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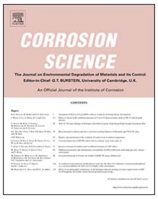

# Synergistic effect of temperature and HCl concentration on the degradation of AISI 410 stainless steel

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## ABSTRACT

The corrosion behavior of AISI 410 stainless steel was investigated in relatively dilute HCl solutions with different concentrations and temperature levels. General corrosion occurred at $\text{pH} < 1.5$ while pitting occurred at $2.25 \le \text{pH} \le 4.25$. Important pitting parameters were evaluated as a function of both temperature and HCl concentration. Critical temperature ($T_{crit}$) increased linearly with pH. Below $T_{crit}$, passive film remained largely intact and sporadic metastable pitting initiated from non-metallic inclusions. Above $T_{crit}$, passivity was completely destroyed and black film consisting of oxy-hydroxide and hydrated oxide formed. Sigma-phase particles were found in this steel and remained un-corroded.

## 1. Introduction

Martensitic steels are essentially Fe-Cr-C alloys that are designed for components requiring high mechanical properties and moderate corrosion resistance. Martensitic stainless steels (SS) exhibit high strength and hardness at relatively low cost, however, they are less resistant to corrosion compared to other types of stainless steels. Among various types of martensitic stainless steels, the 400 series steels have been widely used in petroleum production and refining, turbine components, valve parts, cutlery, fasteners and machinery parts. AISI[1] 410 SS is the classic 12% Cr martensitic stainless steel and is the most popular martensitic grade produced [1]. For instance, 410 SS is commonly used in HCl services, such as distillation column trays in oil refineries, however, its corrosion behavior and related data are not available in major industry standards, for example API 581 [2].

Literature reviews suggest that the corrosion behavior of 410 SS is affected by the following environmental factors: anion species and concentration, pH and temperature. Both uniform and localized corrosion of 410 SS have been investigated at either constant $[H^+]$ or constant $[Cl^-]$ and the simultaneous variation of both species has rarely been reported. Leckie studied the effect of pH on the stable passivity of 410 SS in acidic chloride (0.1 M) solutions, and the critical pH was determined to be 3.6–3.7 by means of anodic-polarization and potential-time techniques [3]. Hashizume et al. measured the depassivation pH of various low carbon 13% Cr steels in 5% NaCl + 0.5% $CH_3COOH$ solution under $H_2S + CO_2$ atmosphere. The depassivation pH was between about 3.6 and 3.8, determined from corrosion rate coupled with visual observation [4,5]. In comparison, 304 SS has a much lower critical pH of 1.4–1.5 in 0.1 M chloride solutions [3] which suggests its higher tendency to spontaneously passivate and better resistance to acid corrosion.

In chloride solutions with very low pH (e.g., < 0.5), it is impossible to induce passivity for most stainless steels [3]. The uniform corrosion rates of 410 SS have been reported to be 12 mm/y in 0.1 M HCl [6] and 22 mm/y (478 $g/m^2$-d) in 1 vol.% HCl [7] at room temperature (RT). Agrawal et al. determined a higher corrosion rate of 69 mm/y (2713 mpy) for 410 SS in 1N $H_2SO_4$ solution after 24 h weight loss at 36.3 °C [8]. Finsgar et al. studied the potential evolution of 410 SS in various industrial cleaning acids (10 wt.%) after 20 h immersion at 25 °C. Their results showed that the corrosion potential was $-0.483\ V_{SCE}$ in $H_2SO_4$ solution and $-0.423\ V_{SCE}$ in HCl solution [9]. To improve the corrosion resistance of 410 SS in the aggressive low pH environment, various mitigation strategies have been found effective including plasma nitriding [7], use of inhibitors such as thiourea and its derivatives [8], and application of intrinsically conducting polymers, such as polyaniline [10].

In less acidic environments, localized corrosion such as pitting has been found prevalent for 410 SS. Halides, especially chloride, play a critical role in passive film breakdown. For instance, pitting of 410 SS heat exchanger tubes occurred after brief exposures to chloride environments. Cross sectional analysis revealed undercutting characteristic of chloride ion pitting and X-ray spectrometry of the pits showed evidence of chlorides [11]. Pourbaix et al. studied the chloride threshold concentrations for 410 SS in 0.1 M $NaHCO_3$ solutions containing

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**Table 1**
Chemical composition (wt.%) of the certified 410 SS material (Fe as balance).

| C | Si | Mn | Cr | Mo | Cu | Ni | Co | Al | P | S | N | Sn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.129 | 0.29 | 0.43 | 12.24 | 0.12 | 0.05 | 0.42 | 0.021 | 0.02 | 0.02 | 0.001 | 0.027 | 0.003 |

chloride. Their results suggested that 410 SS corroded by pitting if chloride concentration reached 2.1 g/L $Cl^-$ (breakdown concentration), but stopped corroding if the concentration fell below 0.24–0.54 g/L $Cl^-$ (protective concentration). When chloride concentration is above the critical concentration, there is a risk of localized corrosion with the presence of oxidizing agents such as $O_2$ and $H_2O_2$. The range of the protective concentration depends on the heat-treatment and the surface state of the metal. They also acknowledged that without the presence of 0.1 M bicarbonate, the chloride breakdown and protective concentrations would be much lower [12]. In his study in neutral NaCl solutions at 80 °C, Atrens found that 12% Cr steel suffered no pitting and no crevice corrosion only in deaerated solutions containing a chloride ion concentration less than about $2 \times 10^{-4}$ N [13]. However, Brigham et al. suggested the presence of chloride is a sufficient but not necessary condition based on their study of 410 SS pitting in sulfate only solutions. They hypothesized that localized breakdown of passivity is due to localized attenuation of surface charge density resulting from the interaction of double layers on passive surfaces. This is a rather general phenomenon that could be observed under appropriate conditions in halide-free systems [14].

Azzerri et al. developed the stability diagrams of 410 SS in chloride containing water (200–35,000 ppm) at three temperature levels (22, 44 and 64 °C). Both the pitting potential ($E_{pit}$) and repassivation potential ($E_{rp}$) were found to obey logarithmic law for 410 SS at all temperature levels [15]. Pahlavan et al. studied the pitting corrosion of 403 SS (martensitic) in halide bearing solutions and found the aggressive nature increases in the following order: $I^- < Br^- < Cl^-$. The dependence of $E_{pit}$ on $\log[Cl^-]$ was determined to be 130 mV/dec, with more noble values for more dilute solutions [16]. Similarly, Atrens found that at 80 °C, both $E_{pit}$ and $E_{rp}$ of 410 SS varied with the logarithm of chloride ion concentration, slopes 183 mV/dec and 142 mV/dec, respectively [13]. Pourbaix et al. found similar trend of $E_{pit}$ and $E_{rp}$ on chloride concentration, which both decrease with increasing chloride concentration, but do not follow the linear relationship of E *vs.* $\log[Cl^-]$ [17].

The pit initiation and propagation behavior of 410 SS has rarely been investigated in comparison to the 300 series austenitic stainless steels. Sulfide inclusions, especially manganese sulfide have been extensively studied as an initiation site for pitting corrosion in austenitic stainless steels [1,18,19]. However, they are not present in 410 SS and no studies appear to have been carried out on sulfides as pit initiation sites for martensitic stainless steels [1]. Therefore, pitting initiation sites are largely unknown for 410 SS. In the case of heat exchanger tubing failure, pitting was found to be random and could not be correlated with any sensitization or metallurgical deficiency in the tubes [11].

The present work aims to investigate the corrosion behavior of AISI 410 SS in relatively dilute HCl environment (pH 0.5–4.25) at different temperature levels (38–93 °C) based on API 581 [2]. Electrochemical techniques such as cyclic potentiodynamic polarization (CPP), open circuit potential (OCP) monitoring and temperature ramping with potentiostatic polarization were utilized to determine critical parameters and their dependence on pH (chloride concentration) and temperature. Various characterization techniques such as 3-D optical microscope, scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) together with selected area electron diffraction (SAED) analysis, and Raman spectroscopy were used to examine the corrosion morphology and surface film information. Lastly, all information was compiled and a diagram of corrosion domains as a function of environmental factors was generated for 410 SS in HCl solution.

## 2. Experimental

### 2.1. Materials and sample preparation

A commercial 410 SS rod material with certificate was used for all experiments. Table 1 gives the specific chemical composition. According to the certificate, the 410 SS rod used in this study was hot rolled, annealed and cold drawn. "Bullet"-shaped electrodes with dimension of L = 30 mm, D = 6 mm, and R = 3 mm (tip) were machined from the rod material and tapped with a threaded hole for electrical connection to a supporting threaded rod [20]. It has been demonstrated that specimen geometry can be very important in determining if pitting and/or crevice corrosion will occur [13]. All tests were performed with partially immersed electrodes and the exact exposed surface area was individually measured after each experiment. This electrode configuration was used to minimize unintended crevice corrosion which occurs frequently on flush mounted electrodes [7], and also had an advantage of mimicking possible waterline corrosion in actual environment. Prior to all tests, the samples were abraded to 600-grit, cleaned ultrasonically in acetone, rinsed with isopropanol and deionized (DI) water and finally blow-dried using compressed argon gas (99.998%). Additional polishing using diamond slurries (i.e., 9 μm, 3 μm and 1 μm) was performed to achieve mirror-like surface for inclusion characterization by SEM.

### 2.2. Electrolyte

All test solutions were prepared with reagent grade chemicals (37% HCl, Fisher Scientific) and DI water with a resistivity of 18.2 MΩ-cm. The solution pH was adjusted to target value immediately before each test at RT (~22 °C) using a calibrated pH meter. The following pH levels were examined: 0.5, 1.25, 2.25, 3.25 and 4.25 [2].

### 2.3. Electrochemical testing

Electrochemical tests were performed using Gamry REF 600+ potentiostat in a polarization cell described by ASTM G5 [21]. A saturated calomel electrode (SCE) was used as reference electrode and a pair of graphite rods were used as counter electrode. A salt bridge separated the compartment where the reference electrode was placed from the testing environment. This was done so that the reference electrode could be maintained at constant temperature (10 °C) through a recirculating water bath. All the potentials are referenced with respect to SCE at 10 °C, if not specified otherwise.

The solution temperature was measured via a K-type thermocouple (Omega) and controlled by a temperature controller (Omega) through a heating mantle (Glas-Col). Both constant temperature heating and temperature ramping experiments were performed. The following constant temperature levels were investigated: 38, 52, 66, 79 and 93 °C [2].

Three types of electrochemical tests were performed, including CPP, OCP measurements and temperature ramping experiments under potentiostatic hold. Table 2 gives the matrix for various tests conducted at different temperature and pH combinations.

The CPP experiments were performed according to the guidelines set forth in ASTM G61 [22]. Prior to testing, OCP was monitored for one