Mechanical Behaviour of Type 316L Austenitic Stainless Steel in Low Pressure Hydrogen Steam Environment

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Abstract. Low pressure superheated H2-steam appears to be an interesting alternative to pressurized water environments, since it is capable of performing accelerated environmentally assisted cracking (EAC) experiments for nickel base and stainless steel alloys. Constant Extension Rate Tensile (CERT) tests were performed with strain rates of 2×10^{-6} or 2×10^{-8} ms^{-1} at 350, 400, 440 and 480 °C on flat tapered specimens of Type 316L austenitic stainless steel. The tapered shape allows the determination of crack initiation over a range of stresses and strains simultaneously on one specimen and therefore the threshold stress value was obtained. The environment was 6 times more oxidizing than the dissociation pressure of NiO. The acquired mechanical properties are summarized and threshold stresses for EAC crack initiation are evaluated.

1 Introduction

The requirements for mechanical tests in specific environments are determined especially by the large number of boiling water reactor (BWR) and pressurized water reactor (PWR) power plants used worldwide and the planned supercritical water reactor (SCWR) concept IV Generation. It has been found that the main contributor to degradation in these power plants is stress corrosion cracking (SCC) [1]. The pressure of reactor environments is high, which increases the costs of building test equipment and also increases the safety risk. Therefore, low pressure superheated hydrogen steam appears to be an interesting alternative, since it can accelerate the oxidation and SCC initiation stages whilst respecting the correct electrochemical corrosion potential (EcP) in a PWR primary water environment [2,3].

2 Investigated Material

An austenitic stainless steel AISI 316L, manufactured by Industeel, Arcelor Group was used in this study. The steel was available in the form of a 15 mm thick sheet, which was hot rolled and subsequently heat treated. Solution annealing was performed at 1050-1100 °C in air. The microstructure consisted of equiaxed grains of austenite and approximately 5% of δ-ferrite longitudinal stringers oriented in the rolling direction. The chemical composition is: Fe ~68 wt.% Cr ~16 wt.% Ni ~10 wt.% Mo ~2 wt.% C <0.03 wt.% (X2CrNiMo 17-12-2). The steel has a relatively high elongation (~44 % for room temperature and ~26 % at 350 °C). As the temperature rises, the yield strength and tensile strengths drop significantly, which means that cold forming is limited to 20-30 % [4]. The degree of cold working (CW) and yield strength have been found to have a significant effect on crack growth behaviour [5].
Generally a cold-worked metal is more susceptible to corrosion than the same material in an annealed state [6]. Susceptibility to environmentally assisted cracking (EAC) has been investigated in [7] for various surface finishes. It was shown to be associated with high residual stresses as well as with ultrafine-grained and deformed layers that reached up to several microns below the surface. The actual stress needed to initiate the EAC may be the sum of the applied and residual stresses. It has been shown in [8] that an intergranular crack could be initiated after disrupting the oxide or metal-oxide interface. As the temperature rises, a higher EAC rate and shorter initiation times can be expected.

3 Specimens
Flat tapered samples were used to study the mechanical behaviour as a function of different strain rates and temperatures in an H₂-steam environment. The specimens presented a nominal thickness of 3 mm. The gauge length was 26 mm long, and 6.4 mm wide at the widest part and 4 mm at the narrowest part. This corresponds to a 3° slope that produces a different stress distribution along the gauge length during mechanical loading. In this way, it is possible to determine at what state of stress the cracks still occur and thus to determine the threshold stress. Collecting data in this way has a huge advantage, as there is no need to perform several experiments using constant cross-section samples with different load levels.

The samples were produced by wire cutting using an electro-spark machine tool with the longer side parallel to the plate rolling direction. After machining, the parallel flat surfaces of the samples were subjected to different surface preparations. The first step was hand grinding with abrasive paper with a roughness of P500 in a direction inclined by 25 ± 10° to the load axis. The other side of the sample was ground with abrasive papers with steps P500, P1200, P2000 and P4000. Each grinding step was applied for a minimum of 2 minutes until the grinding marks appeared to be all parallel. The samples were carefully rinsed with deionized water between each step. After the grinding procedures, the P4000 prepared side of the sample was metallographically polished with a 3 µm and 1 µm diamond paste in order to produce a mirror-finish surface. In between these steps, the samples were washed with soapy water and rinsed with ethanol and dried in a stream of hot air. Each sample was sonicated for 15 minutes and then rinsed again with ethanol and finally dried in a stream of hot air.

Back-scattered electron (BSE) analysis revealed a ~1 µm thin layer with a different microstructure near the surface. This deformed layer is created by mechanical processing of the sample during preparation (grinding and polishing) and it is usually thicker (~1-2 µm) for ground surfaces. This may generate different oxidation in the corrosive environment and also different tensile behaviour of the material. Due to this nano-layer, which is mechanically strengthened and therefore more resistant to intergranular corrosion, different material behaviours can be observed on the ground/polished sides.

4 Test Equipment, Environment and Methodology
The design of the test apparatus for mechanical testing in a low pressure superheated hydrogen steam environment is based on the oxidation system concept developed by Scenini et al. [9]. A similar system is implemented in different independent laboratories [10,11]. A comprehensive study on the thermodynamics of the low pressure H₂-steam environment can be found in Volpe et al. [12]. This concept was applied to the conversion of a corrosion cell originally designed for testing with heavy liquid metals. The description of the cell was published by the authors [13] in 2018.

The environment was set to perform the EAC experiments in a 6 times more oxidizing environment with respect to the dissociation pressure at the Ni/NiO transition \(p_{O2 \text{ Ni} / \text{NiO}}\). This value was calculated considering the ratio \(R_{O2}\) between the \(p_{O2 \text{ Ni} / \text{NiO}}\) over the actual partial pressure in the system \(p_{O2}\). The full calculation depends on temperature and \(H_2/\text{H}_2\text{O}\) ratio and can be found in Volpe et al. [12]. The environment and hence the \(EcP\) was created by directly controlling the hydrogen flow rate and water flow rate at room temperature. A gas mixture of 6.5% hydrogen and 93.5% argon was used to create the atmosphere. The gas mixture flow rate was selected to be 50 ml/min. The water flow was then adjusted according to the required temperature as shown in
Table 1. A high-performance liquid chromatography (HPLC) pump was used. Ultra-pure water with a conductivity of 0.055 μS/cm was used which was obtained from reverse osmosis. The temperatures were 350, 400, 440 and 480 °C. The total pressure corresponded to an overpressure of 0.1 bar (10 kPa) and was given by a structural column of water located at the outlet of the corrosion cell. Nickel plates with a purity of 99.5 wt. % and with dimensions approximately 20×20×2 mm³ were placed near the sample to indirectly monitor the EcP during the test.

| Temp. [°C] | RO2 | Fgas [ml/min] | FH2O [ml/min] | PPR⁻¹ | p O2 [atm] | p H2 [atm] | EcP [mV] | [H2] [ml/kg] |
|------------|-----|---------------|--------------|-------|------------|------------|---------|-------------|
| 350        | 1/6 | 50            | 2.40         | 981   | 2.47×10⁻³⁰ | 0.078      | 24.05   | 8.05        |
| 400        | 2.02| 826           | 2.06×10⁻²⁷   | 0.103 | 26.02      | 28.86      |
| 440        | 1.79| 732           | 2.26×10⁻²⁵   | 0.127 | 27.60      | 80.14      |
| 480        | 1.60| 655           | 1.49×10⁻²³   | 0.152 | 29.05      | 223.46     |

The tapered samples were loaded and strained during constant extension rate tensile (CERT) tests. This technique uses uniaxial tensile testing performed with a very slow constant elongation rate. The displacement rates used were 2×10⁻⁶ m·s⁻¹ (S1) and 2×10⁻⁸ m·s⁻¹ (S2). The lower strain rate was chosen in order to minimize the effect of the mechanical loading on the EAC behaviour. The tests were interrupted when the maximum stress was reached in order to avoid the full rupture of the sample. In this way, deformation regions are not too distorted and they can be retained. Prior to the start of the test, the sample was exposed to the environmental conditions for 120 hours without any relevant force load (the sample was only loaded with ~100 N).

5 Results and Discussion
The CERT tests were performed with the displacement rate S1 (2×10⁻⁶ ms⁻¹) at 400, 440 and 480 °C under the RO₂ = 1/6 H₂-steam environment. No significant variations were observed when the results were compared to the 350 °C load-displacement curve which was published in [14]. However, CERT tests performed with the slower displacement rate S2 (2×10⁻⁸ ms⁻¹) at 350, 400, 440 and 480 °C showed a more substantial trend. Load-displacement curves are shown in Figure 1. It can be seen from the figure that for temperatures above 400 °C there is a change in behaviour: at higher temperatures, less stress is required to reach the same elongation. This effect is also visible if the maximum values are compared (see Table 2). The curve for 350 °C has a completely different trend. This may be associated with the occurrence of environmentally assisted cracks for higher temperatures. These results are consistent with the other already published results [2,3,14,15], where it was determined that temperature 350 °C did not lead to the initiation of EAC in steam.
**Figure 1.** Measured CERT load-displacement curves for 316L tapered samples exposed to the $R_{O_2}=1/6$ $H_2$-steam environment with the displacement rate a) $S_1$: $2\times10^6$ ms$^{-1}$ and b) $S_2$: $2\times10^8$ ms$^{-1}$.

The boundary between the zone with EAC and the zone without EAC was determined on each side of the specimen using scanning electron microscopy (SEM) LYRA3 GMU (TESCAN company). These results are shown in [15]. EAC was visible near the narrow end of the gauge section. Moving the field of view towards the wide end of the gauge section their density declined. The results of the maximum stresses achieved, including the measured threshold values for the formation of corrosion cracks, are shown in Table 2. The results at 350 °C are not shown in the table because the test did not reach the same elongation as Figure 1 shows. In terms of temperature dependence, it can be stated that a clear trend between threshold values for the ground and polished surfaces was not found. At temperatures above 440 °C EAC cracks were observed on the polished surface further from the smallest cross-section, suggesting that a lower stress level was needed to initiate their formation. At 400 °C the cracks were probably more initiated on the rougher ground surface than on the polished surface. Such phenomena can show that for temperatures above 440 °C the final morphology essentially cannot play a crucial role for a given environment. This finding has to be further reviewed for confirmation.

**Table 2.** Maximum achieved stress with measured threshold values for the formation of corrosion cracks for CERT tests with displacement rate $S_2$: $2\times10^8$ ms$^{-1}$.

| Temperature [°C] | Maximum stress [MPa] | Ground surface threshold stress [MPa] | Polished surface threshold stress [MPa] |
|-----------------|----------------------|-------------------------------------|---------------------------------------|
| 400             | 496                  | 386                                 | 412                                   |
| 440             | 489                  | 406                                 | 383                                   |
| 480             | 444                  | 397                                 | 367                                   |

An interesting change occurred when comparing displacement rates for each temperature separately. As Figure 2 shows, the same conclusions as for temperature 350 °C apply to temperature 440 °C (Figure 2a), namely that a lower displacement rate leads to higher strength values. However, the beginning to the $1/4$ deformation range does not correspond to this. A completely different situation occurred for the temperature 480 °C (Figure 2b). On the other hand, a higher displacement rate also leads to higher strength characteristics at this temperature. This indicates that another deformation mechanism may occur with rate changes.
Figure 2. Influence of displacement rate on measured CERT load-displacement curves for samples exposed to oxidizing environment with $R_{O2} = 1/6$ for temperatures a) 440 °C and b) 480 °C.

This is also related to the achieved maximum stress values, which are listed in Table 3. A lower maximum stress was reached at 440 °C for a higher displacement rate ($S_1$: 537 MPa, $S_2$: 549 MPa), similar to that obtained at 350 °C published in [14]. On the other hand, at a temperature of 480 °C, a significantly higher maximum stress ($S_1$: 567 MPa, $S_2$: 490 MPa) was achieved for a higher displacement rate. In this case it can be stated that the lower strain rate allows the EAC crack to develop because the mechanical effect is less evident at this strain rate. Regarding the stress thresholds for corrosion cracking, similar findings were obtained as for the lower displacement rate $S_2$ and the results are shown in Table 3. A marked difference of almost ~100 MPa was observed at 480 °C.

Table 3. Maximum achieved stress with measured threshold values for the formation of corrosion cracks for CERT tests with displacement rate $S_1$: $2 \times 10^{-6}$ ms$^{-1}$.

| Temperature [°C] | Maximum stress [MPa] | Ground surface threshold stress [MPa] | Polished surface threshold stress [MPa] |
|------------------|----------------------|--------------------------------------|---------------------------------------|
| 400              | 443                  | 342                                  | 358                                   |
| 440              | 462                  | 435                                  | 430                                   |
| 480              | 480                  | 450                                  | 351                                   |

6 Summary

The area of interest was environmentally assisted cracking (EAC) in a low pressure superheated hydrogen steam environment 6 times more oxidizing than the Ni/NiO phase transition. It is an approach for accelerating the testing of PWR primary circuit operation conditions. The AISI 316L steel specimen at 350 °C did not lead to the initiation of environmentally assisted cracks, but the occurrence of environmentally assisted cracks was confirmed for temperatures higher than 400 °C. The results obtained from the faster displacement rate $2 \times 10^{-6}$ ms$^{-1}$ ($S_1$) and for 440 °C and 480 °C showed no significant changes in comparison to the 350 °C load-displacement curve. However the temperatures above 400 °C with slower displacement rate $2 \times 10^{-8}$ ms$^{-1}$ ($S_2$) showed a change. The curve for 350 °C has a completely different trend. This was related to the occurrence of corrosion cracks and with reduction in mechanical properties. The more the temperature increases above 400 °C, the less stress is required for the same elongation. At higher temperatures, above 440 °C, EAC cracks were observed on the polished surface further from the smallest cross-section, suggesting that a lower stress level was needed to initiate their formation. It indicates that for temperatures above 440 °C the final morphology essentially cannot play a crucial role for the given environment. This hypothesis was supported by the results for both displacement rates. The lower strain rate allows EAC cracks to develop because the mechanical effect is less evident at this strain rate.
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