A Novel Mini-Autoclave to Study Concurrently the Electrochemistry and *In-situ* Imaging of Precursor Sites for Pitting in Steels in Chloride Containing Environments at High T & P

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ABSTRACT

A Novel Mini-Autoclave where the tests are performed *in-situ* under an aqueous environment (simulated production brine) saturated with CO/H_2S gas mixtures was developed (with similar performance compared to a normal autoclave). The mini-autoclave ultimate limits are 400 $^{\circ}$C and 4000 psi and can stand a mixture of a gases and liquids. The surface of the sample inside the chamber can be photographed and a real time video can be recorded while electrochemical measurements on the Area of Interest (AOI) in the surface of the sample can be done. Typically, small areas (5 μm ≤ AOI ≤ 5 mm) are suitable for imaging using this mini autoclave. In the present study, electrochemical measurements simultaneously with optical imaging and real time videos of UNS S32550 (25% Cr Duplex Stainless Steels) in chloride containing environments at two temperatures 40 $^{\circ}$C (and 582 psi) and 180 $^{\circ}$C (and 900 psi) were used to confirm (visually and electrochemically) the conditions under which the transition from passivity to corrosion could take place. This methodology allowed the real-time *in-situ* anodic polarization of the samples and observation of the precursor sites for pitting above the Critical pitting Temperature on UNS S32550 (25% Cr Duplex Stainless Steels).

Key words: In-Situ, Electrochemistry, DSS, Pitting, CPT, Ferrite, Austenite, Inclusions, Precursor Sites, Temperature, Pressure, HT/HP.

INTRODUCTION

In-situ characterization of corrosion resistant materials (CRAs) offers a new window of opportunities to improve materials and to understand the potential applications limits for those alloys. Of particular relevance is the need to qualify new materials in highly corrosive environments[1]. However, most of the qualification of materials in critical environments is done under aggressive environments at high temperature and high pressure in an enclosed autoclave. Using electrochemical techniques in an enclosed autoclave is typically challenging, but doable. However trying to get visual confirmation in real time of the processes occurring in the sample(s) is only possible if the autoclave can have a window that allows real time imaging and can stand the aggressive conditions as well as high temperature and high pressure.

In the present work, a mini-autoclave with a maximum operational temperature of 400 °C and 4000 psi maximum pressure was developed. The mini-autoclave is capable of operating with a mixture of corrosive gasses and liquids, where electrochemical and/or immersion tests can be performed *in-situ* while simultaneously imaging an Area of Interest (AOI) in the surface of the sample from 5 µm to 5 mm. The surface of the sample inside the chamber (while immersed in the liquid/gas mixture) can be photographed and a real time video can be recorded while electrochemical measurements can be performed.

It is well known that inclusions in commercially available engineering materials are the main cause of pitting in commercial stainless steels[2-5]. From all the main inclusions, MnS in stainless steels have been well studied[5]. However, in highly alloyed materials, like in the case of corrosion resistant alloys (CRAs), the precursor sites for pitting corrosion are more complex intermetallic particles found in the bulk of the alloys[6].

In the present study, electrochemical measurements simultaneously with optical imaging and real time videos of UNS S32550 (25% Cr Duplex Stainless Steels) in chloride containing environments at two temperatures 40 °C (and 582 psi) and 180 °C (and 900 psi) were used to confirm (visually and electrochemically) that pitting corrosion could only developed at the higher temperature (above the Critical Temperature for this alloy). This methodology allowed the real-time *in-situ* anodic polarization of the samples and observation of the precursor sites for pitting above the Critical pitting Temperature on UNS S32550 (25% Cr Duplex Stainless Steels).

EXPERIMENTAL PROCEDURE

Materials

All samples used in the present research were cut from commercially available 25Cr DSS of the type UNS S32550, which were obtained in wrought form (bars of 10 mm diameter). Machining of the samples to 5 mm diameter was necessary to be able to introduce the sample in the mini-autoclave. Table 1 shows the melt composition of the alloy.

Table 1
UNS S32550 Alloy Used in the Present Work

Composition (wt. %)									
Cr	**Ni**	**Mo**	**Cu**	**N**	**Mn**	**Si**	**C**	**S**	**P**
25.92	**5.9**	**3.19**	**1.62**	**0.2**	**0.96**	**0.47**	**0.03**	**0.007**	**0.024**

One main annealing procedure was selected, involving solution treatment at 1020 °C followed by water quenching. This annealing procedure has shown to yield a Critical Pitting Temperature (CPT) of 62 °C[7] in 6% Ferric Chloride test using a modified version of the ASTM G-48[8]. The chemical compositions of both ferrite and austenite phases were determined by Electron Probe Microanalysis (EPMA), as described in the literature[9] and are presented in Table 2.

Table 2

Average Composition of Ferrite and Austenite for UNS S32550 Sample Used in the Present Work

	Composition (wt. %)								
Annealing Temp.	**Phase**	**%**	**Cr**	**Ni**	**Mo**	**N***	**Cu**	**S**	**P**
1020°C	**Ferrite**	**47**	**26.36**	**4.63**	**3.69**	**0.05**	**1.27**	**0.073**	**0.043**
	Austenite	**53**	**23.14**	**7.36**	**2.35**	**0.33**	**1.95**	**0.035**	**0.025**

* Nitrogen in ferrite is taken as fixed at the saturation value of ~0.05%, the rest partitions to austenite

Sample Preparation

The samples were prepared by successive polishing with SiC polishing paper (with running water) followed by ultrasonic cleaning in DI water. A further polishing was done using polishing oil and 6, 1 and ¼ µm diamond paste (In that order). All the samples were cleaned carefully to avoid contact with any particulate other than the diamond polishing pastes and the solvents (and to avoid impinging any foreign material in the surface of the sample). At the end of the polishing, the samples were rinsed with acetone, followed by rinsing with isopropyl alcohol and a final rinse with deionized water (DI). Then the samples were lightly electrolytically etched for 8 seconds in a solution prepared with 40% KOH at an applied voltage of 4 V, to allow the ferrite and austenite to be distinguished under the microscope and inside the mini autoclave. The etching was done in order to remove the air formed oxide (native oxide), to prepare a 'fresh' surface and to find the grains and inclusions for each test. After etching, the whole sample was covered with an insulating lacquer except on the area of interest (normally square regions with approximate area around 300 µm x 300 µm). No crevices were ever observed at the edges of the lacquer and this procedure allowed us to isolate a small part of the surface and consequently to keep the background passive current very low, in the µA, while observing in real time the area of interest.

Experimental Configuration for *In-situ* Microscopy with Concurrent Electrochemistry at HT/HP

Anodic polarizations at high temperature in 3.5% NaCl solution saturated with air at high pressure were done in the mini-autoclave setup (see Figure 1). The mini-autoclave contains a quartz window in one of the sides that allowed connecting a high resolution camera in order to capture the images and videos (in real time) of the surface of the sample that is immersed in the liquid. Figure 1 also shows the mixing autoclave (a 500 ml pre-chamber where the liquid is saturated with the gas), two temperature controllers (for the mini-autoclave and the mixing autoclave) and the additional safety valves that were added to the setup, since the work is done at high temperatures and high pressures.

A potentiostat allowed the collection of the Open Circuit Potential (OCP) at the beginning of the test and while the mini autoclave temperature was increased to the target temperature. Anodic Polarizations were carried out once the temperature was stable at the target temperature. All the electrochemical experiments were carried out using a three-electrode electrochemical cell. A pseudo reference electrode (Pt wire with 1 mm diameter and 3 cm long) electrode was used as a reference electrode. An additional 3 cm long Pt wire (1 mm diameter) was used as the counter electrode. Both, the sample potential and current were collected through potentiostat which was interfaced with the personal computer.

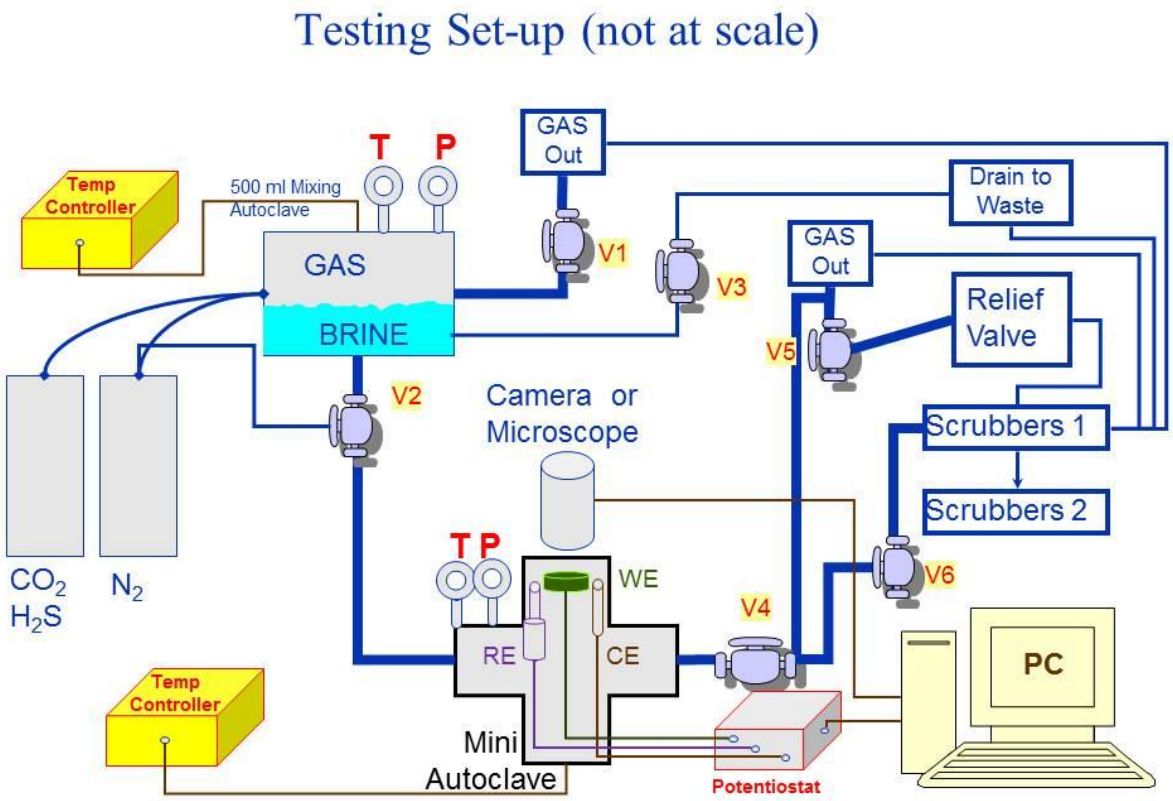

Figure 1: Experimental Setup Used in the Present Work

This configuration (with the high resolution camera) allowed the observation of the surface of the sample, but the resolution and the light input was not sufficiently high to be able to image the grains and inclusions within the surface of the sample. Figure 2 shows three images of the surface of a sample where 2 pits developed (at different times and potentials during the anodic polarization), but the resolution was not sufficiently high to be able to differentiate the grain boundaries in the surface of the sample.

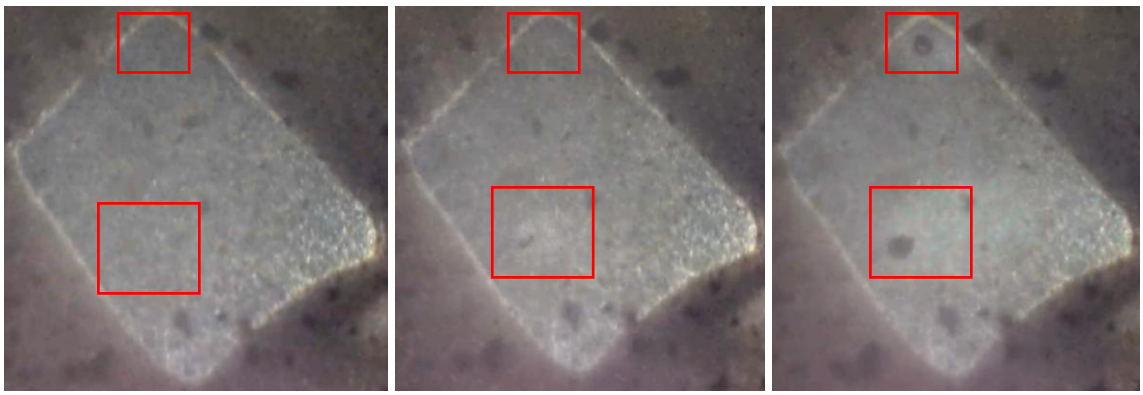

Figure 2: Early Experimental Setup Using a High Resolution Camera with a LED Light Ring

A second configuration that included the use of a stereo microscope (instead of a high resolution camera) and keeping the same configuration as the early configuration was introduced.

At the beginning of the experiments and during temperature ramping, OCP measurements were taken until stable OCP signals were achieved (and videos of the surface). During the anodic polarizations at the target temperatures (40 °C and 180 °C), real time videos of the surface of the samples were collected simultaneously with the anodic polarization. This second configuration allowed the observation of the precursor sites for pitting in the alloy (UNS S32550) in a chloride containing environment in air while the *In-situ* real time monitoring of the surface was done using the stereo microscope.

RESULTS

Figure 3 shows the optical image of sample 1 (annealed at 1120 °C) before the tests (left), after anodic polarization at 40 °C and 582 psi (center) and after (right) anodic polarization at 180 °C (and 900 psi) in the 3.5% NaCl solution saturated with air. Notice that because the sample did not undergo any type of corrosion at the lower temperature (40 °C) in this test, the same sample was used at the higher temperature (180 °C). As it can be seen in the image, the dark region corresponds to the ferrite matrix, whereas the lighter grains correspond to the austenite grains. A few inclusions in the surface are shown as dark spots.

The composition of the inclusions in the samples shown in the matrix and grains has been extensively studied[6,10,11]. It is important to notice that only a few of the inclusions, the very small ones, are clearly in the middle of the either the ferrite matrix or the austenite grains. However, most of the larger inclusions are in the boundary between the ferrite matrix and the austenite grains. This is particularly important, when the main discussion on whether the ferrite or the austenite is the “weaker” (or less corrosion resistant) part of the duplex structure.

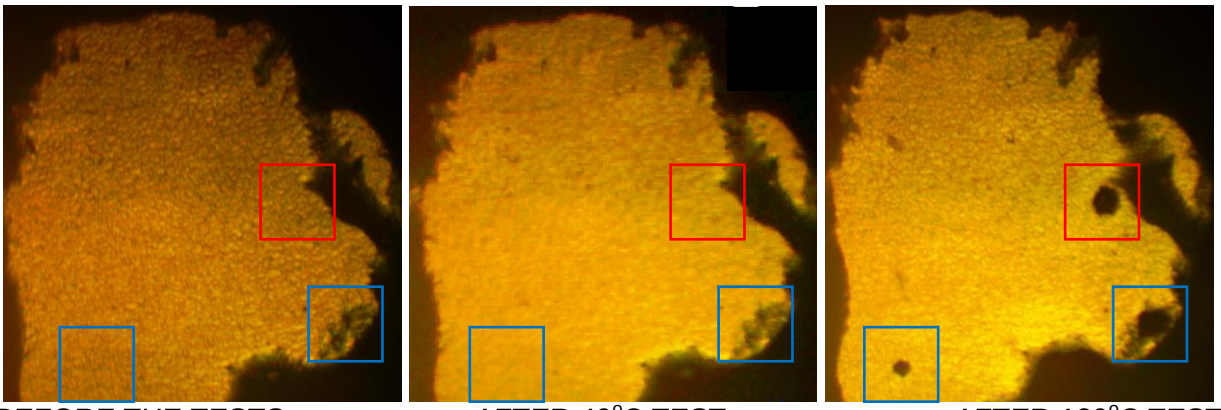

Figure 3: Optical image of UNS S32550 sample before the tests (left), after anodic polarization at 40 °C and 582 psi (center) and after (right) anodic polarization at 180 °C (and 900 psi) in 3.5% NaCl solution saturated with air.

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Figure 4 shows the optical image of sample 1 (annealed at 1020 °C) in the left and the Anodic Polarization taken at 40 °C (and 582 psi) in 3.5% NaCl solution saturated with air at high pressure (in the right). The Anodic Polarization of the sample started at about -200 mV_{Pt} and -8 µA (not shown in Figure 4) and was stopped at +1000 mV_{Pt} and +10 µA (see Figure 4). Only metastable pitting (observed in the anodic polarization transients at higher potentials) was observed in the electrochemical signature, but no changes could be observed in the optical image.

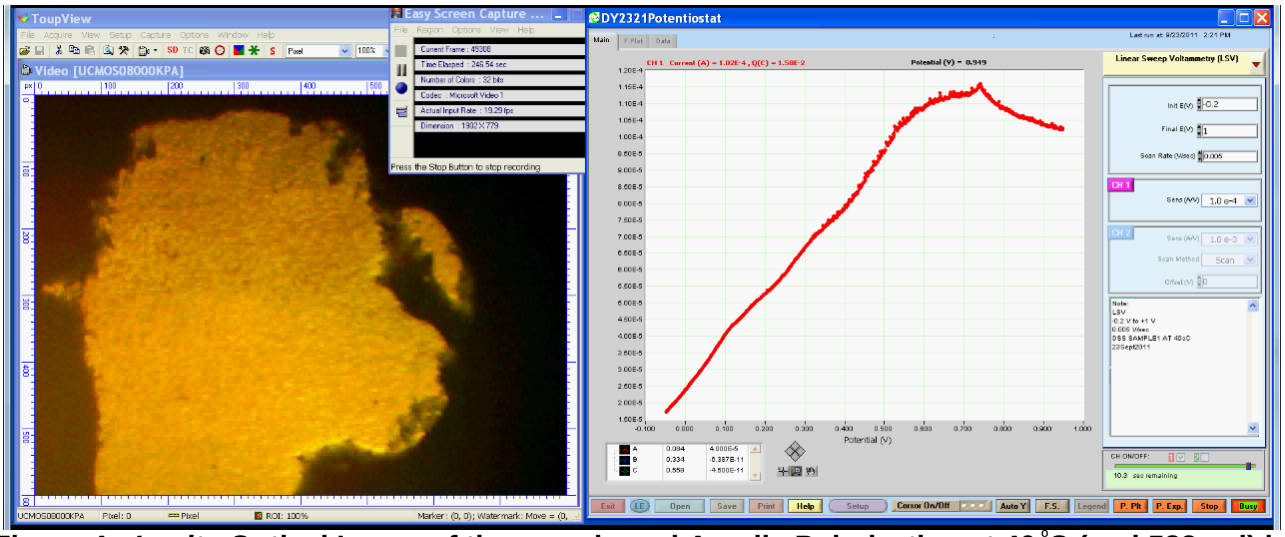

Figure 4: *In-situ* Optical Image of the sample and Anodic Polarization at 40 °C (and 582 psi) in 3.5% NaCl solution saturated with air at high pressure.

Microscopy and Electrochemistry at 180 °C and 900 psi (in 3.5% NaCl and Air)

It is important to understand the electrochemical behavior of DSS when exposed to a chloride containing solution. While testing the DSS below the CPT in neutral NaCl solutions (at ambient pressure), a region of very large peaks associated with metastable pits can be observed at low potentials (typically located between 200 mV_{SCE} and 350 mV_{SCE}), followed by a decrease of activity at higher potentials[6,9,10]. Above the CPT (in Chloride containing solutions, as explained in the literature), stable pits can initiate at the same low potentials where metastable pits start but preceded by only a few metastable events.

Figure 5 shows the anodic polarization curve (in 3.5% NaCl solution saturated with air) of the same area (of the same sample annealed at 1020 °C) at 180 °C (and 900 psi). Notice that the CPT for this sample (annealed at 1020 °C) has been found to be 62 °C[7,9] As described in the previous section, the 40 °C anodic polarization shows passive behavior with only small transients related to metastable pitting at the higher potentials (above +300 mV_{Pt}). However, no pitting corrosion was observed during that experiment. This result is clearly in good agreement with previous measurements in these alloys, except for the fact that metastable pitting continues at higher potentials during the test at high temperature and high pressure (in this work).

Immediately after the 40 °C anodic polarization experiment, the cell was heated until it reached a constant temperature of 180 °C (which is above the CPT in chloride containing solutions for this material[6,9,10]). While heating the sample and solution, the OCP was monitored and imagining of the surface of the sample was conducted (no corrosion was observed under these conditions). Once a stable 180 °C temperature was achieved, an anodic polarization experiment was repeated, but this time while the temperature of the sample and the solution was 180 °C (and the pressure reached 900 psi).

Figure 5 shows the optical image of the area analyzed and the anodic polarization curve of the same sample. The sample developed the first pit at +530 mV_{Pt}. In this case, the real time optical video of the sample surface was collected and was used to determine the first location where the pit started (red square in Figure 5). It has been found that the typical inclusions that undergo pitting corrosion in this material are approximately 2 µm in diameter.

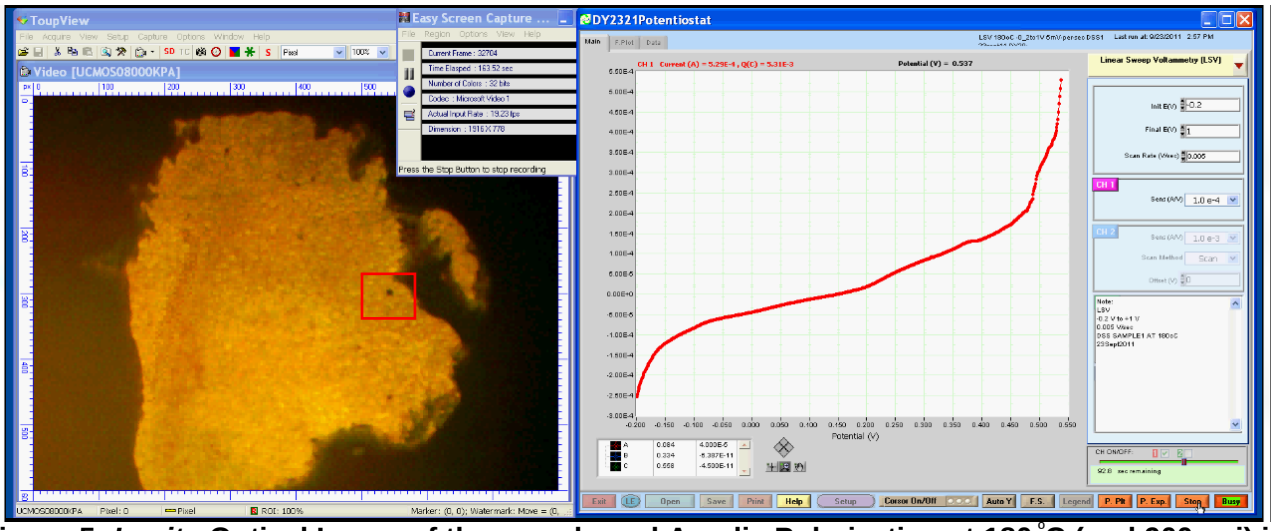

Figure 5: *In-situ* Optical Image of the sample and Anodic Polarization at 180 °C (and 900 psi) in 3.5% NaCl solution saturated with air at high pressure.

Figure 6 shows the optical image of the area analyzed and the anodic polarization curve of the same sample after the second and third pits appeared at +570 mV_{Pt}. Both pits (second and third) appeared almost at the same time.

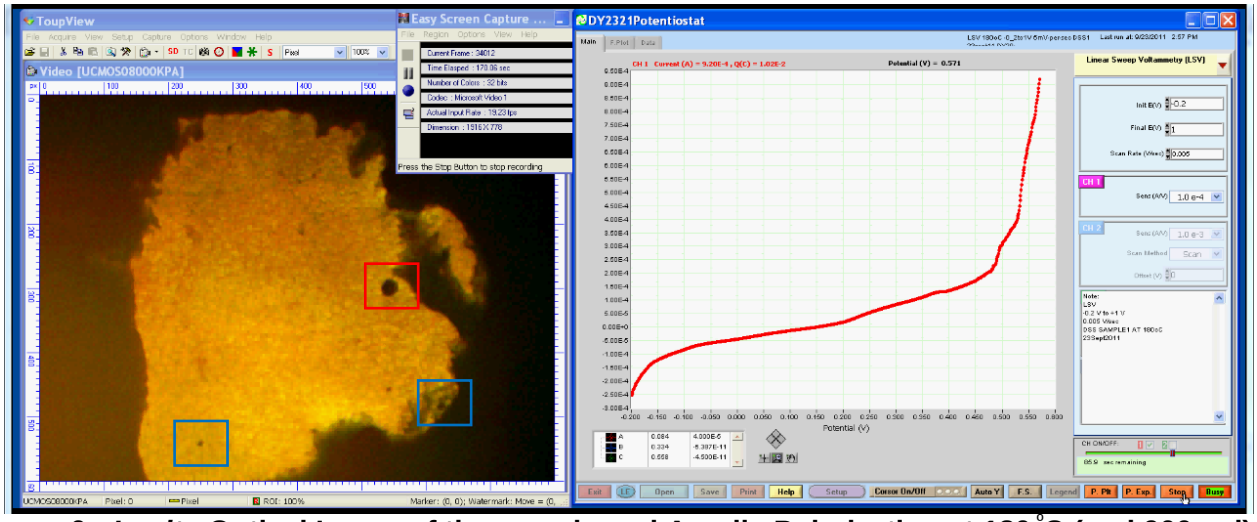

Figure 6: *In-situ* Optical Image of the sample and Anodic Polarization at 180 °C (and 900 psi) in 3.5% NaCl solution saturated with air at high pressure (start of second and third pits).

Figure 7 shows the optical image of the area analyzed and the anodic polarization curve of the same sample at the end of the test and once the three pits have developed at +624 mV_{Pt}.

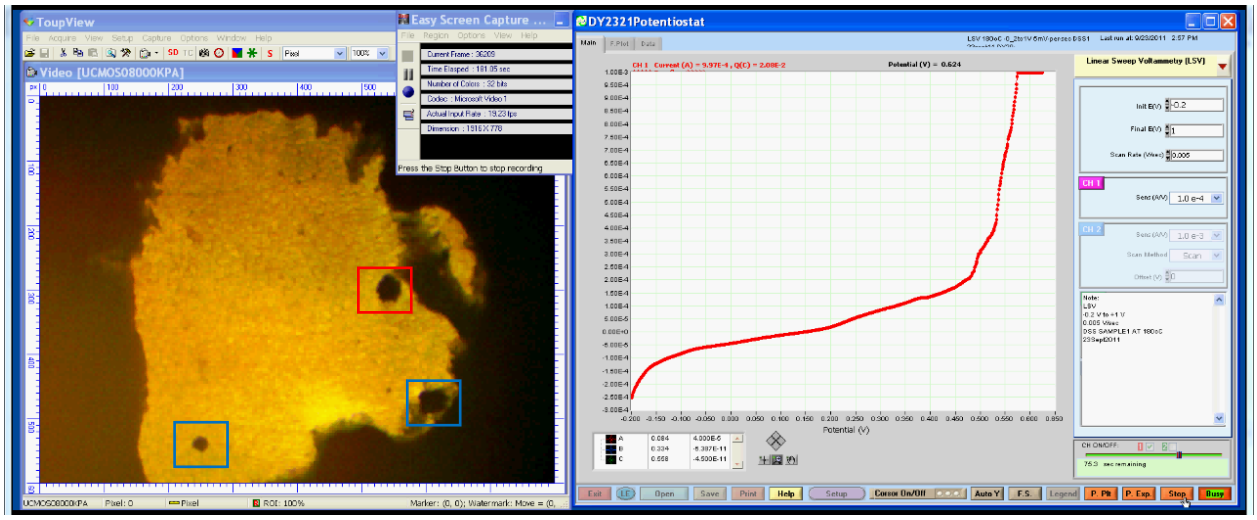

Figure 7: *In-situ* Optical Image of the sample and Anodic Polarization at 180 °C (and 900 psi) in 3.5% NaCl solution saturated with air at high pressure (end of experiment).

CONCLUSIONS

A new mini-autoclave to study *in-situ* in real time the pitting corrosion of materials at high temperature and high pressure was developed. This methodology allowed the real-time *in-situ* determination of the first sites to undergo pitting corrosion in the surface of a 25Cr DSS (UNS S32550 sample 1 annealed at 1120 °C). Currently, experiments under more aggressive conditions (liquid phase containing CO_2 and H_2S) are currently being carried out (both at 40 °C and 180 °C).

Future work will also aim at studying the precursors sites for pitting on other Highly Corrosion Resistance Alloys (HCRAs) as well as on novel metallic coatings (claddings) in real industrial environments (for example in different corrosive gases containing CO_2, H_2S, etc.).

The current threshold for Temperature (400 °C) and Pressure (4000 psi) with this configuration will allow *in-situ* studies in more aggressive conditions.

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