STEELS FOR SOUR SERVICE: RESEARCH IN ESCOLA POLITÉCNICA, UNIVERSITY OF SÃO PAULO (EPUSP)

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Abstract

Microstructure-property relationships for metallic materials are basic requirements for the design of industrial processes to produce special materials, such as HSLA steels. Currently, there is a demand for materials resistant to aggressive environments having chloride, sulfide and carbon dioxide, all of which are corrosive and embrittling to steels. These environments are present in the extraction and transport of oil and natural gas from deep water. Escola Politécnica, University of São Paulo, in its Department of Metallurgical and Materials Engineering, has ongoing research aiming at the development of HSLA steels resistant to corrosion, specifically stress corrosion cracking and susceptibility to hydrogen induced cracking under wet hydrogen sulfide and carbon dioxide environments. These objectives were the scope of a project, supported by CBMM (Companhia Brasileira de Metalurgia e Mineração), which contributed to the construction of a laboratory dedicated to the study of corrosion, embrittlement and stress-corrosion by hydrogen sulfide. Development of experimental methods for the measurement of corrosion resistance, evaluation of the effect of inclusions on corrosion behavior and comparison between API 5L X65 and X80 steels with regard to hydrogen embrittlement are some of the achievements from utilizing such a laboratory. Microstructures under study are the ones of as-rolled plates and of pipes; modified structures are produced in laboratory conditions in the Phase Transformations Laboratory and also in the Department of Metallurgical and Materials Engineering. This paper presents part of the history of the Electrochemical Processes Laboratory, where such corrosion studies are made and gives some important results for production of steels for deep water oil exploitation and future projects.

Introduction

Research and development of HSLA steels has been performed for years in the Department of Metallurgical and Materials Engineering of Escola Politécnica, University of São Paulo (PMT). Microstructure-property relationships are the foundation upon which Prof. Renato Rocha Vieira has built a strong research group, which started in the 1970s. Under his guidance, PMT has produced scientific results closely related to the practice of metallurgical engineering. Over four decades, PMT has constantly upgraded the laboratory, which provides undergraduate and graduate courses with high recognition by national and international evaluation criteria. The Department has received research grants from federal and state institutions such as the National Council for Scientific and Technological Development (CNPq) and the Foundation of the State of Sao Paulo for Research Support (FAPESP).

A recent improvement in the Department has been the construction of a new facility coupled to the “Electrochemical Processes Laboratory” (LPE/-PMT) that has potentiostats and other resources used in electrochemical tests, which has been operating since 1991, the year of the acquisition of the first potentiostat. The "Laboratory of H_2S - Tests with Special Gases" (LabH_2S), Figure 1, was built as part of a research project, sponsored by CBMM, and was opened on 2nd December, 2011.

H_2S gas, used in most of the experiments carried out in this laboratory, has an unpleasant smell and is dangerous to human health and to the environment. Its handling requires special procedures for the safety of users and for the disposal of exhaust gases to the environment. During the planning of the laboratory, there was a constant focus on safety. The facilities feature a gas injection panel with flow control, isolated safety cabinet connected to a chemical scrubber for gas cleaning and neutralization, controlled temperature environment, electrical safety outlets, anti-explosion lighting and light and sound alarms to detect gas leaks.

(a) (b)

Figure 1. (a) Overview of LabH_2S, (b) Safety cabinet for experiments with special gases.

Like all PMT laboratories, this one supports teaching and research, providing training for undergraduate and graduate students of Metallurgical and Materials Engineering.

In recent years, especially in Brazil, oil and gas reserves have been discovered under deep sea waters, where the environment is very aggressive. This gave rise to a demand for high quality special microalloyed steels, to make pipes and machine components, to resist the aggressive environment present at the stages of extraction and transport of these products.

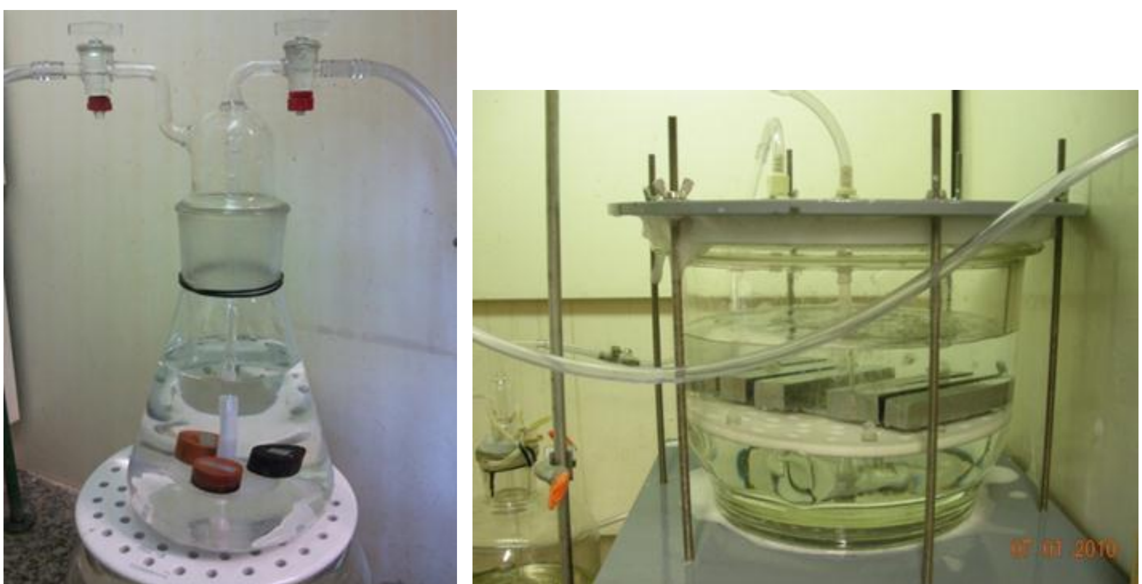
In this context, the objective of LabH_2S, is to support the development of metallic materials for the extraction and transportation of oil and natural gas. As part of the University, an institution of teaching and research, this has been done through research projects at post-graduate (Masters, Doctoral and Postdoctoral) levels, where the results are not only the technical and scientific developments, but also the training of people preparing them for the challenges and needs that will arise in the coming decades. LabH_2S meets a demand of industry for research and human resources, technically and scientifically trained, to work in the field of materials resistant to aggressive environments.

Ongoing research activities include, for instance, studies of experimental methods for measuring corrosion resistance: weight loss and electrochemical tests with the use of potentiostats, Figure 2; evaluation of the influence of inclusions on the morphology of corrosion - uniform and/or localized, Figure 3a, through immersion tests of polished samples, with tests and analysis in a scanning electron microscope (SEM) and analysis by energy dispersive spectroscopy (EDS); tests of Hydrogen Induced Cracking (HIC) in API 5L X65 and X80 pipes according to NACE TM0284-2003 standard, Figure 3b, and examination by optical microscopy and SEM. In all cases, microstructural observations are aimed at understanding the cracking and corrosion mechanisms.

(a)[1] (b)[2]

Figure 2. Electrochemical test; (a) Potentiostat PAR 273A, (b) Electrochemical cell.

[1] Image Author: José Wilmar Calderón-Hernández, PMT, 2012.
[2] Image Author: Henrique Strobl Costa, PMT, 2010.



(a)[3] (b)[4]

Figure 3. (a) Immersion test to examine corrosion morphology,
(b) Hydrogen induced cracking test, according to NACE TM0284-2003.

[3] Image Author: Henrique Strobl Costa, PMT, 2010.
[4] Image Author: Mariana Akemi Okamoto, PMT, 2010.

Results

The studies have been made on HSLA steels in media containing H_2S and can be grouped into the following categories:

- Experimental methods for the evaluation of corrosion resistance;
- Corrosion resistance of different chemical compositions and microstructures;
- Hydrogen induced cracking of API 5L X80 and API 5L X65 steels;
- Relationships between microstructure and hydrogen induced cracking.

The main results obtained through the facilities of LabH_2S are briefly described below.

<u>Experimental Methods for the Evaluation of Corrosion Resistance</u>

Mass loss, Figure 4, and potentiodynamic tests, Figure 5, were performed in different media, in the presence or absence of H_2S for a steel that is used for API 5L X80 pipe production. Mass loss tests showed that dissolved oxygen in aqueous media accelerates the kinetics of uniform corrosion. Deaerated media, with or without addition of H_2S, is much less corrosive. Potentiodynamic polarization curves did not show differences, indicating that this procedure is not suitable for the determination of differences in the corrosion rates. On the other hand, the determination of polarization resistance (Rp) agreed with the results of mass loss experiments, as shown in Figures 4 and 6.

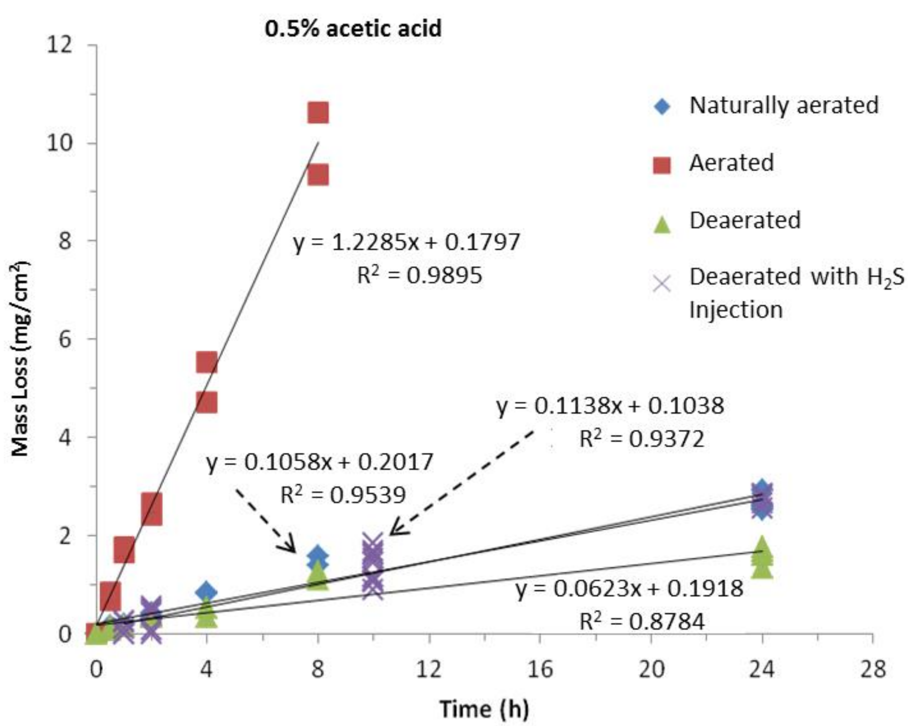


Figure 4. Mass loss in 0.5% acetic acid in different conditions: Naturally aerated solution; Aerated solution; Deaerated solution; Deaerated solution with H_2S injection [1].

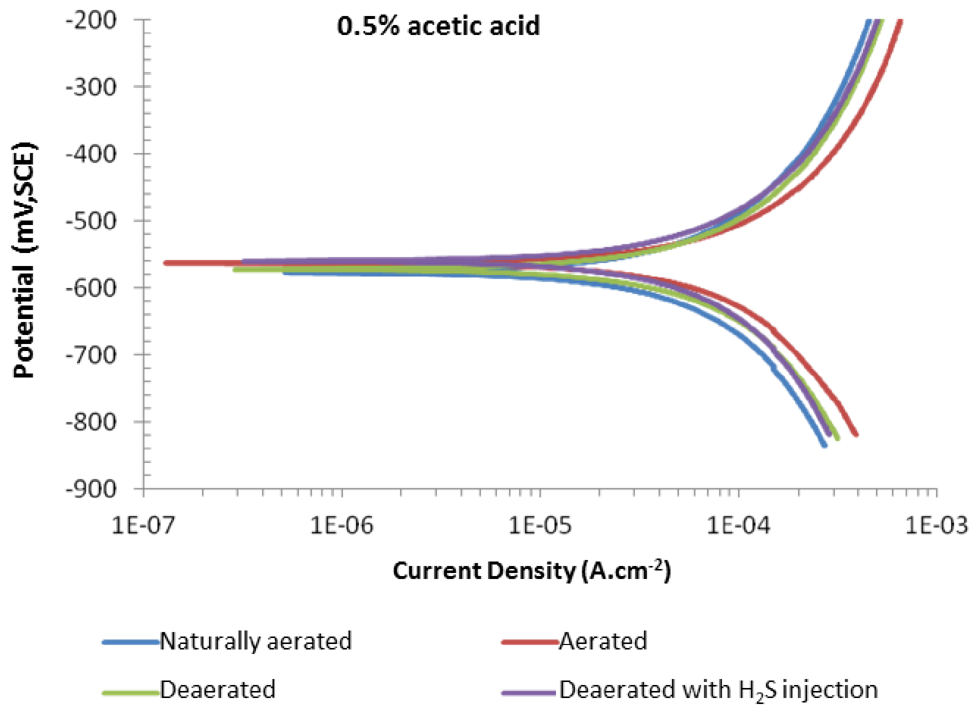


Figure 5. Potentiodynamic curves in 0.5% acetic acid in different conditions: Naturally aerated solution; Aerated solution; Deaerated solution; Deaerated solution with H_2S injection [1]. SCE: Saturated Calomel Electrode.

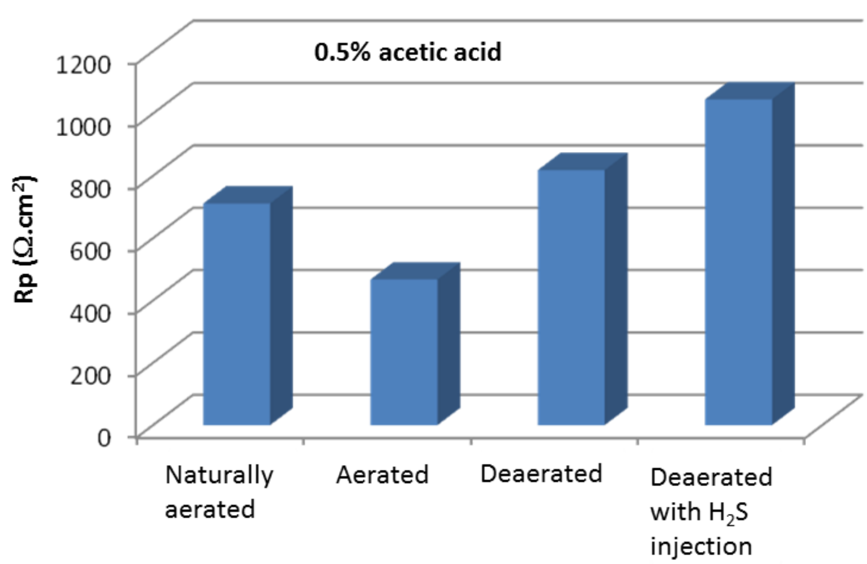


Figure 6. Polarization resistance (Rp) values in 0.5% acetic acid in different conditions: Naturally aerated solution; Aerated solution; Deaerated solution; Deaerated solution with H_2S injection [1].

Results of another study [2], for API 5L X80 pipe material, showed that Rp did not change significantly with the immersion time up to 8h, Figure 7. With this information, the evaluation of corrosion resistance of HSLA steels is now determined by Rp values for immersion times up to 60 minutes only, making the procedure faster.

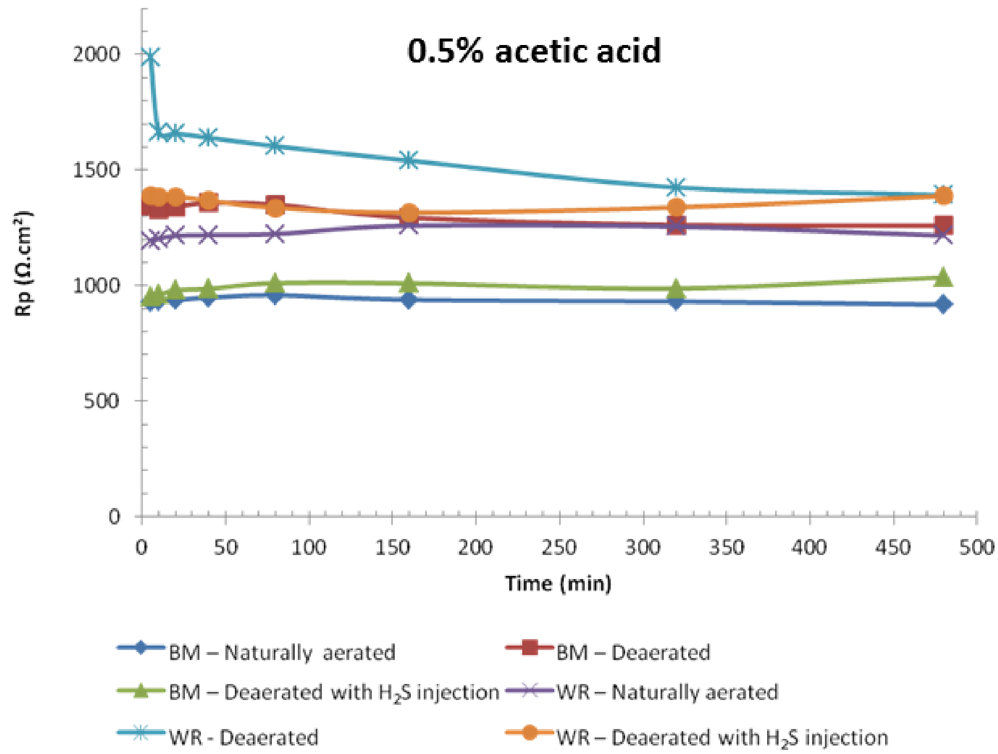


Figure 7. Rp values for different samples of API 5L X80 pipe material in different conditions as a function of immersion time in 0.5% acetic acid. BM: base metal; WR: weld region [2].

Corrosion Resistance for Different Chemical Composition and Microstructure

The method of polarization resistance showed that the steels designed for sour service have better corrosion resistance, Figure 8 [3]. Samples of API 5L X65 pipe material for sour and non-sour service were tested by the polarization resistance method in solution A of NACE TM0284-2003 standard (with injection of H_2S). Results showed similar corrosion morphology in both steels, with preferential corrosion at metal-inclusion interfaces as shown in Figures 9 and 10. The Rp values, as well as the microscopic examination, indicate better corrosion resistance for the sour material, possibly due to the different chemical compositions of the steels and different inclusion densities.

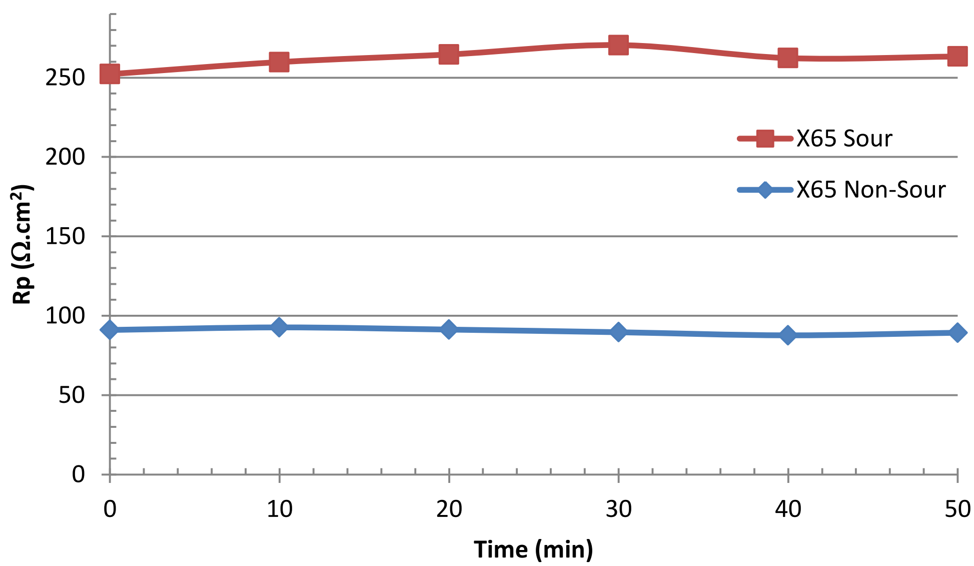
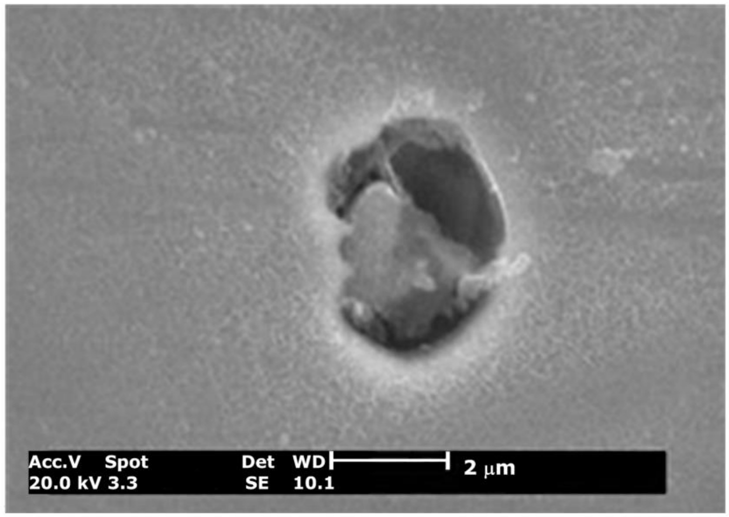


Figure 8. Polarization resistance as a function of immersion time in solution A of the TM0284-2003 standard. Comparison of non-sour and sour service pipes [3].

(a)



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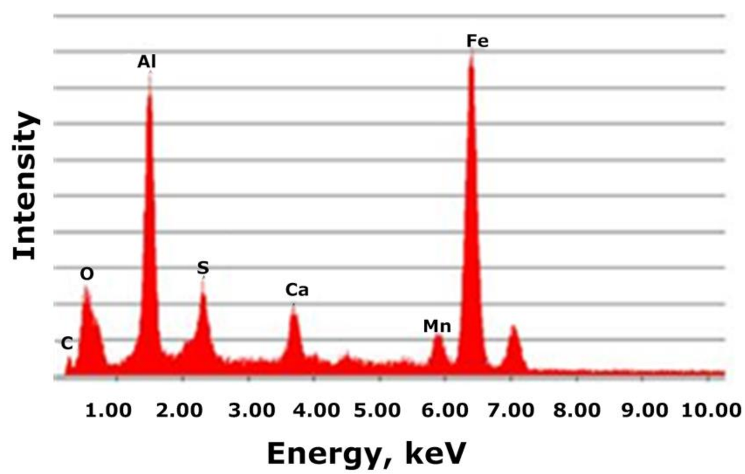
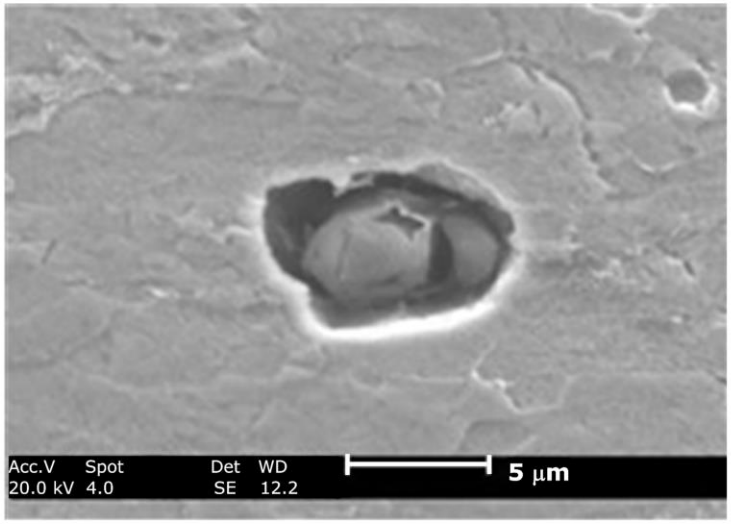


Figure 9. (a) Example of an inclusion present in the X65 sour pipe material and (b) its corresponding EDS chemical analysis.
EDS analysis shows the presence of Al, Ca, S, Mn and Fe [3].

(a)



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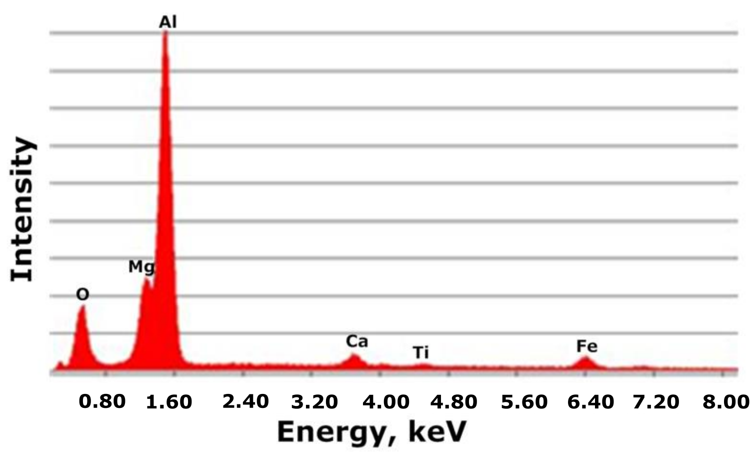
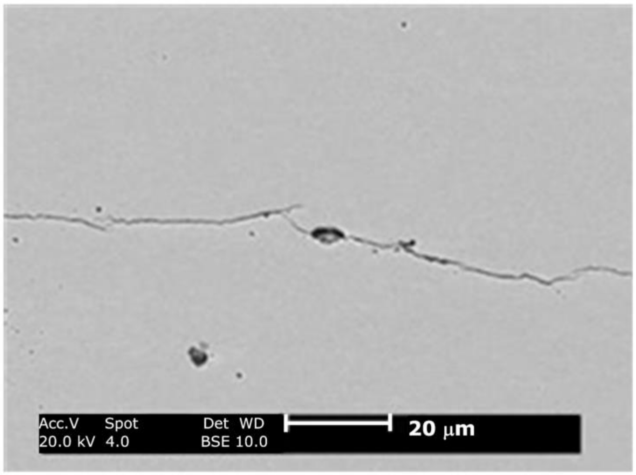


Figure 10. (a) Corrosion around an inclusion in the X65 non-sour pipe after immersion test, (b) EDS analysis shows the presence of Al, Mg and Ca [3].

Hydrogen Induced Cracking of API 5L X80 and API 5L X65 Steels

API 5L X80 and API 5L X65 pipe materials were compared [4] with regards to hydrogen exposure in a corrosive environment in the presence of H_2S (solution A - NACE TM0284-2003). The results show that the X80 pipe, Figure 11, is more susceptible to hydrogen induced cracking than the X65 [4]. X65 pipe material did not show any cracking. Elongated MnS inclusions are sites of crack nucleation while other types of inclusions can help crack propagation. Moreover, rounded inclusions can also nucleate cracks but are thought to be less susceptible to crack nucleation. Inclusion shape control is done in steelmaking by several processes, many of them using Ca treatment. Possibly this is the origin of the Ca detected by EDS analysis, Figures 9b and 10b. Inclusion shape control is not the only way to increase API 5L tubes HIC resistance. Microstructure control is also important for crack nucleation and propagation.

(a)



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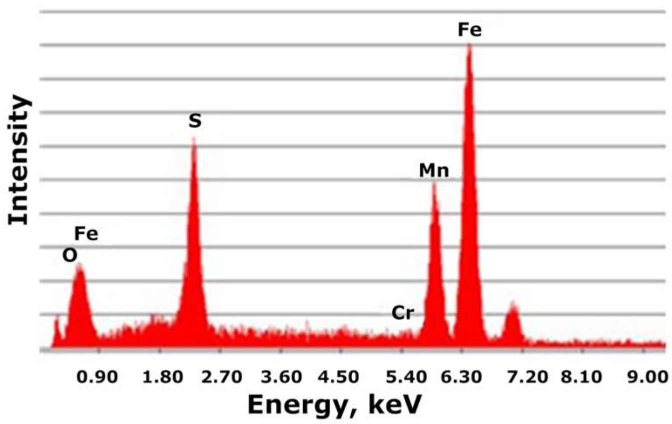
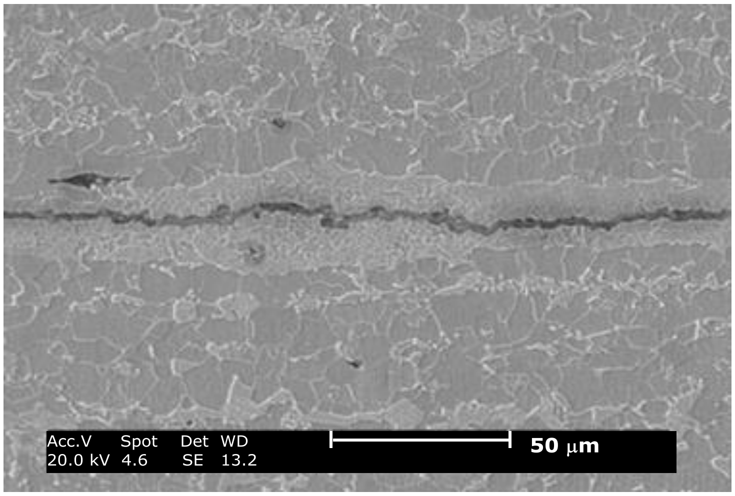


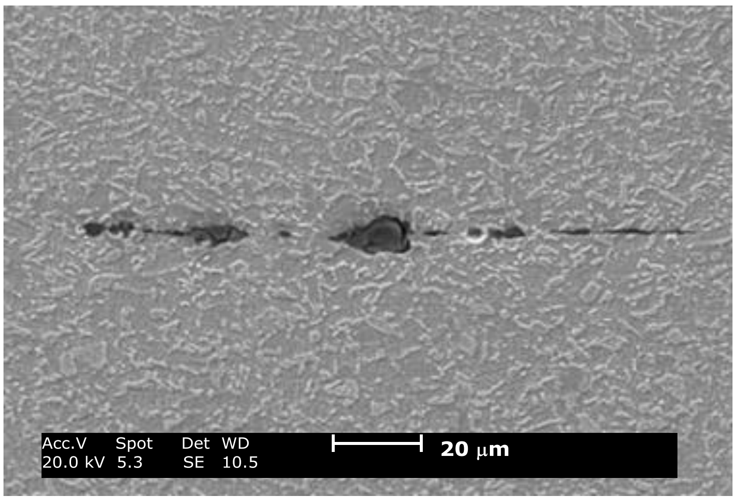
Figure 11. (a) Inclusions on the crack path in X80 specimen, (b) Corresponding EDS analysis showing the presence of manganese and sulphur [4].

Microstructure and Hydrogen Induced Cracking

The effect of different microstructures on hydrogen induced cracking of microalloyed steels, austenitized and subjected to different cooling rates, was studied [5]. Samples extracted from a plate and heat treated in a quenching dilatometer were subjected to hydrogen induced cracking tests (NACE TM0284-2003). Slow cooled samples (cooling rate of 0.5 °Cs^{-1}) showed higher susceptibility to hydrogen induced cracking, with large cracks in the middle of the sample, propagating along segregation bands at the centerline of the plate thickness, as shown in Figure 12a. For cooling rates of 10 °Cs^{-1} and 40 °Cs^{-1}, only small cracks were found in the matrix and micro-cracks nucleated at non-metallic inclusions, as shown in Figure 12b.



(a) 0.5 °Cs^{-1}



(b) 10 °Cs^{-1}

Figure 12. Microstructure of samples subjected to different cooling rates and hydrogen induced cracking test [5].

API 5L X80 pipe material showed a strong relationship between hydrogen induced cracking and the presence of inclusions [5]. In these materials, both the nucleation and the propagation path of cracks produced by hydrogen followed the distribution of inclusions.

On the other hand, the hydrogen induced cracking process in the API 5L X65 pipe material related to the micro-constituents; no relation to the inclusions was observed [6]. The materials with granular and acicular ferrite microstructure and microconstituent MA, Figure 13, were immune to hydrogen induced cracking in tests made in solutions A and B NACE TM0284-2003, while those with banded microstructures of alternating ferrite and pearlite had cracks, Figure 14.

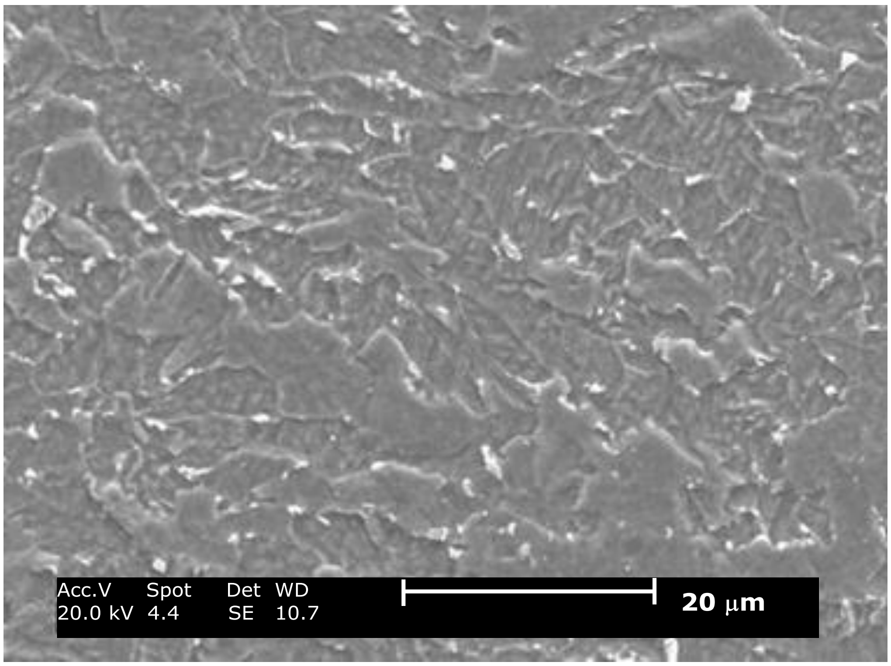


Figure 13. Secondary electron image. Granular ferritic matrix, acicular ferrite and micro-constituent MA. Etchant: Nital 2% [6].

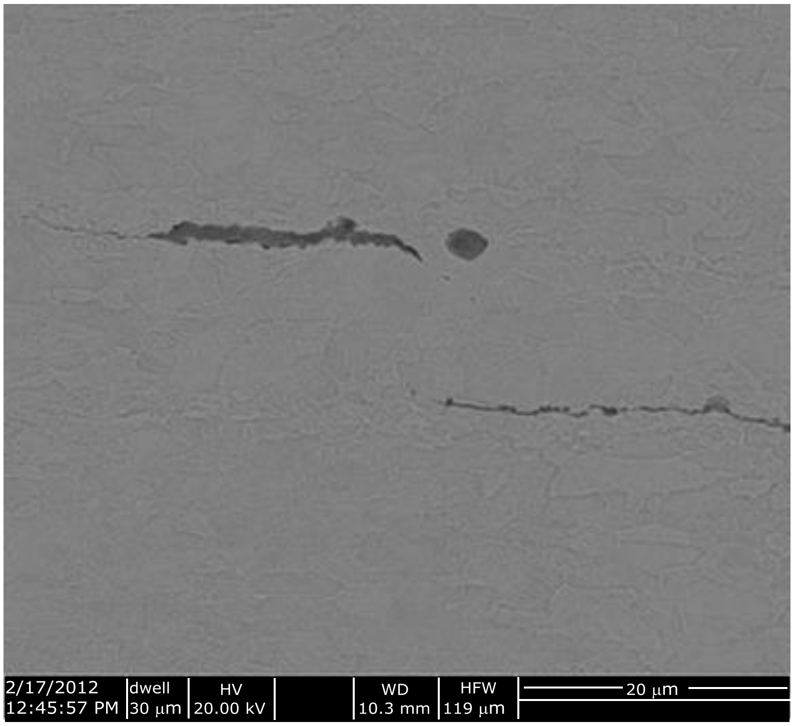


Figure 14. Backscattered electron image of a crack nucleated in the segregation band. Etchant: Nital 2%. Solution A - NACE TM0284-2003. Ferrite and pearlite microstructure [6].

Future Projects

The objective of the current research line is the development of materials to withstand the adverse conditions which are found in the exploitation, refining and transportation of oil and natural gas. There are planned projects involving micro-alloyed HSLA steels, super-martensitic stainless steels and nickel alloys. The materials to be studied are:

- API 5L X65 and X80;
- API 5L X65 containing high Nb;
- API 5L X65 containing high Nb and low Mn content;
- Nb in super-martensitic stainless steels: with Mo, Ti and Nb;
- HSLA clad with INCONEL 625 - nickel alloy.

It is intended to study the mechanisms of failure caused by hydrogen (H_2S), as the embrittling medium, hydrogen induced cracking, sulfide stress corrosion cracking and corrosion resistance itself.

Conclusions

1. Escola Politécnica, University of São Paulo, through its Department of Metallurgical and Materials Engineering, is able to conduct research projects that deal with materials resistant to hydrogen induced cracking and sulfide stress corrosion cracking.

2. Polarization resistance (Rp) is a suitable parameter for determining the corrosion resistance of HSLA steels. The corrosion rate does not change for immersion times as long as eight hours.

3. API 5L X65 pipe material, for sour service, has a higher corrosion resistance than those for non-sour service.

4. The corrosion of microalloyed steels is typically generalized, but there is preferential attack at the interface matrix/inclusion.

5. API 5L X80 pipe material studied has suffered hydrogen induced cracking. Cracks are nucleated at the interface between the matrix and inclusions and propagate following the inclusion path.

6. In pipe material API 5L X65, hydrogen induced cracking depends on the microstructure: ferritic structures such as granular and acicular are more resistant than those with a banded structure of ferrite and pearlite.

Acknowledgements

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