

***In-situ* Pitting of UNS S32550 Duplex Stainless Steel in Artificial Seawater below and above the Critical Pitting Temperature**

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ABSTRACT

This paper demonstrates a novel methodology that can be used to determine the factors that contribute to the initiation of pitting corrosion of Corrosion Resistant Alloys (CRAs) in aggressive environments above the Critical Pitting Temperature (CPT). The work presented here shows, for the first time, simultaneous *in-situ* micro-visualization and anodic polarizations of two microelectrodes made of UNS S32550 Duplex Stainless Steel (DSS) while immersed in artificial seawater. A real time video of the surface of the two electrodes was recorded while anodic polarizations were made at different temperatures below and above the CPT. This methodology allowed the observation of metastable pitting below the CPT of the alloy and stable pitting above the CPT of the 25 Cr DSS.

Key words: CRA, DSS, Pitting, CPT, Ferrite, Austenite, Inclusions, Precursor Sites, Heat Treatment, Temperature, Annealing Temperature, Electrochemistry, Metastable Pitting, Pit Initiation.

INTRODUCTION

The qualification of materials for their use in harsh environments, particularly in the oil and gas industry, requires new techniques and methodologies that can help identify the proper materials for critical applications. Currently, the oil and gas industry is experiencing a high demand for cost effective corrosion resistant alloys (CRAs) which can be used in extreme environments. The qualification methodologies that the industry typically undertakes vary and are often based on one or two international standards. Typically, the engineer applies the standard and bases selection decisions on the pass/fail criteria given by the international standard. The qualification methods do not require an understanding of the material performance in the operating environment. Fundamental research and understanding of the processes that take place in the materials exposed to these harsh environments is normally not within the scope of the measurement task.

Duplex Stainless Steels (DSS) are a cheaper alternative to the Ni-containing alloys and other highly alloyed materials. DSS can be readily available for most applications in the oil and gas industry. However, in most applications, it must be qualified under the typically harsh conditions of the anticipated working environments. DSS is well known for its good mechanical and corrosion resistant properties even in aggressive environments containing CO₂, H₂S and Cl⁻, at elevated pressures and temperatures (HP/HT).

In traditional oil and gas applications, the requirement for the use of a CRA in harsh environments requires the calculation of the Pitting Resistance Equivalent Number (or PREN¹). In most cases the qualification requirements follow Section 6.3 of NACE MR0175². A recent publication³ by the author warns about the use of the PREN as the only qualification requirement for CRAs and suggests that the qualification procedure should include fundamental testing to understand the factors that contribute to the degradation (general corrosion, pitting corrosion, etc.) of the alloy in the given environment.

The main objective of the present study was to develop a methodology that can be used to qualify CRAs in aggressive environments and understand the factors that can contribute to the performance of different alloys. This methodology allows simultaneous monitoring and in-situ imaging of the two CRA surfaces while an anodic polarization in each of the adjacent electrodes is being conducted at high temperatures, below and above the Critical Pitting Temperature (CPT).

EXPERIMENTAL PROCEDURE

Materials

The samples used in the present research were obtained from commercially available wrought 10 mm dia. bars of 25Cr DSS (UNS S32550). The bars were further machined to obtain microelectrodes of approximately 300 to 500 micrometers in each side. The microelectrodes were annealed at 1140°C for 2 hours followed by water quenching. Table 1 shows the alloy composition.

Table 1
25 Cr DSS (UNS S32550) used in the present work (Composition in 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

Sample Preparation

The microelectrodes were mounted in epoxy and then successively polished with 200, 600 and 880 grit SiC paper followed by ultrasonic cleaning in deionized (DI) water. Further polishing with 15 micron, 6 micron and 1 micron diamond paste was done using polishing oil. At the end of each polishing step, the samples were degreased with acetone, then rinsed with isopropyl alcohol and finally rinsed with DI water in that order. All samples were cleaned carefully to avoid contact with any particulate other than the diamond polishing paste and the cleaning solvents (acetone, isopropyl alcohol and DI water). The samples were then dried with high purity compressed air.

Some samples were electrolytically etched for 3-5 seconds in a 20% KOH solution at an applied voltage between 1 or 2 Volts to allow the ferrite and austenite to be distinguished under the microscope. The etching was done in order to remove the native air formed oxide and present a 'fresh' surface and to facilitate the microscopy of the sample. Unfortunately, because side-by-side electrodes

were used to allow simultaneous imaging of both electrodes, the magnification needed to clearly visualize the grains and grain boundaries could not be used during the test.

After etching, two samples were selected for the test. Figure 1 shows a picture of the end of the microelectrode and an optical image of the surface of the two samples immersed in artificial seawater. Sample 1 (triangular shaped area) was approximately 500 micrometers in the two long sides and about 300 micrometers in the third, shorter side. Sample 2 (rectangular shaped area) was approximately 300 micrometers long by 50 micrometers (wide). No crevices were observed at the edges of the sample.

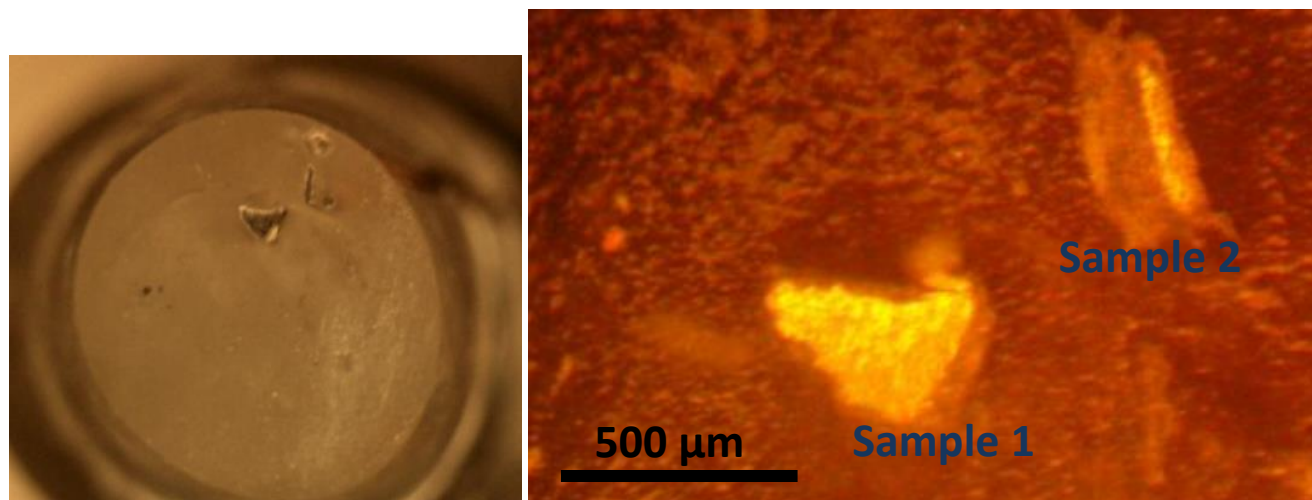


Figure 1: Optical image of Samples 1 and 2. The left image shows the microelectrode mounted with the two samples. The image on right shows the high magnification image of the samples while they were immersed in artificial seawater.

Grain Analysis

The samples were imaged using a conventional optical microscope to select the areas to be analyzed. The ferrite matrix and austenite grains were analyzed by using a Scanning Electron Microscope, equipped with an Energy Dispersive Spectrometer (EDS), which provides X-ray mapping and particle analysis. The chemical composition of the phases was determined by Electron Probe Microanalysis (EPMA), as described in previous publications by the author⁴ and is presented in Table 2.

Table 2
Average composition of Ferrite and Austenite for the UNS S32550 sample annealed at 1140°C used in the present work (Composition in wt%)

Annealing Temp.	Phase	%	Cr	Ni	Mo	N*	Cu	S	P
1140 °C	Ferrite	64	26.37	5.05	3.36	0.05	1.36	0.082	0.038
	Austenite	36	24.04	7.15	2.33	0.47	1.83	0.037	0.027

* Nitrogen in the ferrite phase was estimated to be at the saturation value of ~0.05%. It was assumed that the remaining Nitrogen was partitioned to the austenite

Testing Setup

Anodic polarization measurements for both electrodes were conducted at the target temperature for each test in artificial seawater⁵. A mini-autoclave⁶ was used to perform the tests and is shown in Figure 2. This mini-autoclave has been used for CRA testing in sour conditions⁷ and to image *in-situ* carbon steel corrosion in the presence of microorganisms⁸ as well as investigating the corrosion of CRAs in

different conditions. Details of the testing setup has been published in these references but will be explained in the following paragraphs.

The mini-autoclave contains a quartz window that allowed the connection of a stereo microscope in order to capture the images and real-time videos of the sample surface at magnifications between 40x and 200x. Figure 2 also shows the wiring to connect the samples. Note that in the present case, two working electrodes were used as well as a Pt-wire pseudo reference electrode and Pt-wire counter electrode inside the mini-autoclave. All electrodes were connected to the bipotentiostat that was linked to a laptop computer. A laptop computer was used to simultaneously record the data in real time from the bipotentiostat as well as the images and videos of the surface of the samples. This configuration and methodology allowed the observation of the areas of the two samples that were exposed to artificial seawater.

The stereo microscope equipped with a digital camera was used to image the samples through a quartz window that allowed capturing the images and videos in real time of the surface of the samples while performing the tests. Typically a 40x to 200x magnification can be used in these studies depending on the size of the sample. The anodic polarization for both samples and video recording of the surfaces of the samples were logged onto the computer. The typical video files that contain both the anodic polarizations and the surface of the metal are approximately 100 Mb. Therefore, snapshots of the surface of the samples were used in this article.

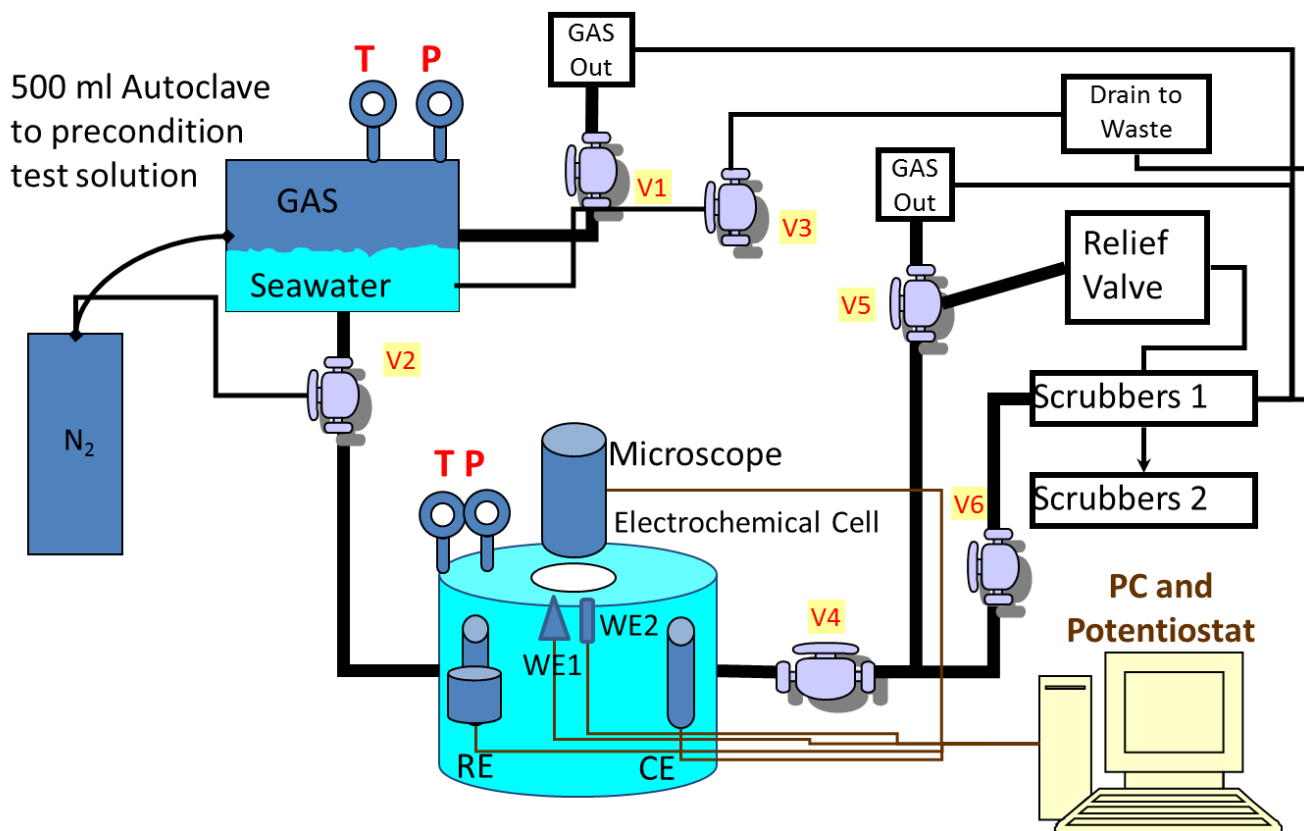


Figure 2: Experimental setup (mini-autoclave) used in the present work.

RESULTS

Anodic Polarization Above and Below the Critical Pitting Temperature (CPT) of the Alloy

Simultaneous anodic polarization of the two samples was undertaken below and above the Critical Pitting Temperature (CPT) of this alloy. The CPT of this alloy has been determined to be 42°C⁹. This CPT has also been confirmed by using multiple anodic polarization tests at different temperatures on large electrodes¹⁰.

Figure 3 shows a snapshot of the data display from a test conducted at 25°C in artificial seawater. The image on the left side shows the surface of the two samples. The image in the center shows the anodic polarization data of both samples (sample 1 on the top and sample 2 below). The temperature inside the mini-autoclave is shown in the meter located in the bottom right of the image and highlighted by the red circle. The anodic polarization plot shows the potential (in Volts) on the X-axis, which is being applied simultaneously to both samples. The test was started at -300 mV vs the Pt pseudo-reference electrode and ended at +800 mV vs the Pt pseudo-reference electrode. The current measured against the Pt counter electrode is shown in the Y-axis of each of the two polarization graphs.

The current measured on Sample 1 (top graph in Figure 3) shows cathodic values near -0.3 μA at -300 mV. The passive current of this sample at this test temperature should be below 0.1 μA ¹. Sample 2 shows slightly different behavior from Sample 1. Sample 2 shows a clear cathodic to anodic transition around -100 mV. The cathodic current was near -1.5 μA at -300 mV. The passive current increased steadily, probably due to the increase in thickness of the protective oxide film in the surface of the sample, until it reached a current of +5 μA at +800 mV. No pitting corrosion was observed in either sample at this test temperature.

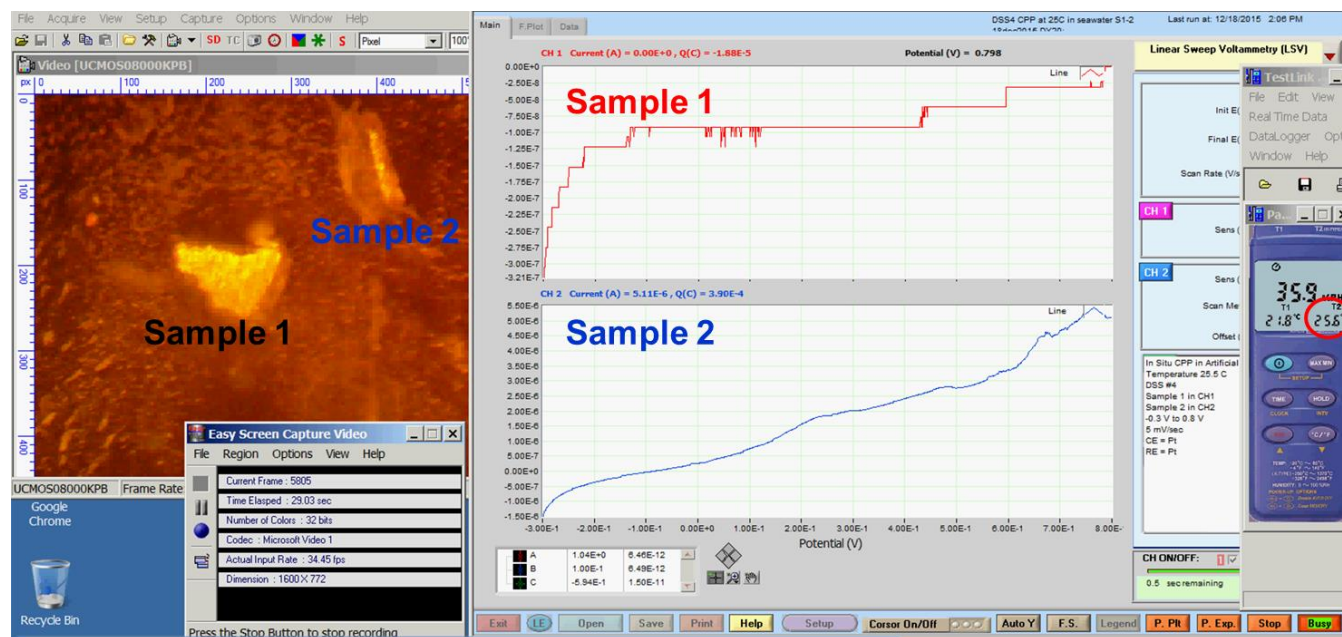


Figure 3: Anodic polarization of the two samples (UNS S32550) in artificial seawater at 25°C

Figure 4 shows a snapshot of the data display of the same test on the same samples, but now conducted at 51°C. Note that this is a temperature that is above the CPT for this alloy in seawater (42°C). Surprisingly, the current measured on Sample 1 (top graph in Figure 4) shows similar passive behavior compared to the test conducted at 25°C. However, Sample 2 now shows the onset of stable

¹ Note that the negative value is probably the result of the real passive current minus the background current of the instrument (in this channel). Therefore the total current shown, although very small, results in a negative value.

pitting at around +350 mV. This is in good agreement with the previous results observed in large samples¹⁰. The passive current increased from around +1 μA to near +10 μA at +700 mV. The optical image of Sample 1 (left side of Figure 4) shows clearly that the sample remains passive contrasting with Sample 2 which shows some corrosion and a decrease in the surface area.

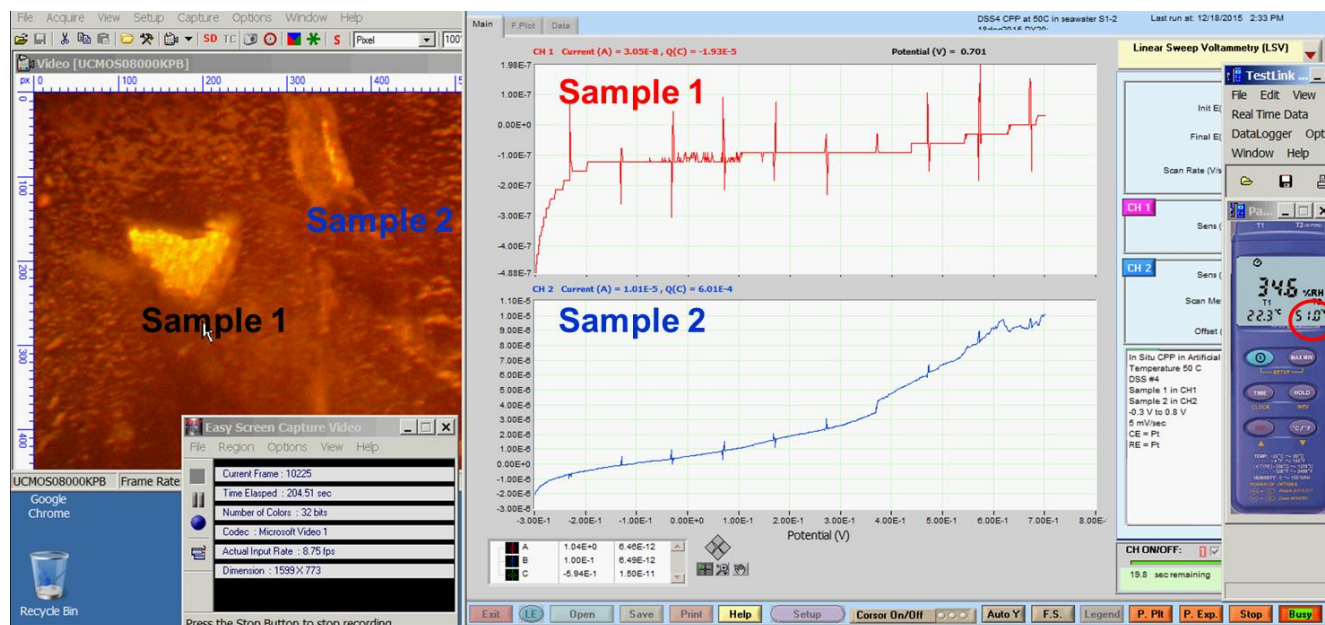


Figure 4: Anodic polarization of the two samples (UNS S32550) in artificial seawater at 51°C

Figure 5 shows a snapshot of the data display for the same test and the same samples, but now conducted at 66°C. In this test, Sample 1 shows the onset of stable pitting above +300 mV and Sample 2 continues pitting on parts of the surface with currents near +10 μA at +700 mV. The optical image of Sample 1 and Sample 2 reveals that samples are pitting, particularly in the sides².

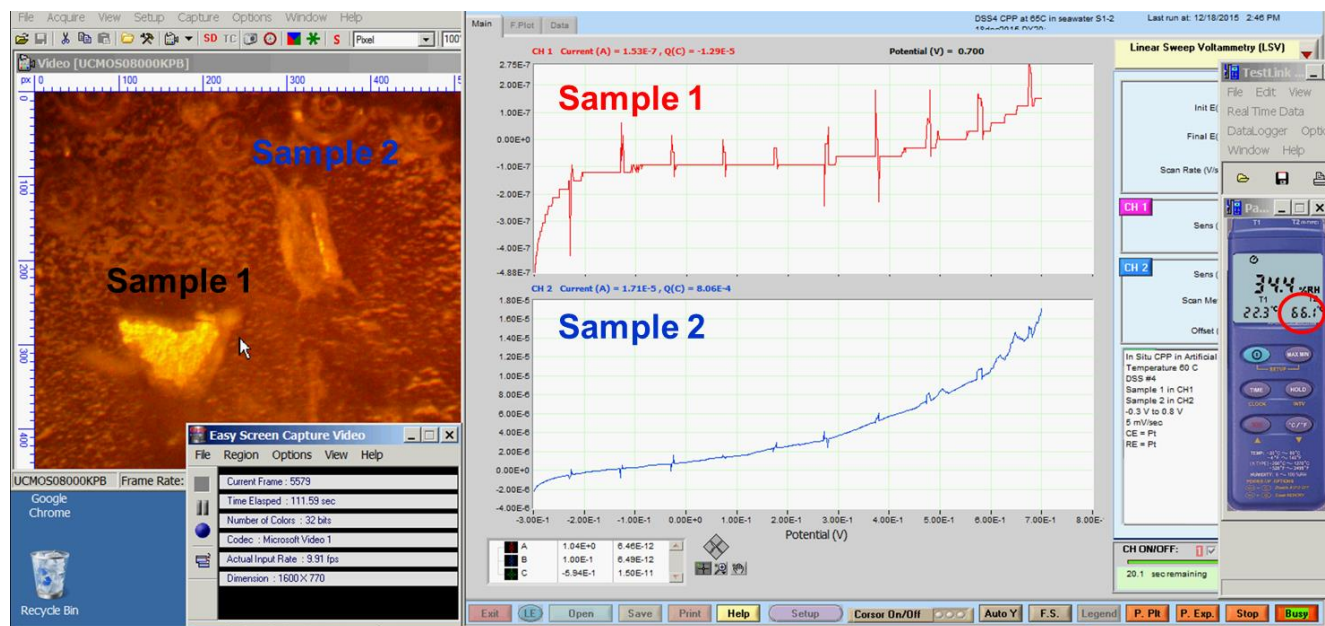


Figure 5: Anodic polarization of the two samples (UNS S32550) in artificial seawater at 66°C

² No crevice corrosion was observed on the edges of either sample. This is consistent with the low currents measured in these experiments.

Figure 6 shows the optical images of the two samples at different test temperatures to facilitate comparison. The arrows show the areas of the samples where pitting corrosion took place during the tests.

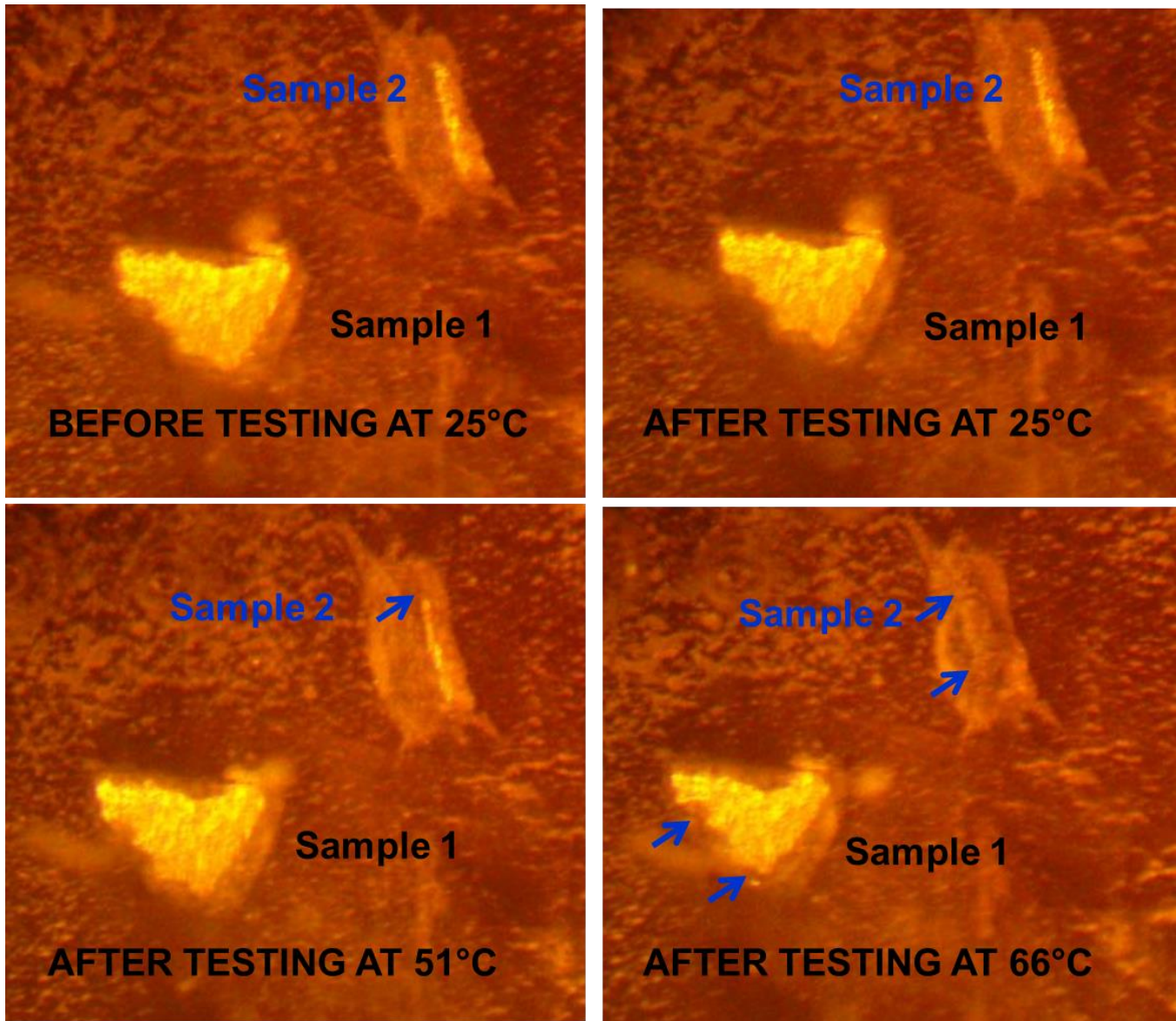


Figure 6: Optical images of the two samples at different test temperatures

DISCUSSION

Anodic polarization of the two samples at 25°C resulted in passive behavior. This is expected for this alloy since the test was conducted below the CPT (42°C). During the anodic polarization conducted at 51°C, which is above the CPT of this material, only the sample with the smaller cross sectional area underwent pitting corrosion, whereas the sample with the largest area remained passive. This is a surprising result since both samples were made of the same material. When the test temperature was increased to 66°C, pitting corrosion developed in both samples.

It is possible to expect that the small sample 'protected' the larger sample when the test was conducted at 51°C. However, at a higher temperature the conditions within the pits reached the critical conditions

described by Galvele's "Pit Stability Product"¹¹. Note that if the samples had undergone crevice corrosion, the measured currents would have been larger and would have probably occurred at much lower temperatures.

Ranking materials based in laboratory tests (particularly the CPT) and comparison of the performance of the alloys in industry environments has been the subject of numerous publications¹². However, in most cases, the tests and interpretation of the results are not consistent between scientist and engineers. The CPT measurements, particularly in highly corrosion resistant alloys, have been one of the few tests that provide a good indication of the performance of the alloys when the tests are done in the same environment as the operational environments of the materials within the industry.

The results obtained using the present methodology can be further used to screen, qualify and understand the interactions between different materials for different applications. This method also provides the materials scientist and developer with an understanding of the microstructural features that may be controlling corrosion performance.

CONCLUSIONS

A mini-autoclave that allows the *in-situ* micro visualization in real time was used to undertake anodic polarizations in artificial seawater of two microelectrodes of 25 Cr DSS (UNS S32550) at different temperatures. Both samples were passive at 25°C. Pitting corrosion was observed only in the sample with the smallest cross sectional area during the tests conducted at 51°C (above the CPT of this material). Both samples developed pitting corrosion at 66°C.

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