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Corrosion Type Diagrams of Cold Rolled Type 316L Stainless Steel in HCl Containing Aqueous Environment

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Abstract

The influence of HCl concentration and temperature on corrosion type, rate, and morphology of annealed and cold rolled type 316L stainless steel has been investigated. Electrochemical polarisation measurements in 0.01 - 3 M HCl at temperatures up to 80 °C were conducted, to establish corrosion type diagrams. These diagrams can be applied to describe the transition between uniform corrosion, pitting, and mixed mode, uniform with pitting corrosion. The transition boundaries are predominantly dependent on temperature and HCl concentration. Cold rolling had only minor effects on the transition temperatures for the different types of corrosion.

Introduction

Corrosion type diagrams of austenitic stainless steels in HCl environments were reported in the 1970s and 1980s [1], [2], indicating that the occurring corrosion type is depending on the HCl concentration at room temperature. Increasing HCl concentrations changed the corrosion type from uniform corrosion, to a combination of uniform and pitting corrosion, followed by uneven general corrosion attack [1]. Another investigation [2] highlighted the role of chloride concentration and acidity (HCl), indicating that both parameters affect the corrosion type. However, no information is available of how these different corrosion types and morphologies are influenced by temperature, microstructure condition, and under atmospheric droplet exposure conditions.

Material and Methods

A mill annealed type 316L austenitic stainless steel with the chemical composition of (wt.%) 16.7 Cr, 10.1 Ni, 2.04 Mo, 0.019 C and 0.049 N was used in this study. The sheets had dimensions of 1000 mm x 1000 mm x 1 mm (L x W x T) from which 250 mm x 30 mm x 1 mm (L x W x T) strips were cut for cold roll processing. The strips were uni-directionally cold rolled along the width of the sheet, with the thickness (T) vertical to the rolling plane. Thickness reductions of 5 %, 10 % and 20 % were chosen to introduce small amounts of cold work, which are referred to as 5 % CR, 10 % CR and 20 % CR.

All specimens were prepared with SiC-grinding paper to a 1200 grit finish. Electrochemical tests were carried out using an Avesta-cell at room temperature, 40 °C, 60 °C and 80 °C, using HCl concentrations ranging from 0.01 M to 3M. A saturated Ag/AgCl electrode was used as the reference electrode and a platinized Ti-electrode as counter electrode. All potentials were converted to NHE (normal hydrogen electrode). The polarisation experiments were carried out using an IVIUM-Compactstat potentiostat at a scan rate of 1 mV/s, with the current response recorded at a rate of 1 Hz. Prior to all scans, the open circuit potential (OCP) was measured.

Results and Discussion

The effect of HCl concentrations on the corrosion resistance of type 316L stainless steel is shown in Figure 1a, indicating different material response depending on the HCl concentration. With increasing HCl concentration the corrosion type changes from pitting corrosion only, observed for 0.01 and 0.1M, to uniform and pitting corrosion (0.7 and 1.5M) and finally to uniform corrosion only (3M). The direct dissolution of the material in 3M HCl is indicating that the passive film is not stable under this condition. This is in good agreement with Pourbaix diagrams for chromium and iron [3].

The less concentrated 0.7 and 1.5M HCl electrolytes exhibit a mix-mode corrosion attack of uniform and pitting corrosion. During polarisation the surface first undergoes active dissolution (active loop), before the surface electrochemically passivates. The passivation is associated with a sudden drop in current density from the active loop, with the potential of this drop occurring as a function of HCl concentration. Localised corrosion was observed by further anodic polarization for samples that first underwent first anodic dissolution (0.7 - 1.5 M HCl), or by directly entering the passive region (< 0.7 M HCl). The passive layer breaks down when the critical pitting potential (E_{pit}) is reached.

Figure 1b shows the influence of electrolyte temperature on the corrosion response of as-received type 316L stainless steel in 1.5M HCl. Higher temperatures lead to decreasing pitting potentials [4], [5], while simultaneously increasing the critical potential to reach passivation. The combination of both affects the width of the passive region, indicating narrower regions for higher electrolyte temperatures. At some point, between 60 and 80 °C, the passive region completely disappears, indicating a corrosion type change from mixed mode – uniform and pitting corrosion, to uniform corrosion only. This suggests that not only the HCl concentration but also the temperature affects the corrosion type.

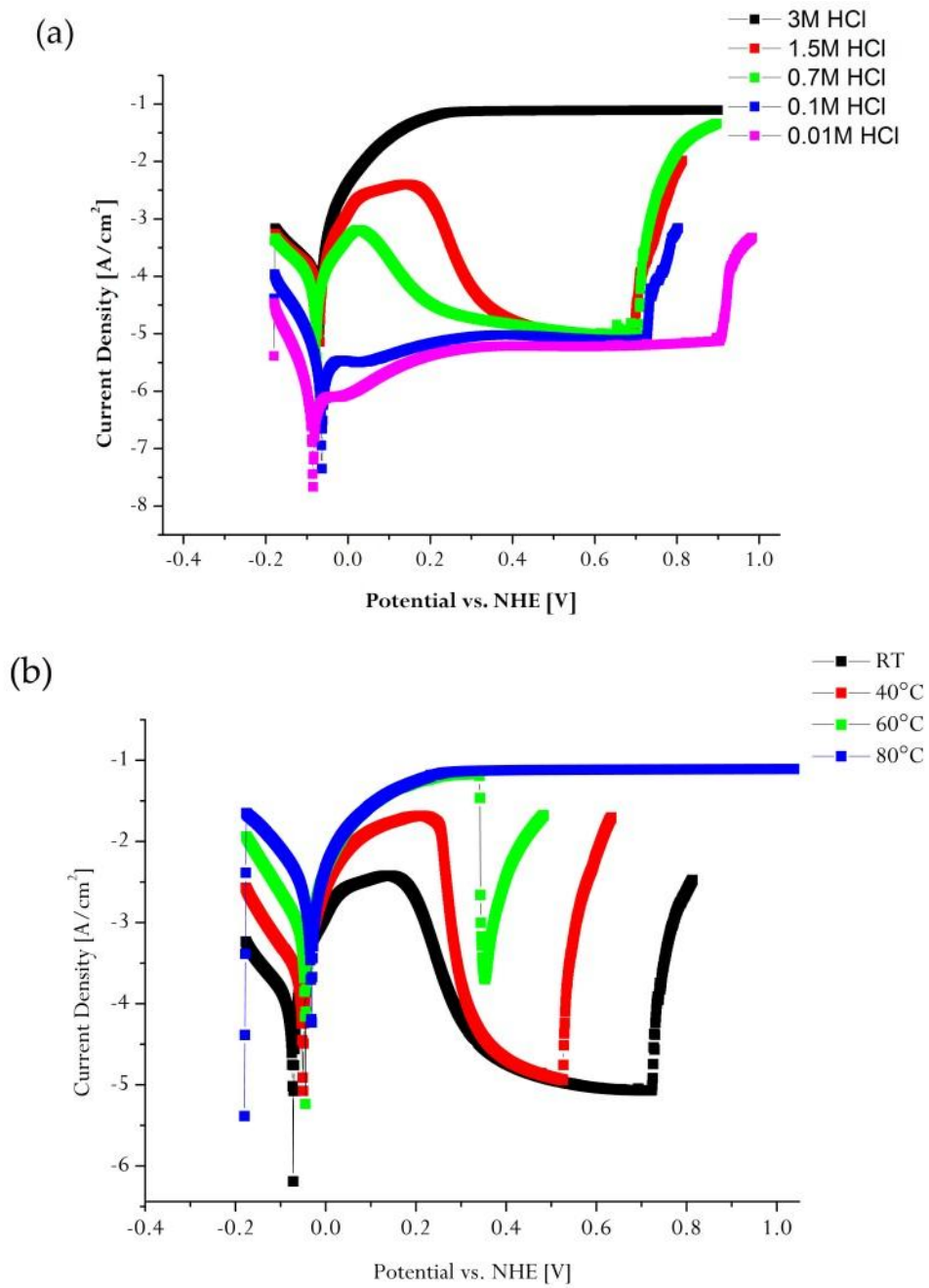


Figure 1: (a) Potentiodynamic polarization scans of as-received type 316L stainless steel in various HCl solutions at RT. (b) Influence of electrolyte temperature on pitting potential, active loop, and the passive range of the as-received microstructure in 1.5 M HCl.

Corrosion Type Diagram

A corrosion type diagram for as received type 316 stainless steel was generated by adjusting the HCl concentration in 0.05M increments at a given temperature. All samples were analysed after corrosion testing using Keyence VK-X200K 3D laser scanning confocal microscope (LSM) to determine the corrosion type.

The same methodology was also applied with CR5, CR10, and CR 20 samples. Figure 2 shows a corrosion type diagram for all investigated microstructures, with representative LSM images for each corrosion type. The error bars represent the scatter of HCl concentrations for which two different corrosion types were observed. The three observed corrosion types and associated boundaries are referred to as pitting corrosion (P), mixed mode uniform and pitting corrosion (P+U), and uniform corrosion only (U). The transition between the types of attack occurs towards lower HCl concentrations with increasing temperature, and are for room temperature in good agreement with literature data [1][2]. The influence of cold rolling is also shown in Figure 2, indicating no significant difference compared to the as-received condition. This is expected, as the pitting corrosion and passivation potentials of cold rolled and as-received condition are similar.

In the mixed-mode region (P+U), the corrosion type depends on the applied potential, as in the active loop, before passivation occurs, only uniform corrosion occurs. With further polarization the formed passive film breaks down resulting in localised corrosion attack. Therefore, the corrosion type in the (P+U) region depends on the applied potential.

With increasing HCl concentration the corrosion type changes as suggested to uniform corrosion only (U), indicating that the passive layer is not stable under the more severe conditions. The direct metal dissolution for higher HCl concentrations is supported by Pourbaix diagrams for iron and chromium, with both indicating no passive condition for low pH values [3].

Corrosion type diagrams with immersion in HCl electrolytes (under open circuit conditions) without electrochemical polarisation, and after exposure to HCl laden droplet deposits have also been obtained, and are reported in [5].

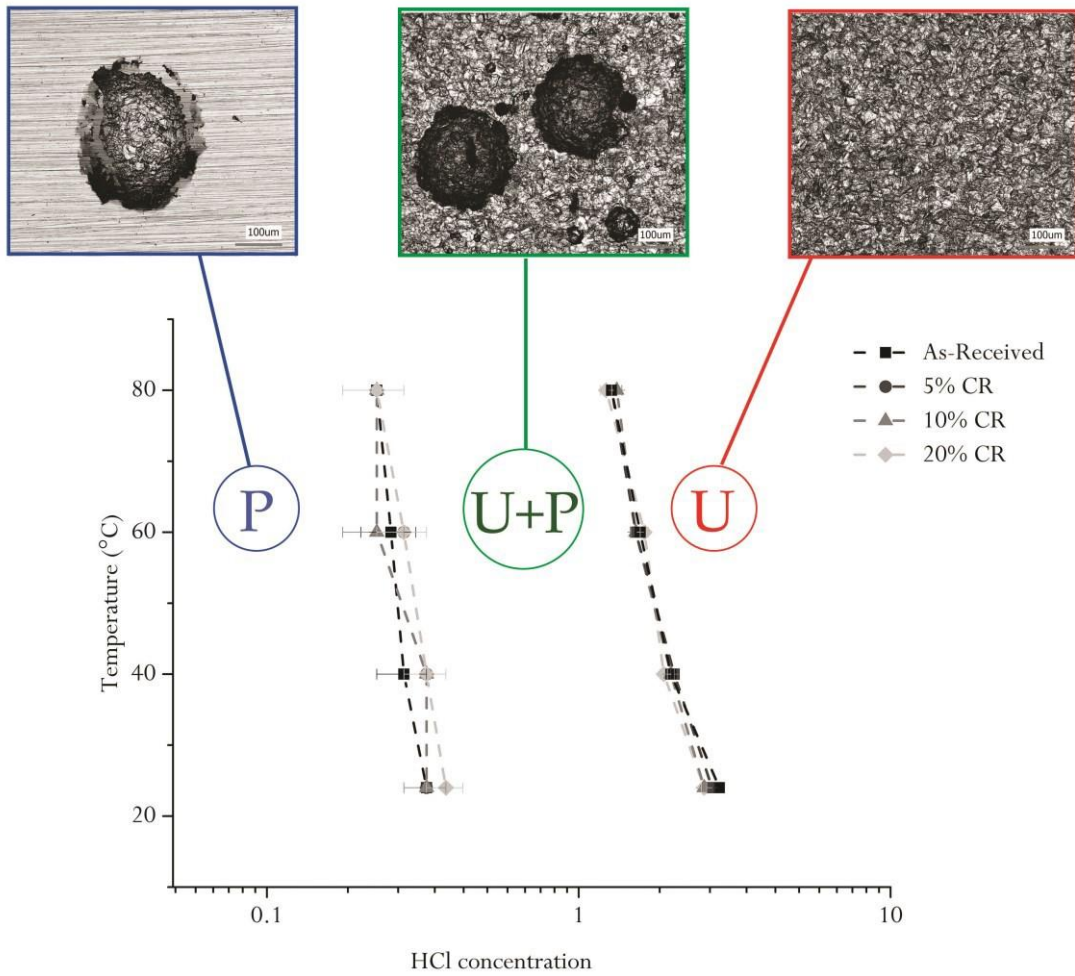


Figure 2: Corrosion type diagram as a function of temperature, HCl concentration and microstructure condition, with representative images for each corrosion type.

Conclusion

- Corrosion types for as-received and cold rolled type 316L stainless steel are introduced as a function of HCl concentration and temperature.
- The corrosion type is changing with increasing HCl concentration from pitting (P) to mixed-mode (P+U), to uniform corrosion (U) only.
- Cold rolling had no significant effect on the transition boundaries from one to another corrosion type, compared to the as-received microstructure condition.

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