COBEM 2021 26th International Congress of Mechanical Engineering

ABCM Associação Brasileira de Engenharia e Ciências Mecânicas
November 22-26, 2021, Virtual Congress, Brazil

COB-2021-1680
ON THE EFFECT OF PRE-STRAIN ON HYDROGEN EMBRITTLEMENT SUSCEPTIBILITY OF STRUCTURAL STEEL

Cláudio Augusto Gomes Filho
Pontifical Catholic University of Minas Gerais, Department of Mechanical Engineering, Av. Dom José Gaspar 500, Belo Horizonte (MG) 30535-901, Brazil.
cagf94@gmail.com

Erberte Marcio Costa
Pontifical Catholic University of Minas Gerais, Department of Mechanical Engineering, R. Rio Comprido, 4580, Contagem (MG) 32010-025, Brazil.
erberte@pucminas.br

Pedro Brito
Pontifical Catholic University of Minas Gerais, Department of Mechanical Engineering, Av. Dom José Gaspar 500, Belo Horizonte (MG) 30535-901, Brazil.
pbrito@pucminas.br

Abstract. *In numerous offshore or coastal applications, structural steels are subject to environmental degradation. In particular, condensation near crevices which appear in bolted or riveted joints may become acidified intensifying corrosion rates and causing embrittlement because of hydrogen absorption. In the present work, a systematic investigation of the hydrogen embrittlement of AISI 1020 steels submitted to different levels of preliminary plastic strain was performed. Tensile test samples were prepared from hot-rolled bars, which were annealed and subject to different levels of plastic strain in uni-axial tension (0.0, 6.0 and 12.0% after yielding). Hydrogen permeation was accomplished by cathodic charging in neutral 0.6M NaCl and acid 0.5M* H_2SO_4 *solutions for 24 hours with a 30mA/cm*^{2} *current. The results obtained revealed that the structural steels, under the tested conditions, were less susceptible to embrittlement when exposed to the neutral solution but suffered significant losses in ductility in the presence of acid.*

Keywords: *hydrogen embrittlement, mechanical properties, structural steel, cathodic charging.*

1. INTRODUCTION

Building materials used in port infrastructure (*e.g.* bridges, marine structures, pipelines and sea vessels) are constantly subjected to environmental degradation, which compromises structural integrity and safety leading to elevated maintenance costs (Blekkenhorst *et al*., 1986, Guedes Soares *et al*., 2011). Apart from corrosion (or in association with corrosion processes), structural materials employed in coastal or offshore applications may experience impairments in mechanical properties caused by the exposure to hydrogen (Louthan, 2008).

Hydrogen damage in metallic materials is commonly explained by two mechanisms identified as Hydrogen Enhanced Local Plasticity (HELP) and Hydrogen Induced Decohesion (HEDE). In HELP, it is proposed that hydrogen increases dislocation activity allowing void formation and assisting crack propagation: overall, the material experiences losses in strength while a macroscopic ductile fracture behavior is observed. In HEDE, the accumulation of hydrogen atoms is considered to reduce cohesive energy of the metallic matrix facilitating crystal cleavage (Beachem, 1972, Birnbaum and Sofronis, 1994).

Because of the importance of hydrogen absorption on the mechanical properties of metallic materials, numerous studies have been published regarding hydrogen embrittlement mechanisms of different alloys, such as stainless steels (Martin *et al*., 2012, Wang *et al*., 2014), high strength steels (Nanninga *et al*., 2010, Pérez Escobar *et al*., 2012, Brandolt *et al*., 2016) and Al-alloys (Ribeiro *et al*., 2019). Considerably less information is available, however, for low carbon steels in general as mentioned in a recent investigation (Wasim and Djukic, 2020).

In the present work, the susceptibility to hydrogen embrittlement of mild steel as a function of preliminary strain is investigated. The imposition of strain prior to hydrogen exposure increases crystal defect density, which is expected to potentialize hydrogen damage in the material (Koyama *et al*., 2017). In practical terms, structural steels are employed in numerous conditions which may frequently involve a certain level of pre-existing plastic strain, such as in cold-drawn bars or tubes, rolled sheets, as well as local strains caused by machining or welding operations. Therefore, it is important to understand the influence of previous mechanical loads associated with the presence of hydrogen for the safe commissioning of engineering materials in hydrogen-containing environments, particularly considering the widespread use of low carbon steel as structural elements.

2. EXPERIMENTAL PROCEDURE

The material used in the present work were AISI 1020 low carbon steel circular bars, initially received in the hot-rolled condition. From the initial bars, tensile test specimens were prepared with a 67.0 mm gauge length and 9.0 mm cross-section diameter. Prior to mechanical testing, the specimens were submitted to isothermal annealing at 900°C for 40 minutes to allow microstructure homogenization. This was considered important since the initial rolling parameters employed for producing the AISI 1020 bars were unknown and because different previous manufacturing techniques (rolling, drawing, extrusion, etc) induce different microstructure modifications and strain states, which may affect the hydrogen susceptibility behavior.

The effect of pre-strain on the hydrogen susceptibility was assessed by submitting the specimens to uni-axial tension in an EMIC 10000 universal tensile testing machine until 6.0 and 12.0% levels of plastic strain (post-yielding) were observed, after which the samples were unloaded. The engineering strain values were calculated from the sample displacement and the engineering stress values by the applied force which was measured using a load cell. The procedure is illustrated graphically in Figure 1, which depicts a force-displacement diagram obtained from an annealed 1020 steel specimen with indications of the displacements imposed to produce the desired levels of pre-strain. The samples were loaded, and the displacement was registered until elongations of 4- and 8-mm post-yielding were reached, which corresponded to strain levels of 6.0 and 12.0%, respectively, considering the gauge length of 67 mm.

After pre-straining, the sample microstructure was characterized by optical microscopy and microhardness measurements were performed along the samples' cross sections using a HMV-1 Shimadzu microhardness tester with a 0.025 gf load and 20 s load time. The final gauge length dimensions (diameter × length) of the pre-strained specimens, after removal of the residual oxide scale developed previously during the annealing treatment were ⌀8.88±0.04×67.05±0.07 mm, ⌀8.59±0.04×69.95±0.21 mm and ⌀8.32±0.02×73.88±0.37 mm, for the 0.0, 6.0 and 12.0% levels of pre-strain, respectively. The pre-strained tensile test specimens (0.0, 6.0 and 12.0%) were subsequently separated into two groups: the first was submitted to tensile testing directly after unloading while the second was submitted to tensile testing after exposure to hydrogen by cathodic charging. The procedures were performed by polarizing the tensile test specimens in 0.6M NaCl and 0.5M H_2SO_4 (containing 0.25mg/l $NaAsO_2$) solutions at 30mA/cm^2 for 24 hours, as in a previous investigation (Queiroga *et al.*, 2019). All tensile tests were performed at a strain rate of 0.003 s^{-1}.

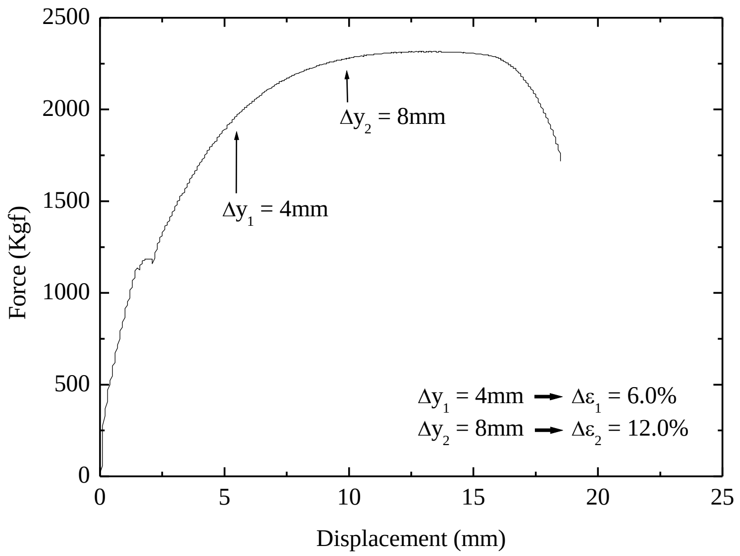

Figure 1. Force-displacement diagram obtained from annealed AISI 1020 specimens, with indications of the preliminary displacements (Δy) imposed to obtain the desired pre-strain (Δε) levels of 6.0 and 12.0%.

3. RESULTS AND DISCUSSION

3.1 Properties of pre-strained specimens

The results of hardness measurements performed along the cross-section of pre-strained specimens is presented in Figure 2, while the corresponding microstructures are shown in Figure 3(a-f). As expected, plastic deformation led to hardening of the materials, with average hardness values of 150±5, 176±8 and 205±6 HV0.025 for pre-strain values of

0.0, 6.0 and 12.0%, respectively. As shown in Figure 2, the hardness increase was also homogenous along the sample cross section, with no significant differences observed (in a given specimen) over the cross-section. This result could also be expected since the uni-axial tensile loads imposed to the materials did not produce necking and therefore introduced uniform plastic strain.

Concerning the microstructure of the tested materials, it was not possible to notice significant changes among the different samples. The microstructure of the annealed samples presented in Figures 3(a, d) is composed of pro-eutectoid ferrite and pearlite colonies, which is typical for low carbon steels. It is possible to notice that the microstructure is homogenous, with no signs of the banded structures of pearlite and elongated ferrite grains which are characteristic of the hot-rolled condition observed in the materials prior to annealing. The imposition of 6.0 and 12.0% levels of plastic strain led to hardening and presumably an increase in defect density but did not produce noticeable changes in microstructure, as shown in Figures 3(b, c, e, f).

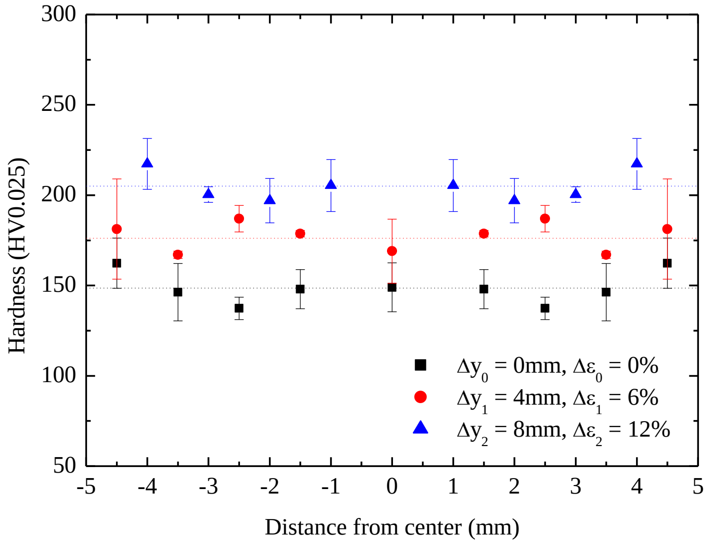

Figure 2. Hardness distributions along the cross-section of samples with pre-strain (Δε) levels of 0.0, 6.0 and 12.0%.

3.2 Influence of hydrogen on tensile properties

After initial characterization of the annealed and pre-strained AISI 1020 steel samples, the materials were submitted to cathodic charging and tensile tests. The introduction of hydrogen was performed by cathodic polarization in both acid (0.5M H_2SO_4 with 0.25mg/l $AsNaO_2$) and neutral (0.6M NaCl) solutions. In aqueous solutions, the available hydrogen ions react at the negatively charged (cathodic) metal surface to form hydrogen gas:

$$2H^+ + 2e^- \rightarrow H_2, \quad (1)$$

The reaction (1) normally occurs in two steps, being hydrogen adsorption (2) followed by the recombination of adsorbed hydrogen atoms (3):

$$H^+ + e^- \rightarrow H_{\mathrm{ads}}, \quad (2)$$

$$H_{\mathrm{ads}} + H_{\mathrm{ads}} \rightarrow H_2, \quad (3)$$

In this process, the adsorbed hydrogen atoms (H_{ads}) are introduced into the metal lattice. Therefore, after cathodic polarization, the AISI 1020 samples are expected to exhibit an increased hydrogen concentration. It is worth noticing that the presence of hydrogen ions in real applications can be observed even in solutions which are not nominally acid around crevices or in cracks developed on the materials surface.

The results of tensile tests performed on the annealed and pre-strained 1020 steel specimens are presented in Figure 4(a-c) for pre-strain levels of 0.0, 6.0 and 12.0%, respectively. The hydrogen charging conditions are indicated in each case. It is worth observing that in all tested conditions, fracture was preceded by some amount of plastic deformation, which led to a ductile fracture surface.

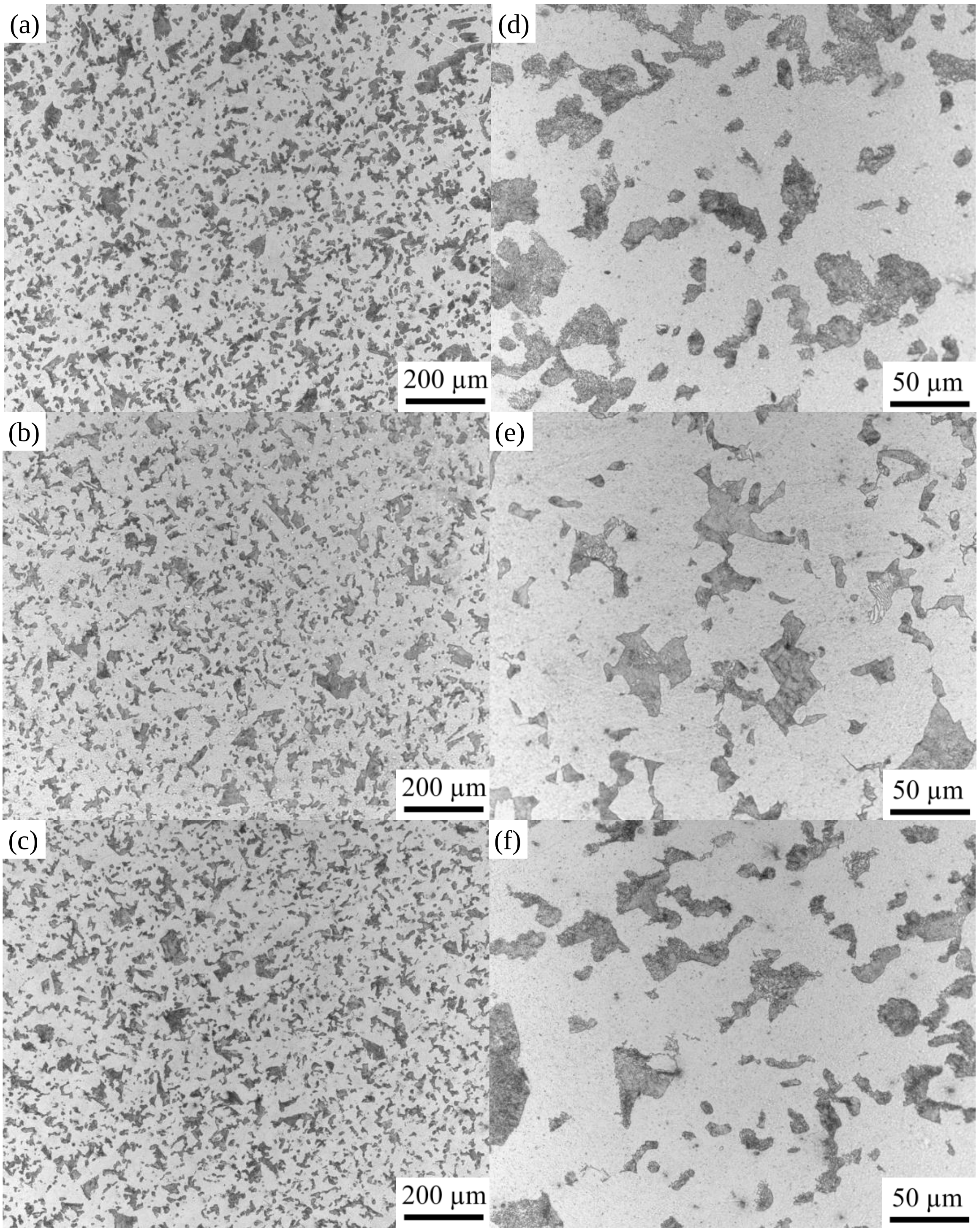

Figure 3. Microstructure of samples submitted to 0% pre-strain (a, d), 6.0% pre-strain (d, e) and 12.0% pre-strain (c, f). Nital 2% etch.

It was possible to notice that even in the annealed condition, the presence of hydrogen led to a decrease in the materials ductility. In case of Figure 4(b), which concerns the material pre-strained at 6.0%, the reduction in ductility was significantly larger for the sample charged in the 0.5M H_2SO_4 relative to the sample exposed to 0.6M NaCl. This can probably be explained by the larger availability of hydrogen ions in the acid solution. The ductility loss was not, however, followed by a reduction in mechanical strength since yield strength and tensile strength for the samples remained essentially unaltered by the presence of hydrogen.

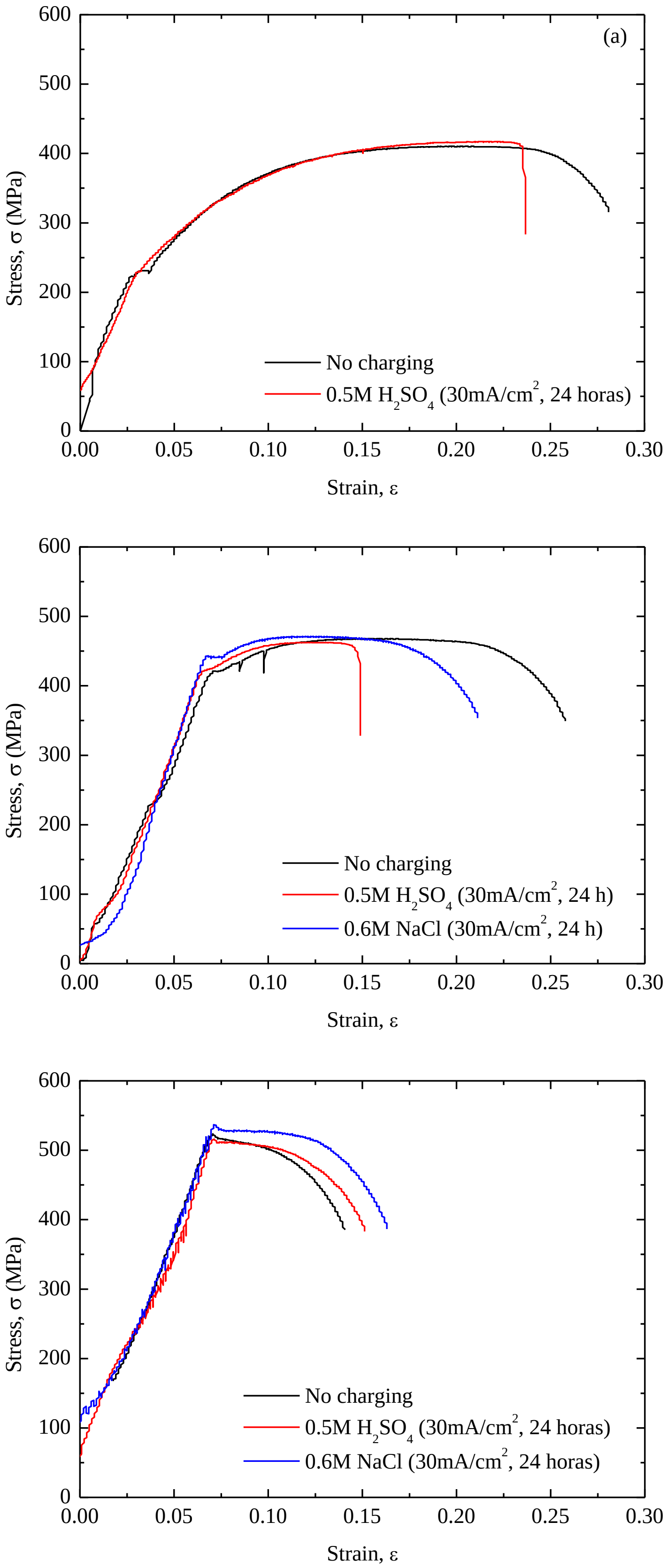

Figure 4. Stress-strain diagrams obtained with and without hydrogen charging for AISI 1020 steels submitted to (a) 0.0, (b) 0.06 and (c) 0.12 pre-strain.

The results obtained agree with previous reports, which have shown that plastic deformation increases hydrogen embrittlement susceptibility. According to Toribio and co-workers (Toribio *et al.*, 2011), plastic strain increases hydrogen solubility and consequently hydrogen absorption. Li and co-workers (Li *et al.*, 2014) investigated the influence of pre-strain on hydrogen susceptibility of high strength steels and also noticed an increase in embrittlement levels up to pre-strain values of 7%. Concerning pre-strained AISI 304 stainless steels (Wang *et al.*, 2014), ductility losses have been observed continually with pre-strain levels. In the case of the AISI 304 steels, however, the loss of ductility for higher pre-strain levels (>10%) because of the formation of strain-induced martensite.

The results presented in Figure 4(c) did not, however, confirm the existence of a continuous trend of increased hydrogen susceptibility with pre-strain, since all 12.0% pre-strain samples exhibited similar tensile behavior. In the present work, the results presented in Figure 4(c) indicate marginally superior ductility in samples tested after hydrogen charging in H_2SO_4 and NaCl, although the difference falls within the tests standard deviation. It is worth noticing that in the case of the 12.0% plastically pre-strained specimens, the yield point already corresponds to the maximum stress level observed during tensile testing, with relatively little subsequent plastic deformation. This can be evidenced by the fact that no further increases in strength are observed upon yielding (yield strength and tensile strength are effectively the same after 12.0% pre-strain). As such, a relatively smaller increase in dislocation density is expected in the already strain-hardened material. Similar results have been observed for AISI 310 austenitic stainless steels, for which hydrogen embrittlement was found to increase initially but ceased with pre-strain levels of 30% (Ji *et al.*, 2014). The behavior of AISI 310 steels differs from the behavior registered for AISI 304 steels (Wang *et al.*, 2014) due to the absence of martensite formation in the former steel (the AISI 310 steel exhibits larger Ni quantities that stabilize austenite). Since hydrogen damage depends on the interaction between dislocations and the hydrogen atoms, which is a dynamic process, it might be necessary to reduce the strain rate in the tensile tests performed on the samples with higher levels of pre-strain. Nevertheless, further investigations would be required to elucidate the observed behavior, *i.e.* that a significant decrease in ductility caused by hydrogen permeation was observed for 6.0% pre-strain but not for 12.0% pre-strain.

The tensile test results are further analyzed in Figure 5, which summarizes the trends observed between yield strength and tensile strength with pre-strain (with and without hydrogen charging) and in Figure 6, which reports variations in ductility as a function of pre-strain (also with and without hydrogen charging). It is clear that the hydrogen charging process did not in fact negatively impact yield and tensile strength, as shown in Figure 5 (the results concerning charging performed in 0.6M NaCl were omitted for clarity). It also becomes evident, by analyzing the results presented in Figure 6, that ductility of all tested samples remains unaltered by the charging process for higher (12.0%) levels of pre-strain, as observed previously.

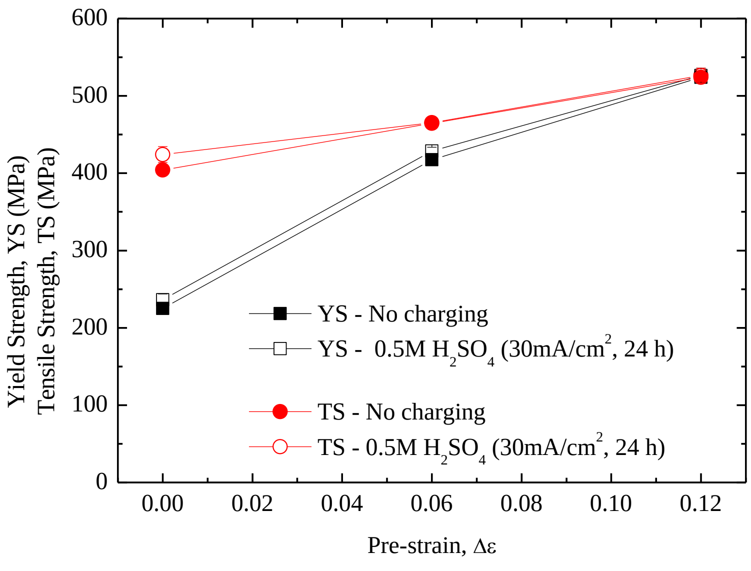

Figure 5. Variation of Yield Strength (YS) and Tensile Strength (TS) with respect to pre-strain (Δε) for samples with and without hydrogen charging.

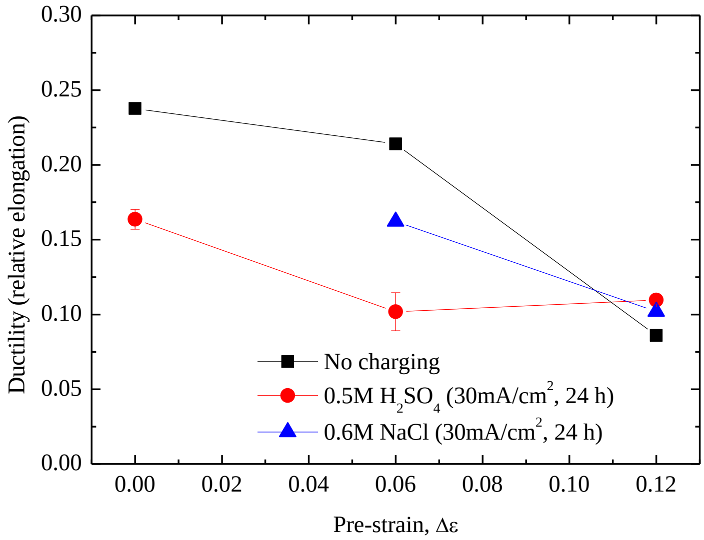

Figure 6. Variation of ductility (determined from the relative elongation) with respect to pre-strain (Δε) for samples with and without hydrogen charging.

4. CONCLUSIONS

In the present investigation, the susceptibility to hydrogen embrittlement of a AISI 1020 structural steel in the annealed and pre-strained conditions submitted to cathodic polarization in 0.5M H_2SO_4 containing 0.25mg/l $NaAsO_2$ and 0.6M NaCl solutions was analyzed. The following conclusions could be drawn:

1. The acid medium (0.5M H_2SO_4 containing 0.25mg/l $NaAsO_2$) led to more severe embrittlement for the same current density in comparison to the 0.6M NaCl solution.
2. The hydrogen charging processes performed on all tested materials did not alter mechanical strength (yield and tensile strength), but a loss of ductility was observed on most test conditions.
3. For higher levels of plastic pre-strain (12.0% post yielding), no significant decreases in ductility were observed, regardless of charging conditions.

5. ACKNOWLEDGEMENTS

Author C. A. Gomes Filho is grateful to the scholarship received by Companhia Vale do Rio Doce (project “Cátedra Equipamentos Portuários”). P. Brito is a CNPq fellow (“Produtividade em Pesquisa” grant number 315533/2020).

6. REFERENCES

Beachem, C. D., 1972. “A New Model for Hydrogen-Assisted Cracking (Hydrogen "Embrittlement")”. *Metallurgical Transactions*, Vol. 3, pp. 437–451.

Birnbaum, H. K., and Sofronis, P., 1994. “Hydrogen-enhanced localized plasticity—a mechanism for hydrogen-related fracture”. *Materials Science and Engineering: A*, Vol. 176, No. 1-2, pp. 191–202.

Blekkenhorst, F., Ferrari, G. M., Van Der Wekken, C. J., and Ijsseling., 1986. “Development of high strength low alloy steels for marine applications: Part 1: Results of long term exposure tests on commercially available and experimental steels”. *British Corrosion Journal*, Vol. 21, No. 3, pp. 163–176.

Brandolt, C. S., Gonçalves, F. V., Savaris, I. D., Schroeder, R. M., and Malfatti, C. F., 2016. “The influence of the tempering temperature on hydrogen embrittlement in carbonitrided modified SAE 10B22 steel”. *Materials and Corrosion*, Vol. 67, No. 5, pp. 449–462.

Guedes Soares, C., Garbatov, Y., and Zayed, A., 2011. “Effect of environmental factors on steel plate corrosion under marine immersion conditions”. *Corrosion Engineering, Science and Technology*, Vol. 46, No. 4, pp. 524–541.

Ji, H., Park, I-J., Lee, S. -M., Lee, Y. -K., 2014. “The effect of pre-strain on hydrogen embrittlement in 310S stainless steel”, *Journal of Alloys and Compounds*, Vol. 598, pp. 205-212.

Koyama, M., Rohwerder, M., Tasan, C. C., Bashir, A., Akiyama, E., Takai, K., Raabe, D., and Tsuzaki, K., 2017. “Recent progress in microstructural hydrogen mapping in steels: quantification, kinetic analysis, and multi-scale characterisation”. *Materials Science and Technology*, Vol. 33, No. 13, pp. 1481–1496.

Li, X., Wang, Y., Zhang, P., Li, B., Song, X., Chen, J., 2014. “Effect of pre-strain on hydrogen embrittlement of high strength steels”, *Materials Science and Engineering A*, Vol. 616, pp. 116-122.

Louthan, M. R., 2008. “Hydrogen Embrittlement of Metals: A Primer for the Failure Analyst”. *Journal of Failure Analysis and Prevention*, Vol. 8, No. 3, pp. 289–307.

Martin, M., Weber, S., Izawa, C., Wagner, S., Pundt, A., and Theisen, W., 2012. “Influence of machining-induced martensite on hydrogen-assisted fracture of AISI type 304 austenitic stainless steel”. *International Journal of Hydrogen Energy*, Vol. 36, No. 17, pp. 11195–11206.

Nanninga, N., Grochowsi, J., Heldt, L., and Rundman, K., 2010. “Role of microstructure, composition and hardness in resisting hydrogen embrittlement of fastener grade steels”. *Corrosion Science*, Vol. 52, No. 4, pp. 1237–1246.

Pérez Escobar, D., Verbeken, K., Duprez, L., and Verhaege, M., 2012. “Evaluation of hydrogen trapping in high strength steels by thermal desorption spectroscopy”. *Materials Science and Engineering A*, Vol. 551, pp. 50–58.

Queiroga, L. R., Marcolino, G. F., Santos, M., Rodrigues, G., Santos, C. E., and Brito, P., 2019. “Influence of machining parameters on surface roughness and susceptibility to hydrogen embrittlement of austenitic stainless steels”. *International Journal of Hydrogen Energy*, Vol. 44, No. 54, pp. 29027–29033.

Ribeiro, E. M. P., Machado, G. H. L., Araújo, M. P. C., Rocha, R. V. R., and Brito, P. P., 2019. “Influence of surface roughness on the hydrogen embrittlement behavior of AA6351 aluminum alloy”. In *Proceedings of the 25th ABCM International Congress of Mechanical Engineering - COBEM 2019*. Uberlândia, Brazil.

Toribio, J., Kharin, V., Lorenzo, M., Vergara, D., 2011. “Role of drawing-induced residual stresses and strains in the hydrogen embrittlement susceptibility of prestressing steels”, *Corrosion Science*, Vol. 53, No. 11, pp. 3346-3355.

Wang, Y., Wang, X., Gong, J., Shen, L., and Dong, W., 2020. “Hydrogen embrittlement of catholically hydrogen-precharged 304L austenitic stainless steel: Effect of plastic pre-strain”. *International Journal of Hydrogen Energy*, Vol. 39, No. 25, pp. 13909–13918.

Wasim, M., and Djukic, M. B., 2020. “Hydrogen embrittlement of low carbon structural steel at macro-, micro- and nano-levels”. *International Journal of Hydrogen Energy*, Vol. 45, No. 3, pp. 2145–2156.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.