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The influence of calcareous deposits on hydrogen uptake and embrittlement of API 5CT P110 steel

Leonardo Simoni*, Júlio Queiroz Caselani, Leandro Brunholi Ramos, Roberto Moreira Schroeder, Célia de Fraga Malfatti

PPGE3M/DEMET, Federal University of Rio Grande do Sul – UFRGS,Av. Bento Gonçalves, 9500, Porto Alegre, RS, Brazil

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ABSTRACT

The effect of calcareous deposits on hydrogen uptake and embrittlement of API 5CT P110 steel was investigated using the electrochemical hydrogen permeation and slow strain rate techniques. A deposit with two distinct layers was formed at $-1000\,mV_{SCE}$, comprising an initial Mg-rich layer followed by a Ca-rich layer whereas at $-1500\,mV_{SCE}$ the deposit was porous and rich in Mg. The formation of calcareous deposits did not significantly alter hydrogen uptake and embrittlement at $-1000\,mV_{SCE}$ whereas at $-1500\,mV_{SCE}$ they were increased. A mechanism was proposed to explain the different roles of calcareous deposits in hydrogen absorption and embrittlement.

1. Introduction

Increasing energy demand has driven the development and exploration of new oil and gas fields around the world, many of which are offshore. Many of the materials used in offshore exploration adopt the cathodic protection technique to minimise or prevent corrosion in a range of structures such as pipelines and well casings [1–3]. When cathodic protection is used, as structures are cathodically polarised, oxygen reduction (1) and water dissociation (2) reactions occur on the metal surface.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (2)$$

In either case, hydroxyl ions are produced resulting in increased pH in the solution adjacent to the metal surface. Consequently carbonate ion concentration is enhanced at the metal/solution interface due to the modification of inorganic carbonic equilibrium. Thus, as a result of the higher interfacial pH and higher carbonate ion concentration at the interface, inorganic compounds whose solubility product is exceeded, such as calcium carbonate (3) and magnesium hydroxide (4), can precipitate.

$$Ca^{2+} + CO_3{}^{2-} \rightarrow CaCO_{3(ppt)} \quad (3)$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_{2(ppt)} \quad (4)$$

It has been shown that the critical pH for the precipitation is ~7.5 for $CaCO_3$ and ~9.5 for $Mg(OH)_2$ (brucite) precipitation [4,5]. Mixed deposits of calcium carbonate and magnesium hydroxide are generally called calcareous deposits. It is known that these deposits decrease the corrosion rate and the current demand of cathodic protection by progressively decreasing the active metal surface and hindering the oxygen transport to the metal surface [6–11]. The composition and morphology of calcareous deposits is dependent on many factors, such as the applied potential, the concentration of dissolved oxygen, the pH, the pressure, the temperature and the flow of the electrolyte, among others [8,12,13]. Barchiche et al. [10] performed X-ray diffraction (XRD) analysis of the outer layers of calcareous deposits formed on rotating steel electrodes in the 10–30 °C range and suggested that for potentials between −900 and $-1100\,mV_{SCE}$ the deposits were composed by aragonite whereas a combination of aragonite and brucite was found at $-1200\,mV_{SCE}$. They also observed that the deposit was composed exclusively by brucite at potentials more negative than $-1300\,mV_{SCE}$. However, it has been established that below the aragonite crystals observed

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* Corresponding author.
E-mail address: lss.simoni@gmail.com (L. Simoni).

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on the outer surface there exists a Mg-rich inner layer, presumed to be magnesium hydroxide [4,5,14].

The hydrogen evolution induced by the applied cathodic potential in certain circumstances results in hydrogen embrittlement of the protected material. It is known that hydrogen evolution occurs in stages, and can lead to entry of hydrogen into the metal lattice [15–17]. Once it has been absorbed, hydrogen can be found either in normal interstitial sites or trapped in defects such as grain boundaries, vacancies and interfaces [18]. These hydrogen traps play an important role in hydrogen diffusion and distribution in steels, and are usually classified as irreversible (traps with high activation energy) and reversible (traps with low activation energy). The absorbed hydrogen has a significant impact on a material's mechanical and microstructural properties. Depending on the conditions and the material, several mechanisms of hydrogen embrittlement have been proposed. The most cited ones are HELP (hydrogen enhanced localised plasticity) and HEDE (hydrogen enhanced decohesion). The former is based on slip softening due to enhanced dislocation movement in some crystallographic planes at crack tip caused by atomic hydrogen [19,20], while the latter supposes that hydrogen decreases the cohesive force between atoms in the metal lattice, at grain boundaries and at interfaces [18,21]. Thus it results in the nucleation of microcracks, resulting in fracture.

The relation between calcareous deposit formation, hydrogen uptake and embrittlement is still not clear. Some researchers have studied and discussed the effect of deposit formation on hydrogen absorption using electrochemical hydrogen permeation techniques but there is no consensus concerning their results. After electrochemical hydrogen permeation tests with galvanostatic charging, Chyn Ou and Wu [22] concluded that calcareous deposit formed either by $Mg(OH)_2$ or by $CaCO_3$ decrease the hydrogen uptake. Olsen and Hesjevik [23] also concluded that the presence of calcareous deposits decreased hydrogen entry in supermartensitic stainless steels by a factor of two or three. Turnbull and Hinds [24] reported that the calcareous deposits formed in artificial seawater in permeation tests at $-1000\,mV_{SCE}$ decreased the hydrogen uptake on supermartensitic stainless steel in comparison with tests carried out in 3.5% NaCl solution. However the authors concluded that the difference was not significant and should not be relied upon. Recently, results obtained by Smith and Paul [25] also showed a slightly lower hydrogen uptake (measured by thermal desorption) in artificial seawater in comparison with 3.5% NaCl solution at $-1100\,mV_{SCE}$. However, Lucas and Robinson [26] and Hamzah and Robinson [27] observed the opposite behaviour of calcareous deposits, i.e., hydrogen absorption was higher in seawater than in 3.5% NaCl solution at different cathodic potentials (from $-850\,mV_{SCE}$ to $-1300\,mV_{SCE}$). In addition, Zucchi et al. [28] used the slow strain rate technique (SSRT) to study the hydrogen embrittlement of duplex stainless steel. They attributed an increase in elongation in tests performed at $-1200\,mV_{SCE}$ compared with $-1000\,mV_{SCE}$ and $-900\,mV_{SCE}$ to the formation of calcareous deposits on the specimens surfaces. Increases or decreases in elongation in SSRT tests compared with tests performed in air are usually used as a parameter to measure hydrogen embrittlement or stress corrosion cracking susceptibility [28,29]. Thus, these studies indicated a decrease in susceptibility to hydrogen embrittlement caused by the precipitation of calcareous deposit.

Despite these published studies, there are still some unclear points in the understanding of this phenomenon, and there remain no focused studies on the calcareous deposit effect on the correlation between hydrogen uptake and hydrogen embrittlement. In addition, there are almost no studies to date concerning the hydrogen effect on API 5CT grade P110 steel, a well casing material that is often used in offshore oil and gas industries. As this material is usually cathodically protected the formation of calcareous deposits on its surface is expected. The main objective of the present work is to investigate the effect of calcareous deposits on hydrogen uptake and embrittlement of API 5CT P110 steel. To accomplish this, electrochemical hydrogen permeation tests and SSRT were used in ASTM D1141 artificial seawater, in artificial seawater without calcium and magnesium ions, and in 3.5% NaCl solution.

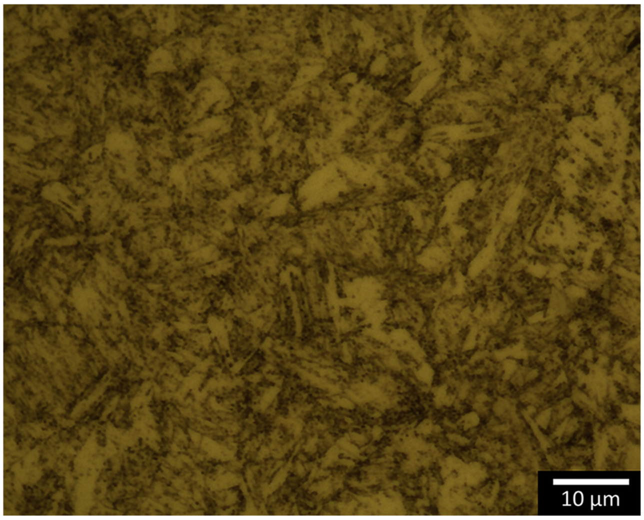

Fig 1. Microstructure of API 5CT grade P110 steel composed of tempered martensite, upper bainite and dispersed carbides, observed by optical microscopy.

2. Experimental procedures

2.1. Preparation of specimens and solutions

The specimens were cut from an API 5CT grade P110 steel seamless pipe with an external diameter of 170 mm and a thickness of 12.7 mm supplied by Petrobras S.A. The chemical composition of this steel is given in Table 1 and the microstructure (composed by tempered martensite, upper bainite and dispersed carbides) is shown in Fig. 1.

The specimens for electrochemical permeation tests were cut by wire electroerosion into samples of $22 \times 25 \times 1\,mm^3$. The surfaces were then prepared as follows:

1. Mechanical wet grinding of the surface in contact with the cathodic cell down to 600 grit SiC emery paper. The surface in contact with the anodic cell was wet ground down to 1200 grit SiC emery paper;
2. Electrodeposition of a thin palladium coating (less than 0.1 µm thick) onto the surface in contact with the anodic cell. The electrodeposition was carried out in a 28% $NH_4OH + 5\,g\,L^{-1}$ $PdCl_2$ solution with a cathodic current density of $2\,mA\,cm^{-2}$ for 90 s, as described by Manolatos and Jerome [30]. The importance of the palladium coating has previously been discussed in several studies [31–33];
3. Degreasing with acetone and ethanol.

The specimens for SSRT were machined according to NACE TM 198-2004 for subsize specimens [34]. Prior to each test, the surface of the specimens was sequentially wet-ground down to 600 grit SiC emery paper and degreased with acetone and ethanol. Note that the surface preparation for the SSRT specimens and for the cathodic side of the electrochemical hydrogen permeation specimens is the same, in order to have the same finish on the surface for hydrogen entry.