacuum.\textsuperscript{22} The electrochemical potential of the electrons, \(\alpha\), is defined as the work to remove one mole of electrons from the infinity (i.e. in vacuum) to the Fermi level inside the metallic phase and is given by Eq. 1.

\[
\Phi \text{N}_\alpha = -\alpha = -\mu_e - F X_w
\]

where \(\Phi\) is the \(\text{ewf}\), \(\mu_e\) is the Fermi level of the electrons in the metal, the \(X_w\) is potential drop across metal surface, \(N_\alpha\) and \(F\) are the Avogadro and the Faraday constants.\textsuperscript{23} Thus, the potential \(\Phi/\mu_e\) (\(e\) being the elementary charge) has bulk and surface contributions. For a metal covered by an oxide film, the potential drop can be expressed as:

\[
X_w = \frac{\mu_{\text{ox}} - \mu_e}{e} + F_b + \beta_{\text{ox/air}}\]

This equation shows that the contact potential difference between the metal and the oxide is proportional to the difference in Fermi levels of the electrons in the metal (\(\mu_e\)) and in the oxide (\(\mu_{\text{ox}}\)). \(F_b\) is the potential drop in the oxide, and \(\beta_{\text{ox/air}}\) is a contribution accounting for the potential drop of adsorbed molecules on the oxide surface. For an iron oxide film, \(\mu_{\text{ox}}\) is governed by the ratio of activities [Fe\(^{3+}\)] / [Fe\(^{2+}\)] whereas for stainless film, both chromium and iron species have to be taken into account.\textsuperscript{24} In a corrosive environment, the SKP measures the potential corresponding to the corrosion potential.\textsuperscript{25} In dry air conditions, the measurement relates to the potential of steel in the passive state controlled by red-ox potential of the surface species.\textsuperscript{24,26} In addition, it was shown that the potential of stainless steel is influenced by the oxide film thickness,\textsuperscript{20} the potential being more positive for a thicker film. Thus, probe-working electrode Volta potential difference relates to electrochemical potential of the working electrode given relative to a reference electrode.

The SKP equipment (UBM Messtechnick) uses vibration capacitor principle to measure the surface distribution of the Volta potential. For measurements in situ under load, a constant load cell with fixed tensile sample was inserted in the SKP chamber.\textsuperscript{20} The experiments were performed in laboratory air at ambient temperature 22°C and at 50% RH. The reference electrode was a needle of a Ni-Cr alloy with a tip diameter of 100 \(\mu\text{m}\) allowing a lateral resolution in the range of 100 \(\mu\text{m}\). In a first step, a topography profile was measured. Then, the SKP scanning of the sample was performed with a constant probe-to-sample distance (50 \(\mu\text{m}\)) and a vibration amplitude of 20 \(\mu\text{m}\) at a frequency of 2 kHz. In standard measurements, the data recording density was 16 points/mm along the X-axis and 4 points/mm along the Y-axis. Before the measurements, the potential of the probe was calibrated with respect to a saturated Cu/CuSO\(_4\) electrode. All SKP potentials are given versus the standard hydrogen electrode (SHE).

**Table I.** Chemical compositions of the investigated materials [wt\%].

| Material    | Fe   | C    | Si   | Mn   | P    | S   | Cr | Ni  | Mo  | N   |
|-------------|------|------|------|------|------|-----|----|-----|-----|-----|
| 301 LN      | 534  | 8 46 | 4.65 | 0.32 | 0.03 | 0.012 | 17.60 | 6.55 | 0.17 | 0.138 |
| SAE 1008    | 285  | -    | -    | -    | -    | -    | -  | -   | -   | -   |

**Figure 1.** Sketches of the samples used. a- carbon steel sample, b- stainless steel 301 LN sample. The dimensions are given in mm.
Figure 2. Averaged potential distribution with error bars across the notch for carbon steel electrode under the load 200 MPa (a) and 260 MPa (c) and in 24 h after unloading 200 MPa (b) and 260 MPa (d). The measurements were carried out in air at 50% RH.

(pH = 9.2). A 3-electrode cell was used including a Pt wire counter-electrode and Ag/AgCl saturated electrode as a reference.

Local electrochemical Impedance Spectroscopy (LEIS) measurements were performed with a home-made setup in a borate electrolyte with an AC perturbation of 25 mV peak-to-peak, the potential of the sample was referred to SHE. LEIS mapping was performed at a constant frequency of 5 kHz. The local probe consisted of a Ag/AgCl bi-microelectrode of 50 μm in radius used as local potential sensors.27 The local potential difference measured was amplified using a home-made differential amplifier and converted to a local current density using ohm’s law.28 It is thus used to measure the local impedance using a multichannel frequency response analyzer, allowing the simultaneous measurement of both local and global electrochemical impedances.29 The 301 LN samples were pre-strained to a 10% tensile strain. Before the LEIS experiments, the air formed oxide film was reduced at −1.2 V / SHE for 10 min. The mapping was performed at fixed potentials at −0.1 and +0.4 V / SHE. In addition, LEIS was measured for 301 LN steel and carbon steel at the center of the notch as function of the load.

Surface analyses by XPS, AFM and light topography profiling.— The oxide film on deformed steel surface was characterized by X-ray Photoelectron Spectroscopy (XPS, Thermo VG Thetaprobe). The 301 LN steel oxide layer composition was analyzed using a two-layer oxide film model that consisted of an iron oxide (Fe2O3) outer layer and a chromium oxide (Cr2O3) interlayer.30 The notch area contained the residual stress due to previous yielding and the location without the stress (i.e. outside the notch area) were analyzed.

The influence of plastic deformation on surface topography and roughness was studied by Atomic Force Microscopy (AFM, Bruker nanoscope multimode 8) using the tapping mode (cantilever frequency of 354.83 kHz). The probe (RTESP MPP-11100) showed a typical tip curvature between 5 and 10 nm.

The evolution of the surface roughness after straining or sample grinding was studied with a profilometer (Veeco, WYKO Surface Light Profiler).

Results

Influence of the strain on the Volta potential of carbon steel.— The Volta potential difference was measured on tensile specimens under load to reach elastic stresses of 200 and 250 MPa in the work area. The initial potential for a non-deformed surface was uniform and close to 300–330 mV, whereas when the measurements were performed under the applied load, the potential in the notch area decreased by 21+/−20 mV (200 MPa) and 28+/−20 mV (250 MPa) compared with surrounding surfaces (Figures 2a, 2c). The data calculated by averaging the potential above and around the notch areas and contain confidence interval (error bars). Then, the sample was unloaded and the measurement was repeated after 24 h of exposure after unloading (Figure 2, curves b, d). The scattering of the potential increased and the potential drop in the notch was lower. Thus, elastic deformation only slightly decreased the Volta potential of the carbon steel. This is in agreement with literature data for other materials, e.g. the elastic stress can decrease or increase potential of Al, Cu or steel for 5–10 mV.20,31–34

Figure 3a shows the distribution of the potential across a carbon steel sample under the load of 310 MPa. This is higher than the yield strength (285 MPa) and the measurement of elongation gives the plastic strain close to 10%. SKP showed the area of low potential of 200 mV in the notch relative to the surrounding surface. Another sample was strained to 15% (330 MPa) and the potential drop in the notch area compared with the surrounding was about 100–150 mV (Figure 3b). Logically, it can be expected that increase of the strain will proportionally decrease the potential. However, the experimental data (Figures 3a, 3b) showed that the dependence is more complex.
The potential can be a function of the thickness of oxide layer and the rate of the loading that can influence on the dislocations pattern (e.g. formation of the cells with high plastic strain\(^{11,13}\)). However, these parameters were not controlled in this study. The formation of slip bands in the strained area is shown by AFM topography in Figure 3c. The results showed that prior tensile plastic deformation increased slightly the thickness of iron oxide layer, from about 2.2 nm to about 2.7 nm. Moreover, the analysis of the O1s peak showed an increase of the contribution of OH\(^-\) group with the plastic deformation (see Figure 4B). It is thus concluded that the passive film of the strained area was more defective and had an increased content of iron hydroxides.

The potential distribution was measured 1 month after unloading. Long-time exposure in a dry air atmosphere led to an increase of the Volta potential to a level 50–80 mV more positive relative to the area surrounding the notch. A possible explanation is that the relaxation of the pre-stressed oxide film resulted in an increase of the oxide film thickness, which is in line with XPS measurements. On the other hand, healing of the defects in the freshly formed oxide by oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) may have also played a role and increased the potential of the gauge section during ageing.

**LEIS measurements of the strained carbon steel surface** —The effect of the stress was studied by local electrochemical impedance spectroscopy in boric/borate aqueous electrolyte. It is possible to compare the impedance for the strained and non-strained areas. The carbon steel sample was strained using the constant load cell and the stress was controlled by a load sensor. The local impedance was monitored by performing a measurement at a single location at the center of notch simultaneously with the global impedance, which corresponds to an averaged value over the whole exposed surface to the electrolyte. Figure 5 shows that the load (300 MPa) increased the local capacitance from 2 to 3.4 \(\mu F/cm^2\). In first approximation, this increase of capacitance can be seen as a thinning of the passive film when increasing the mechanical stress. A similar effect can be the result of increasing the real surface of the working electrode, for instance due to increasing of the surface roughness.

The yield stress is 285 MPa, as shown in Table II, and the tensile strain increases the capacitance during both the elastic and plastic deformation. Conversely, to the local capacitance, the global measurement shows a constant value of the mean capacitance whatever the mechanical load. Thus, the local variation of the impedance due to the strength has only a light contribution on the global EIS response indicating that the local variation of the capacitance is localized above the notch area only, and can be monitored only with the help of a spatially resolved techniques.

The open circuit potential (OCP), which was monitored using an Ag/AgCl reference electrode, decreased due to straining from \(-0.12\) to \(-0.38\) V/SHE. This effect was observed only after reaching the yield stress. A negative shift of the OCP can be related to the formation of defects or to the decrease of the oxide film thickness due to local breakdown in the film. Interestingly, the OCP value, which is a global measurement, appears to be sensitive to local modifications of the oxide film.

The sample was unloaded and LEIS was monitored during exposure in the electrolyte. After 12 h of exposure, the OCP increased by 40 mV to reach \(-0.34\) V/SHE and the local capacitance decreased from 3.4 to 2.5 \(\mu F/cm^2\). Thus, defects in the oxide film repair and in absence of loading the surface can partially re-passivate. The LEIS data in electrolyte are in line with SKP measurements in air.
Figure 4. A- averaged potential distribution with error bars across the notch area. 1-potential of initial surface, 2-potential of the surface under the load (310 MPa); 3,4 –potential of the unloaded surface measured in dry air 5%RH (4) and in dry nitrogen 5%RH (3) atmospheres. B- XPS spectrum, OH<sup>-</sup>/H<sub>2</sub>O and iron oxide contribution on the O1s peak (a) reference unstrained area and (b) plastic strained area.

Figure 5. Influence of the mechanical load on the local (1, 2) and global (3, 4) capacitances of the carbon steel in borate electrolyte. The measurements 2 and 4 were performed after unloading.

**SKP and XPS measurements of austenitic 301 LN steel.**—The sample of stainless steel 301 LN with reduced thickness in the gauge section was loaded up to 650 MPa. This stress was higher than the tensile strength (Table II) and the Volta potential in the area of the notch decreased by 250 mV. Figure 6 shows the potential distribution across the tensile specimen under the load and after unloading. The data across the profile were averaged and the error bars are shown in the figure. The length measurement confirmed a notch elongation of about 10%. The sample was unloaded and the potential distribution was measured in 24 h after unloading (Figure 6, curve 2). The potential in the area of notch was decreased by the plastic strain compared with areas outside the notch, and it is in agreement with the potential variations for 301 LN stainless steel<sup>[35]</sup> and <i>et al.</i> for duplex stainless steel. Visual observation and AFM topography show...
The reference spectrum XPS was used to analyze the influence of previously applied strain on the potential drop across the oxide film. Thus, grazing angle potential; 20 the thinner the oxide layer, the more negative the potential when compared to rough surface. Thus, the effect of the surface roughness due to plastic deformation on the potential had to be studied.

The surface topography was measured for previously strained to 10% elongation carbon steel sample inside and outside of the notch in rectangles of 740 × 440 μm². A 4-fold average roughness increase from 110 nm to 466 nm due to plastic strain was found, whereas it reached a 7-fold factor (from 92 nm to 690 nm) for stainless steel sample under the same experimental conditions.

Influence of the surface roughness on the volta potential.—It was assumed 11–34 that the formation of dislocations can change the potential drop across the metal/air interface due to variation in the atomic density and accordingly to the interfacial dipole moment (Eq. 1), resulting in a decrease of the \( \text{ewf} \) at locations of peaks at the rough surface. On the other hand, semiconducting oxide film covered the steel surface. Variation of the atomic density can differently change the potential distribution across the 301 LN steel surface with high roughness due to plastic deformation on the potential had to be studied. The surface topography was measured for previously strained to 10% elongation carbon steel sample inside and outside of the notch in rectangles of 740 × 440 μm². A 4-fold average roughness increase from 110 nm to 466 nm due to plastic strain was found, whereas it reached a 7-fold factor (from 92 nm to 690 nm) for stainless steel sample under the same experimental conditions.

To mimic the effect of the roughness, the samples were ground using SiC emery paper of different grits. Initially, the 301 LN steel surface was ground using SiC #4000 paper to a low roughness factor (31 nm). Then, a part of the treated surface was ground with SiC #80 paper creating an average roughness of 589 nm, that is, a roughness close to that of 301 LN steel after yielding. The stabilization of the oxide film was achieved by exposing the sample for 3 days in dry air. It is noteworthy that no significant modifications of the thickness and the elements distribution occurred in the oxide film for 301 LN steel surface after grinding with different roughness. 35 Figure 9 shows the potential distribution across the 301 LN steel surface with high (left hand side of the cartography) and low (right hand side of the cartography) roughness. Interestingly, the area with the lowest roughness showed a 30 mV higher potential relatively the area with a high roughness.

Similar experiments were performed for carbon steel for which the smooth surface showed only an increase of 10 mV of the Volta potential when compared to rough surface. Thus, the effect of the roughness on the potential was much lower compared with effect of the yielding. It is probable that the difference in Volta potentials (Figure 9) is related to residual stress that originates from the grinding. 16,36 On the other hand, measurements of capacitance showed that rougher steel surface may lead to higher disordering of the surface oxide, which can also change the electronic properties of the film. 37

![Figure 6](image1.png)  
**Figure 6.** Averaged potential distribution with error bars across gauge section of 301 LN steel sample under the load (1) and in load-free conditions (2). The measurements were carried out in air at 50% RH.

![Figure 7](image2.png)  
**Figure 7.** Photograph of the sample (a) and AFM topography of the strained area (b). The sample was loaded at 650 MPa corresponding to 10% plastic strain. Some slip bands are indicated by white arrows.

![Figure 8](image3.png)  
**Figure 8.** XPS of the Fe2p envelope in unloaded (reference), tensile strained specimen 301 LN steel. Potential distribution is shown at Figure 6.
SKP and LEIS study of strained zones of 301 LN steel.—It is also important to evaluate the effect of straining in the presence of the electrolyte. The area of the notch and around the notch was exposed to a borate solution in a conventional electrochemical cell. The air formed oxide film was reduced at $-1.2$ V (SHE) for 10 min and the steel sample was polarized at fixed potentials for 1 h. The sample of 301 steel was then strained to 10% of elongation in the electrolyte under polarization. The SKP measurements were performed in air after rinsing the unloaded sample in deionized water and drying in a stream of dry air. The potential profile (Figure 10a) shows the potential distribution across the notch for the sample polarized at $-0.1$ V/SHE. This potential is close to the OCP measured for of the steel in borate electrolyte. The profile shows low potential areas in the middle part related to the notch where the potential drop reached about 300 mV.

Figure 10b shows the potential distribution for steel after an anodic polarization of 0.4 V/SHE. Some locations inside the notch exhibited increased Volta potential and some of them show low potential. The potential contrast between strained and non-strained area increased to 500 mV. Thus SKP visualizes the areas with residual stress which have low ability to passivate the surface.

The LEIS was applied using the same setup. The measurements of the capacitance were performed in situ during elastic deformation in the range 0–125 MPa in borate electrolyte. The LEIS data show that stress increased the capacitance at the center of the notch from 2.3 to 2.4 $10^{-6}$ F/cm² (data are not shown). Thus, elastic tensile strain shows only minor influence on the properties of the steel surface.

The same experiment was performed on 301 LN steel with a pre-strained sample used for SKP measurements corresponding to 10% of elongation (Figure 10). Before LEIS measurements the oxide film was reduced at $-1.2$ V (SHE) for 10 min. Figure 11 shows the distribution of the capacitance across the non-strained and strained areas. In that case, the deformation results in a significant increase of the capacity from about 2.3 to 4.5 $10^{-6}$ F/cm² above the deformed area with a well-defined transition zone.

Discussion

SKP measures the Volta potential ($\Phi/e$) in air close to the metal surface. On an absolute potential scale, the potential of the metal covered by semiconducting oxide film can be expressed as:

$$\frac{\Phi}{e} = -\frac{\mu_{\text{ox}}}{e} + \Delta \chi_{\text{ox}} + \Delta \chi_{\text{air}} = -\frac{\mu_{\text{ox}}}{e} + \frac{q}{C_{\text{ox}}} + \frac{q}{C_{\text{air}}}$$

Where $\mu_{\text{ox}}$ is the chemical potential of the electron in the metal bulk, $\Delta \chi_{\text{ox}}$ - the potential drop in the oxide film (metal-oxide interface) and $\Delta \chi_{\text{air}}$ - the potential drop in the air gap. Eq. 3 shows the relationship between the measured potential and the corresponding capacitances ($C_{\text{ox}}, C_{\text{air}}$) and the charges stored at this interface ($q$).

Due to electroneutrality, the charges of adsorbed species (e.g. $O_2^-$) are compensated by the same amount of charges in the oxide (e.g. holes) resulting in band bending of both electronic and valence bands in the oxide. The capacitance of the oxide film is reciprocal to the potential drop. Thus, SKP and EIS (or LEIS) measurements are inter-related and can be used in a complementary fashion to evaluate the effect of the mechanical stress on the properties of the steel surface.

According to fundamental definitions, $\Delta \chi_{\text{air}}$, the electrode potential is defined by the energy level of the electron or metal ion. The steel electrode has both electronic and ionic energy levels and the ionic and electronic potentials can be correlated. Thus, the potential of the metal can be represented in terms the real free energy of metal ion that is measured by the corresponding reference electrode in the electrolyte. The same potential corresponds to the real free energy of the electron at the Fermi level of the metal and can be measured using SKP. Thus, the mass transfer between metal and environment correlates with electron transfer and the Volta potential measured by SKP is related to electrochemical potential of the steel (Eq. 1).

The SKP study showed that tensile plastic deformation of austenitic and carbon steels decreased the electrode potential. The stress can influence the chemical potential of the electron in the metal ($\mu_{\text{ox}}/e$) or the potential drop across the metal/oxide/air interface (Eqs. 1 & 3). The calculation within the self-consisting Kohn–Sham method for elastically deformed metal crystals showed that tensile strain de-
creased the density of the atoms packing and concentration of the
electrons that can decrease $\text{ewf}$ in the range $30–40$ mV for Al and Cu
(111 and 100 planes).$^{39}$ The stress can influence the potential drop
across metal/vacuum interface due to the change of the distance be-
tween surface atoms, while the change of the chemical potential of the
electron (Fermi energy) in the metal bulk was negligible. Thus, the
properties of the material bulk were not altered by the stress, which
is in agreement with calorimetry measurements and thermodynamic
definition of Hoar.$^9$ It can be assumed that the stress mainly influenced
the potential drop across metal/oxide and oxide air/interfaces. The po-
tential mainly decreased when the specimen was loaded over the yield
strength, leading to the formation of dislocations. Plastic strain in the
range of $10–15\%$ decreased the potential of $200–300$ mV for 301 LN
steel and around $200$ mV for the carbon steel. Similar effects were
found for the yielding of Cu and Al.$^{31–33}$ The further increase of strain
showed only small influence on the potential. Application of strain to
301 LN steel sample higher than $20–30\%$ (data not shown) did not
lead to extra drop in potential. Thus, it is possible to point out that,
defects in the oxide film and locations with thin oxide film were cre-
ated by tensile plastic stress through dislocations and emerging slip
bands. The potential drop across the passive oxide film was decreased,
creating areas of high corrosion activity.

The degradation of the passive oxide film due to the residual stress
after tensile deformation was also shown by LEIS for the 301 LN steel.
SKP and LEIS have near the same level of spatial resolution. Higher
capacitance was obtained on surface with emerged dislocations com-
paring with the unstrained reference. The strained area with increased
capacitance (Figure 11) corresponded to area with decreased of po-
tential measured by SKP (Figure 10). Thus, the potential drop in the
oxide film is reciprocal to film capacitance (Eq. 3).

The effect of dislocations on properties of passive films is not well
defined. It may be induced by slip lines or pile-ups of the dislocations.
The yielding increases the surface roughness to factors of 4 (carbon
steel) and 7 (stainless steel). Increase of the real metal surface relates
to decreasing the density of the material. New surfaces can result in a
lowering of the oxide thickness that can play an important role in the
initiation of stress corrosion cracking of stainless steels.$^{40,41}$ It is
thus possible that areas with low oxide thickness are created under stress
due to the oxide film rupture or emerging of the slip bands.$^{42}$
It is gradually different from the roughness created by the grinding
(Figure 9). In the last case, the compressive stress can be developed and
no significant decrease of the material density takes place. The
schematic of the strained surface is given in Figure 12.

For practical case, it is important to compare data obtained in air
and in electrolyte. In the electrolyte, a cathodic polarization for the
reduction of the air formed oxide was applied. After electrochemical
treatment the notch obtained lower potentials comparing with strained
in the air. It can be due to the concomitant effect of the hydrogenation
and stress on the steel. Thus, it is in line with observation that both
the stress and hydrogen entry decreases OCP.$^{43}$

A similar effect of cold work or straining on the capacitance of the
oxide film was observed in few studies.$^{15–17,40,41,44}$ In these works, the
effect of mechanical work was explained by increasing the densities
of the donors or acceptors that changes the properties of the semi-
conducting oxide film. On the other hand, it was observed that stress has
only a small influence on the flatband potential of the oxide films. The
results of this work show that plastic stress increases the capacitance
and decreases the potential drop in the oxide film. Emerging of dislo-
cations create a defective oxide film that is prone to anodic dissolution
in form of pitting corrosion or stress corrosion cracking.

Conclusions

1. It was demonstrated that SKP and LEIS are local electrochemical
techniques that are able to visualize the distribution of the residual
stress with similar spatial resolution. The plastic tensile deformation
decreased the electrochemical potential of carbon and austenitic steels measured in air. The strain increased the capacitance of the steels in the borate aqueous electrolyte.

![Figure 12. Sketch of the steel surface created by a tensile plastic deformation.](image-url)
2. It was shown that plastic strain creates dislocations and emerging the dislocations that create defects in the oxide film. The dislocation pile-ups and sliding lines showed low electrochemical potential and they are prone to local corrosion.

3. Local probe techniques – SKP in air and LEIS in the aqueous electrolyte – demonstrated that residual stress decreased the ability of the steel to passivate the surface either in the air or in the electrolyte.

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