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HYDROGEN EMBRITTLEMENT IN AISI 4340 STEEL (AMS 6415S) QUENCHED AND TEMPERED

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Abstract. *The phenomenon of hydrogen embrittlement in AISI 4340 steel was investigated due to the fact that it is a high strength low alloy steel quite susceptible to this phenomenon. The analysis was done through the fracture toughness test by bending based on ASTM E 399-09. Specimens were machined with crack plane L-C, quenched at 845 °C and tempered at three different temperatures (350 °C, 400 °C and 500 °C). The hydrogen loading was made by means of an electrochemical cell where the specimens were immersed in a solution of 0.01 M sulfuric acid by applying a current density of 10 mA/cm² and three different hydrogenation times, in order to obtain three levels of contamination. After the tests were performed fractographies of the specimen fracture surfaces for each condition of temper and contamination by hydrogen, with observed changes in the micromechanisms of fracture for the different conditions. The test results of fracture toughness by bending were correlated with the micromechanisms of fracture, the microstructure and hydrogen contamination. Under conditions of tempering of 400 °C and 350 °C, AISI 4340 steel proved to be very susceptible to hydrogen embrittlement, with reductions of 10% and 20%, respectively, on the values of fracture toughness of contaminated specimens. The same was not observed in AISI 4340 quenched and tempered at 500 °C, which did not presented embrittlement.*

Keywords: *Hydrogen Embrittlement, Fracture Toughness, AISI 4340 Steel*

1. INTRODUCTION

AISI 4340 steel quenched and tempered has excellent combined properties of strength, fatigue resistance and especially fracture toughness (Silva and Mei, 1988), which is used in aerospace, automotive, marine and petrochemical industry, in components subjected to dynamic loads, such as shafts, gears, landing gears, clamping pins and safety parts.

A serious problem afflicting AISI 4340 steel is hydrogen embrittlement. It causes significant reduction on fracture toughness of the material, so it becomes more brittle, causing a reduction in ductility, enabling the initiation and propagation of cracks, causing blisters on the surface, internal voids and changes in the yield strength (Dini, 1993).

Corrosive environments such as marine and industrial environments, industrial processes such as electrodeposition, acid pickling and cathodic electrolytic degreasing are sources of contamination by hydrogen (Jansen and Tomachuk, 2008a; Jansen and Tomachuk, 2008b). In cathodic protection process of steel in harsh environments there is also generation of hydrogen, and although the cathodic protection of steel, it also exposes it to hydrogen embrittlement (Wang, 2009). During pig iron production process, in blast furnaces occurs contamination by hydrogen, because when hot air is insufflated in one of the process stages, if there is moisture in the air, the following reaction will occur (Silva and Mei, 1988):

$$C + H_2O \leftrightarrow CO + H_2 \quad (1)$$

Thus, the generated hydrogen is easily absorbed by the liquid iron and may lead to embrittlement.

The metallic hydrogen adsorbed on the surface of a metal can follow two paths: if it combines with another hydrogen adsorbed, they form molecular hydrogen and released as a gas; or it can diffuse inside the metal, causing the problem of embrittlement due to its distortion of the crystal lattice or its accumulation in traps.

Besides the diffusion, there is a theory that hydrogen transport may also occur through the dislocations present in the crystal lattice, which function as paths for the passage and retention of hydrogen. The hydrogen transport by these dislocations may be many orders of magnitude greater than associated to diffusion (Hertzberg, 1996).

The metallic hydrogen present in the crystalline structure of the metal, when combined with other increases in volume. This volume increase inside the material may cause embrittlement, because it creates a distortion in the crystal lattice, increasing stresses and reducing the strength of the bonds between the metal atoms.

This type of embrittlement, called *internal hydrogen embrittlement*, can be explained by the following equation:

$$c_H = 135\sqrt{p_{H_2}}\, e^{(-6500/RT)} \quad (2)$$

where c_H: hydrogen concentration (ppm), p_{H_2}: hydrogen pressure (MPa), R: universal gas constant and T: temperature.

According to this equation, each dissolved ppm of hydrogen results in a pressure of 2 x 10^5 MPa. This is sufficient to cause damage in the crystal lattice. The embrittlement occurs because the hydrogen excess dissolved and dispersed in inclusions, pores or microcracks, generates high pressure, resulting in cracks (Woodtli and Kieselbach, 1999).

The martensitic structure of AISI 4340 steel quenched and tempered is characteristic by having great hardness due to distortion, which the carbon atoms cause in the crystal lattice of the steel. This distortion, combined with the high hydrogen diffusion capacity, increases the residual stresses in it, further increasing the hardness and consequently causing embrittlement that can lead to brittle fractures (Liu, et al., 2008). Importantly, the susceptibility of steel AISI 4340 quenched and tempered to hydrogen embrittlement is observed when it has hardness above about 40 HRC (ASM Handbook, Vol. 11, 2002).

Two important models that try to explain the micromechanisms causing embrittlement of metals are the "Hydrogen enhanced local plasticity" (HELP) and the "Hydrogen-induced decohesion" (HEDE). In HELP model, the atomic hydrogen diffused in the steel crystalline lattice increases the mobility of dislocations present in it, causing a reduction in shear strength of the same. This decrease in the shear strength enables the formation of microvoids (dimples) that connect along preferential slip planes resulting in highly localized fracture. HEDE model affirm that the atomic bonds at the tip of a crack are weakened by the expansion of the crystal lattice caused by the presence of hydrogen. Thus, the energy required to cause the fracture is reduced, resulting in brittle fracture in macroscopic aspect (Wang, 2009).

Besides these, there are models that affirm that grain boundaries, dislocations, carbides and non-metallic particles can act as hydrogen traps. Since these defects are usually located near the grain boundaries, there is a tendency for accumulation of hydrogen in these regions, making the connections between the grains boundaries weakened, leading to intergranular fractures (Lee, et al., 2004; Liu, et al., 2008; Nanninga, et al., 2009).

Grain boundaries act as preferential sites for hydrogen, because this region has a thickness of two to five interatomic distances. The contours of the atoms have a coordination number smaller than the atoms inside the grains, then these atoms connections are incomplete. This discontinuity is associated with a high energy that can trap hydrogen (Padilha, 2000).

The objective or this paper is the analysis of the fracture toughness, by using bending specimens, and the micromechanisms of fracture of the AISI 4340 steel (AMS 6415S), in three different conditions, quenched at 845 °C and tempered at three different temperatures (350 °C, 400 °C and 500 °C), contaminated with hydrogen, by meaning of an electrochemical cell where the specimens were immersed in a solution of 0.01 M sulfuric acid by applying a current density of 10 mA/cm² and three different hydrogenation times, in order to obtain three levels of contamination.

2. MATERIALS AND METHODS

The material in this study was AISI 4340 steel ingots rolled up in a cylindrical cross-section diameter of 58 mm with a final rolling temperature between 800 and 850 °C, annealed at a temperature of 660 to 680 °C for 5 hours with air cooling and machined to a diameter of 50 mm. Its chemical composition, according to standard AMS 6415S, is shown in Tab. 1.

Table 1. Chemical composition of AISI 4340 steel as-received (AMS 6415S, 2007).

Element		wt%								
		C	Mn	Si	P	S	Cr	Ni	Mo	Cu
AMS 6415S Standard	Minimum	0.38	0.65	0.15	-	-	0.70	1.65	0.20	-
	Maximum	0.43	0.85	0.35	0.025	0.025	0.90	2.00	0.30	0.35
Measured		0.38	0.73	0.27	0.006	0.003	0.74	1.60	0.23	0.02

Specimens for fracture toughness testing were machined according to ASTM E1820 - 08a and ASTM E399 - 09 (Fig.1).

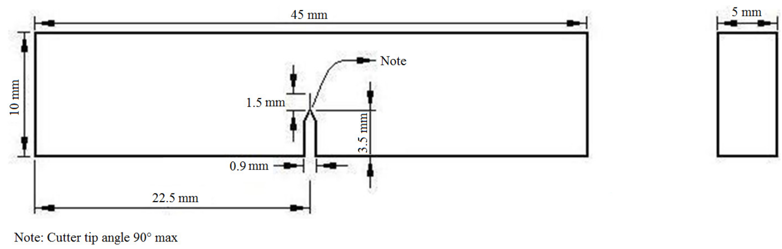


Figure 1. Specimen dimensions (ASTM E 1820 – 08a, 2009; ASTM E 399 – 09, 2009). The fatigue pre-carck size is about 1.5 mm.

The specimens were heat treated by annealing at 845 °C for 1 hour to obtain a full austenitization followed by quenching in oil at room temperature, resulting in a martensitic structure. Immediately after quenching, tempering treatments were performed at three different temperatures (350, 400 and 500 °C) by 1 hour for each block of specimens, with air cooling, obtaining tempered martensitic structure. The sequence of heat treatment is summarized in Fig. 2.

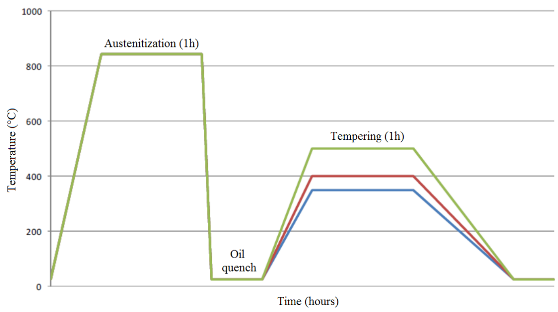


Figure 2. Sketch of heat treatments of the specimens

Hydrogen loading of 3, 6 and 9 hours were conducted in a beaker with H_2SO_4 solution with concentration of 0.01M, responsible for hydrogen generation, a titanium wire (to make contact) attached to the specimen, which is the working electrode, two lead plates, which are the counter electrode, and the reference electrode saturated calomel. All of this assembled on a magnetic stirrer to prevent that the bubbles formed during the reaction becoming trapped on the working electrode surface, inhibiting the adsorption of hydrogen on the specimen. The apparatus was connected to a potentiostat/galvanostat for applying a current density of 10 mA/cm^2 on the specimens and inducing reaction (Fig. 3).

For each tempering condition, microstructural characterization also has been made, using the following procedure:

a) Grinding on silicon carbide (SiC) grinding papers with particle size in the following order: 100, 220, 320, 400, 600, 800, 1200 mesh to removal of the risk of the previous stage;

b) Polishing with diamond pastes of 6 and 1 µm until complete removal of scratches left on the grinding step to obtain a mirror surface;

c) Washing the surface with alcohol in ultrasonic equipment for a finer cleaning;

d) Observation of the resulting surface (before etching) in an optical microscope for viewing the amount of inclusions present;

e) Etching with a 2% nital solution (2% nitric acid and 98% alcohol) with a mean time between 15 and 20 seconds to reveal the microstructure;

f) Observation of the microstructure in optical microscope and also in scanning electron microscope (SEM).

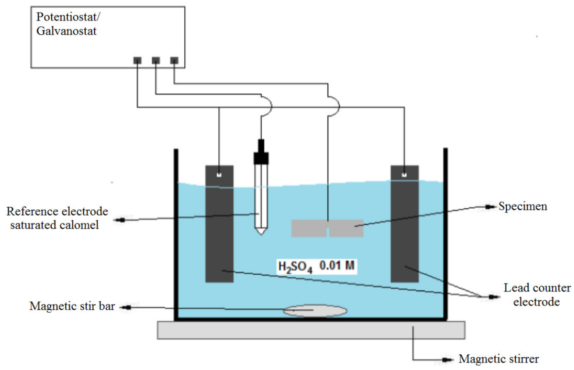


Figure 3. Assembly sketch for hydrogen charging

The number of specimens for each test condition is summarized in Tab. 2.

Table 2. Number of specimens for each test condition

Hydrogen loading in 0.01M sulfuric acid	Tempering		
	350 °C	400 °C	500 °C
Without hydrogen loading	3	3	3
3 hours hydrogen loading	3	3	-
6 hours hydrogen loading	3	3	3
9 hours hydrogen loading	3	3	3

Finally, for each condition, was determined the Rockwell C hardness of the material.

After the apparent fracture toughness (value of fracture toughness out of ASTM requirements) testing for each condition, the fracture surfaces obtained were observed in a scanning electron microscope for each condition in order to connect the fracture mechanism to the hydrogen loading time, the microstructure and the corresponding hardness of each heat treatment.

3. RESULTS AND DISCUSSION

The AISI 4340 steel microstructures in laminate state and tempering for each condition are shown in Fig. 4 to 7.

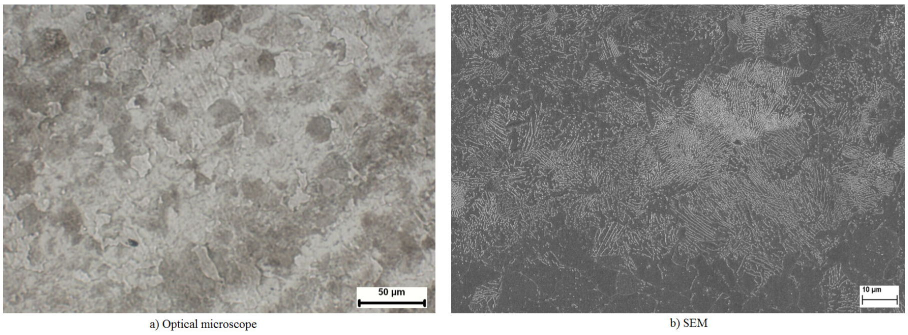


Figure 4. Microstructure of AISI 4340 steel in laminate state

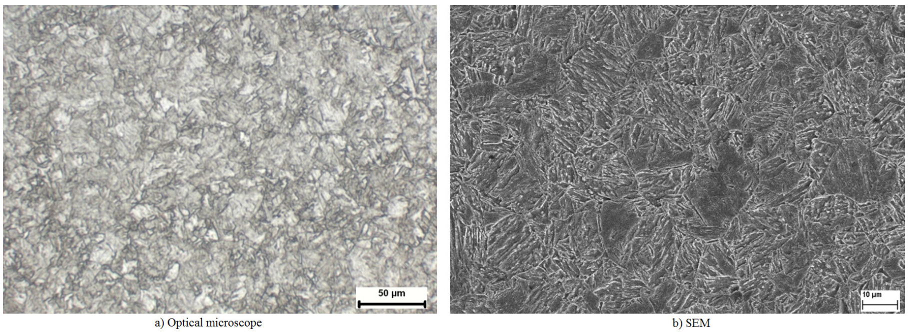


Figure 5. Microstructure of AISI 4340 quenched and tempered at 500 ^{o}C

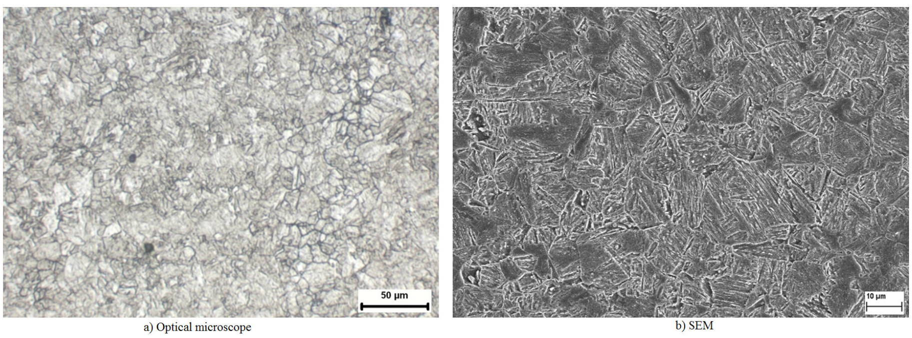


Figure 6. Microstructure of AISI 4340 quenched and tempered at 400 ^{o}C

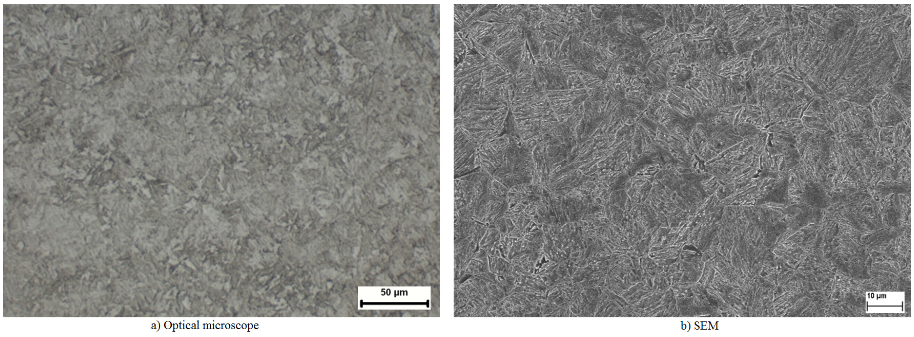


Figure 7. Microstructure of AISI 4340 quenched and tempered at 350 °C

From Fig. 4, on the image obtained by SEM (scanning electron microscope), it is possible to observe the ferritic-pearlitic structure in thee steel without heat treatment, wherein the lamellar phase shows the pearlite (cementite and ferrite) while the dark phase shows proeutectoid ferrite.

In Fig. 5, 6 and 7 is possible to observe a martensitic microstructure in which there is a refinement of the structure as the tempering temperature is lower, as expected.

The mechanical properties of the specimens were obtained from Rockwell C hardness measurements were related to literature for each tempering condition (ASM Handbook, Vol. 1, 1993). A summary is shown in Tab. 3.

Table 3. Results of mechanical properties and results from ASM Handbook.

	Rockwell C Hardness (HRC)	Standard deviation (HRC)	Rockwell C Hardness (ASM Handbook, Vol. 1) (HRC)	Yield strength (ASM Handbook, Vol. 1) (MPa)	Tensile strength (ASM Handbook, Vol. 1) (MPa)
As-received condition	19	0.56	-	-	-
Tempered at 500 °C	39	1.05	41	1112	1233
Tempered at 400 °C	45	1.61	47	1353	1475
Tempered at 350 °C	47	1.28	49	1457	1580

The results of the apparent fracture toughness tests conducted based on ASTM E 399-09 are presented in Fig. 8.

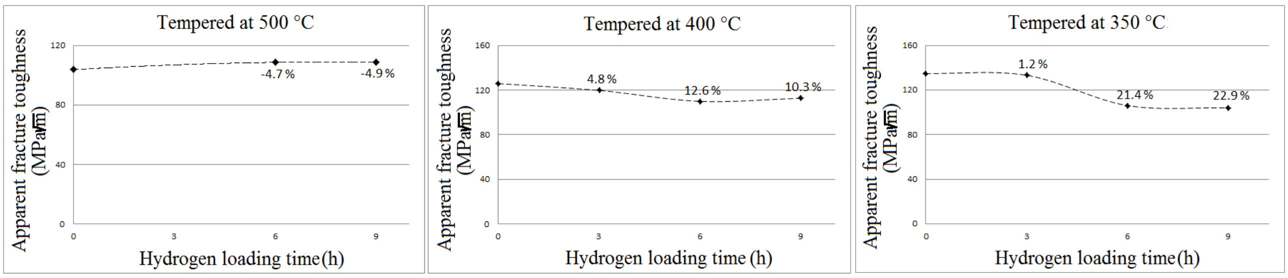


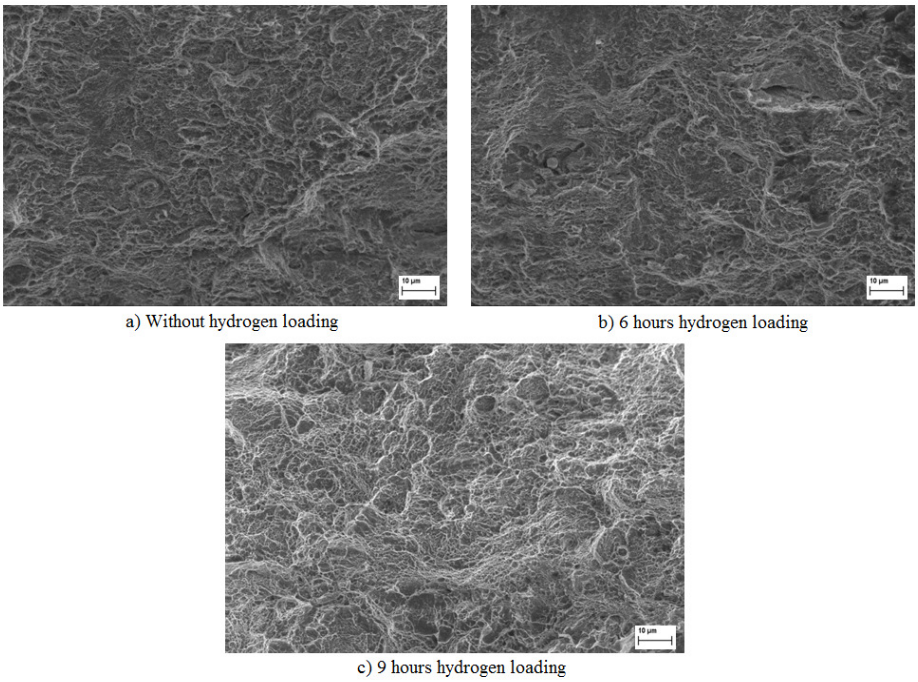
Figure 8. Apparent fracture toughness for tempering at 500, 400 and 350 °C respectively

By analysis of Fig. 8, it can be seen that there was no hydrogen embrittlement in steel tempered at 500 °C, even after 6 and 9 hours hydrogen loading. There wasn't any significant variation in values of the apparent fracture toughness. This result may be because of the low hardness produced by tempering at 500 °C, resulting in a higher fracture toughness, which leads the material not to be susceptible to this phenomenon at low hardness.

In the case of tempering at 400 °C, it is possible to observe a significant reduction in apparent fracture toughness, 12.6% for 6 hours and 10.3% for 9 hours, indicating that these hydrogenation periods were sufficient to embrittle the steel. These results are in agreement with the expected, because with an average hardness of 45 HRC, the metal already become brittle enough to be susceptible to the phenomenon. It is still possible to observe that the hydrogenation time of 6 hours was enough to saturate the crystalline structure of the steel by hydrogen, because even after the increase in charging time to 9 hours there was no significant change in apparent fracture toughness, keeping around 10% compared to non-hydrogenated.

In the case of tempering temperature of 350 °C was verified that the samples that have passed to this heat treatment showed the greatest variations in the apparent fracture toughness for cases of hydrogenation of 6 hours and 9 hours, which showed average reductions of 21.4% and 22.9%, respectively. These values on the engineering standpoint are very important reductions. This can be explained by the hardness of the resulting heat treatment, which was 47 HRC, with steel having a decrease in fracture toughness and therefore susceptible to embrittlement. In this case it is also noted that there is no great change in the values of the apparent fracture toughness for load times of 6 and 9 hours, showing that just as in the case of tempering at 400 °C, 6 hours of charging hydrogen was enough to saturate the steel structure.

From the test specimens it was also possible to analyze the fracture surfaces for each test condition. The results are shown in Fig. 9 to 11.

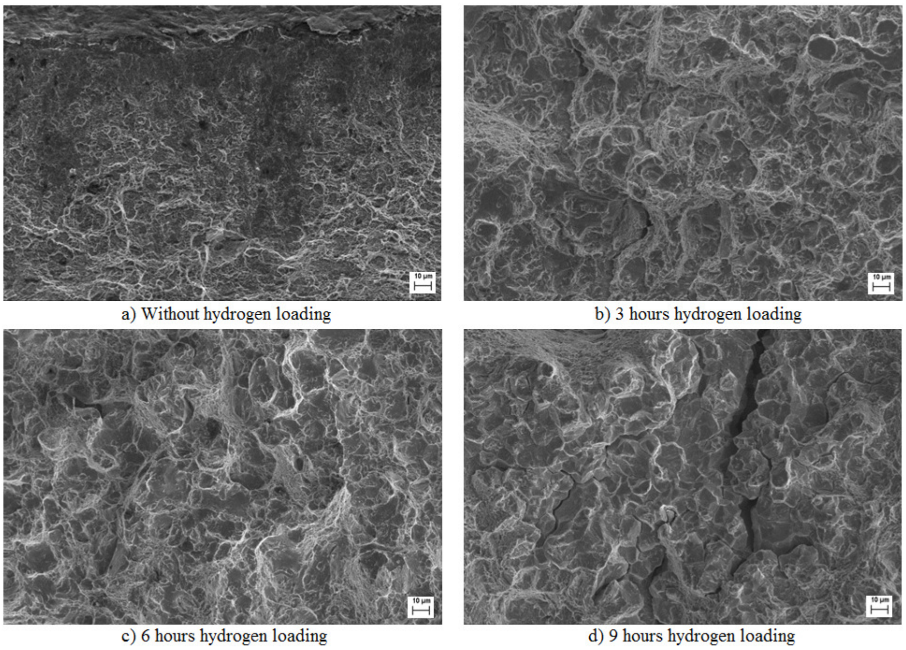


a) Without hydrogen loading b) 6 hours hydrogen loading c) 9 hours hydrogen loading

Figure 9. Fracture surfaces in AISI 4340 steel quenched and tempered at 500 °C analyzed in SEM

From Fig. 9 it can be seen that all cases resulted in microvoid fracture type (dimples), so the hydrogenation of 6 and 9 hours caused no negative effect on the crystalline structure of the steel. This indicates a fracture surface consistent with the results of the hardness, which showed a value of 39 HRC, below the threshold required to cause embrittlement, and the apparent fracture toughness test, which showed no significant changes, with the three tests (hardness, apparent fracture toughness and fractography) complementing each other.

Figure 10 shows the fracture surfaces for the tempering temperature of 400 °C.



a) Without hydrogen loading b) 3 hours hydrogen loading c) 6 hours hydrogen loading d) 9 hours hydrogen loading

Figure 10. Fracture surfaces in AISI 4340 steel quenched and tempered at 400 °C analyzed in SEM

In this case, it is possible to observe changes on the fracture micromechanism of hydrogenated specimens. For the case without hydrogen charging, the observed fracture surface is predominantly dimples. For the case of hydrogenation for 3 hours, despite not having been a wide variation in the value of fracture toughness, it can be seen on the fracture surface there is an initiation of an intergranular fracture surface in a dimples "matrix", with the initiation of secondary cracks. With the increase in hydrogenation times for 6 to 9 hours, there is an increase in intergranular fracture surface and reduction of microvoid fracture surface, indicating that there was a higher embrittlement in these cases. Furthermore, there is an increase of secondary and Y-shaped cracks, reinforcing the assertion of hydrogen embrittlement, as these cracks forms in triple points, in other words, triaxiality stress points, which are preferred regions for precipitation of hydrogen. It is also noted a concordance between the results of hardness test, since this is a higher hardness steel (45 HRC) making it more susceptible to the phenomenon, and apparent fracture toughness, which had reductions in order of 10% in the steel hydrogenated for 6 and 9 hours compared to non-hydrogenated. Comparing the results of the apparent fracture toughness and fractography of specimens tested, it can be concluded the predominance of hydrogen embrittlement due to microinclusions (traps) in this type of steel. This is usually associated with grain boundaries and leads to intergranular fracture (Lee, et al., 2004; Liu, et al., 2008; Nanninga, et al., 2009) and there is no occurrence of cleavage fracture, characteristic of HEDE mechanism or dimples (in the case of hydrogenated specimens), which characterizes the HELP mechanism.

Figure 11 shows the fracture surfaces to tempering condition of 350 °C.

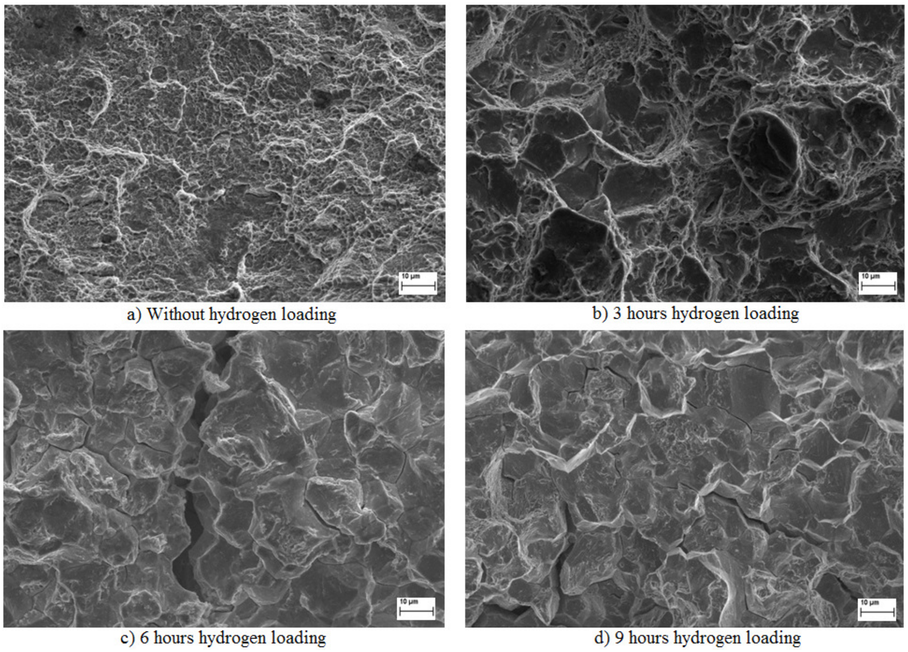


Figure 11. Fracture surfaces in AISI 4340 steel quenched and tempered at 350 °C analyzed in SEM

According to Fig. 11, it is verified that this was the case with the greatest change of the non-hydrogenated steel fracture surface compared with hydrogenated. The non-hydrogenated steel fracture surface was almost predominantly dimples. With 3 hours hydrogenation, although showing no major changes in the apparent fracture toughness, occurs the beginning of the transition from dimples fracture to intergranular, which indicates a start of embrittlement. The hydrogenation for 6 and 9 hours showed a fracture fully intergranular, with the appearance of secondary and Y-shaped cracks, reaffirming the reductions of around 20% in value of the apparent fracture toughness, indicating a high degree of embrittlement.

In the same way that 500 and 400 °C tempering, the tempering at 350 °C shows a correlation between the hardness value, which was 47 HRC, indicating high susceptibility to the phenomenon, and the apparent fracture toughness. Just as happened with the steel tempered at 400 °C, there is a predominance of embrittlement due to imprisoning associated with grain boundaries leading to intergranular fracture in the weakened steel, with no indication in any of the samples tested of the HELP or HEDE micromechanism, which would lead to dimple fracture or cleavage, respectively.

4. CONCLUSIONS

After analyzing the results of apparent fracture toughness along with hardness testing and fracture surfaces for all conditions used in this study is possible to pointing out the following conclusions:

a) The hardness of 40 HRC is the minimum necessary for AISI 4340 steel to show susceptibility to hydrogen embrittlement, because it generates lower yield strength values and tensile strength, making it more ductile steel. For values smaller than this, as was the case of steel AISI 4340 quenched and tempered at 500 °C, which showed hardness of 39 HRC, yield strength of 1112 MPa and tensile strength of 1233 MPa, it suffered no embrittlement after loaded with hydrogen for 6 and 9 hours, with no significant changes in their values of the apparent fracture toughness or on its fracture surface, that remained dimple, independent of the hydrogen loading condition;

b) The AISI 4340 steel quenched and tempered at 400 °C, with measured hardness 45 HRC, yield strength 1352 MPa and tensile strength 1475 MPa, showed a high degree of embrittlement, with reductions greater than 10% in their values of apparent fracture toughness for hydrogen loading conditions of 6 and 9 hours, together with a change of predominantly dimples fracture micromechanisms to almost predominantly intergranular fracture with the appearance of secondary and Y-shaped cracks;
c) The steel quenched and tempered at 350 °C, with measured hardness 47 HRC, yield strength of 1457 MPa and tensile strength of 1580 MPa, was the one that showed greater susceptibility to the phenomenon of hydrogen embrittlement, resulting in reductions in values of apparent fracture toughness higher than 20% for loads of 6 and 9 hours, with a change of predominantly dimples fracture micromechanisms to predominantly intergranular fracture, also with the appearance of secondary and Y-shaped cracks.

For the parameters used in the hydrogen loading, which were contaminated with 0.01 M H_2SO_4 solution, with application of current density of 10 mA/cm^2, 3 hours charging time was not enough to cause significant reductions in toughness values the apparent fracture. While the time of 6 hours of charging is enough to weaken the structure of the tempered steels at 400 °C and 350 °C, being also a time close to the saturation into the crystal lattice of this alloy, because increasing load time to 9 hours did not show much variation in the apparent fracture toughness compared to 6 hours.

5. ACKNOWLEDGEMENTS

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