

## MECHANICAL AND STRUCTURAL BEHAVIOUR OF X 65 CONTINUOUS CASTING STEEL UNDER HYDROGEN EMBRITTLEMENT INFLUENCE

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### ABSTRACT

*The paper presents experimental results of the mechanical tests (alternating plane bending and Charpy impact) performed on samples obtained from X 65 PSL 2 steel slabs. Samples were taken from different batches, cast at the same continuous casting machine. Since metallographic analyses indicates a heterogeneous micro and macrostructure, the samples were collected from different areas of the slabs (surface and middle).*

*In order to highlight the influence of hydrogen embrittlement on mechanical characteristics of steel, some specimens were hydrogenated into hydrogen sulphide environment, for different periods of time. There were calculated the hydrogen embrittlement degree and the structural heterogeneity degree of the slabs structure with data from the two types of the mentioned tests. It is found that the hydrogen embrittlement mainly influences the fatigue characteristics. The structural differences between surface and middle of the slabs are mainly highlighted by the impact tests.*

**Keywords:** continuous casting slabs; X 65 steel; hydrogen embrittlement; alternating plane bending test; Charpy impact test

### 1. INTRODUCTION

Continuous casting is the most efficient and fastest way to obtain solid metal [1]. The literature contains few references related to hydrogen effects on mechanical components made from slabs obtained by continuous casting. The most of the researches and the existing standards are related to the characterization of the steel after rolling.

The hydrogen embrittlement of the steel [2, 3] is the cause of many damages that occur in oil refineries [4], in oil pipelines [5, 6, 7], in storage or containment of hydrogen gas, in power plants [4], in means of transport [8] and can produce premature wear of the tribosystems [9, 10]. These damages, some very serious, have demonstrated the necessity to study the influence of hydrogen on metals. Therefore, profile organizations have being appeared, such as EFC (European Federation of Corrosion), NACE International (National

Association of Corrosion Engineers) and others studying different materials in different conditions and they have developed standardized test methods [11, 12].

Initial hydrogen (called “metallurgical hydrogen”) can occur in steel during elaboration and continuous casting. Additional hydrogen can occur as a result of the influence of the environment in which steel components work. In the presence of the mechanical stress, the influence of hydrogen may increase the degradation of components, such as pressure pipe carrying oil and gas [6, 7]. The X 65 PSL 2 steel (according standard API 5 L) studied in this paper, is used in construction of oil pipelines. Within these steels, at the existing “metallurgical hydrogen”, the hydrogen from certain harmful compounds of oil products (mainly hydrogen sulphide) is added. Most oil deposits that are exploited now are infested with hydrogen sulphide. Therefore, a good resistance to embrittlement is required for this steel.

During the hydrogen embrittlement in H<sub>2</sub>S medium, atomic hydrogen is produced by hydrogen sulphide dissociation, while the corrosion process takes place in hydrated environment. The final reaction is [13, 14]:



There is not a general model to explain all cases of hydrogen embrittlement [2, 3, 15, 16]. The existing theories do not exclude any of them, being complementary. This highlights the complexity of phenomena that occur in embrittlement process. The best known is the mechanism based on hydrogen pressure in the traps, developed by Zapffe and Sims [13, 14]. In this mechanism, after adsorption of atomic hydrogen in metal, its diffusion and accumulation occur in the traps, which are usually crystalline structure defects (nonmetallic inclusions, voids, grain joints, interfaces, etc.). Here, the hydrogen recombination takes place, resulting molecular hydrogen, with a greater volume than that of the atomic hydrogen. This creates a high pressure in traps, which can lead to micro cracks in steel, if a critical threshold is reached.

The present work aims to determine the influence of hydrogen embrittlement of steels obtained by continuous casting technology. It was examined the hydrogen embrittlement on variable loading and impact behaviour of hydrogenated samples obtained from different areas of the slabs. The influence of interaction between microstructure of different areas of slabs and embrittle action of hydrogen was also analyzed on the above mentioned mechanic characteristics.

In order to simulate environmental conditions caused by hydrogen sulphide in the oil industry installations using X 65 steel, sets of samples from different areas of the slabs were treated in hydrogen sulphide environment, for different periods of time.

## 2. MACRO AND MICROSTRUCTURAL STATE CHARACTERIZATION OF CONTINUOUS CASTING SLABS

**Sampling.** For this study, there were several batches. The average chemical composition of them is presented in Table 1.

**Table 1 The average chemical composition of the batches**

Average chemical composition [%]											
C	Si	Mn	P	S	Al	Cr	Ni	As	Ti	Nb	Ca
0.062	0.28	1.60	0.015	0.006	0.030	0.267	0.077	0.002	0.014	0.057	0.0007

In their sections in terms of structure, continuous casting slabs are heterogenous because the slab surface quickly solidifies into mold (at the beginning of "metallurgical length"), while the middle of it much later, at the end of the "metallurgical length" (Fig. 1).

Given the heterogeneity state of slabs obtained by continuous casting technology, a sampling strategy was necessary to be developed. In order to do this, blocks were cut with a length of 200 mm from the slabs of X 65 PSL 2 steel, belonging to different batches, cast at the same continuous casting machine. These blocks have the width and the height of the slabs (250 mm and 1550 mm, respectively) [18]. The blocks were separated from slabs during casting with the help of the torch procedure (Fig. 1). Resulting blocks were cut into five smaller blocks (Fig. 2), from which heat affected zones were removed using a circular saw.

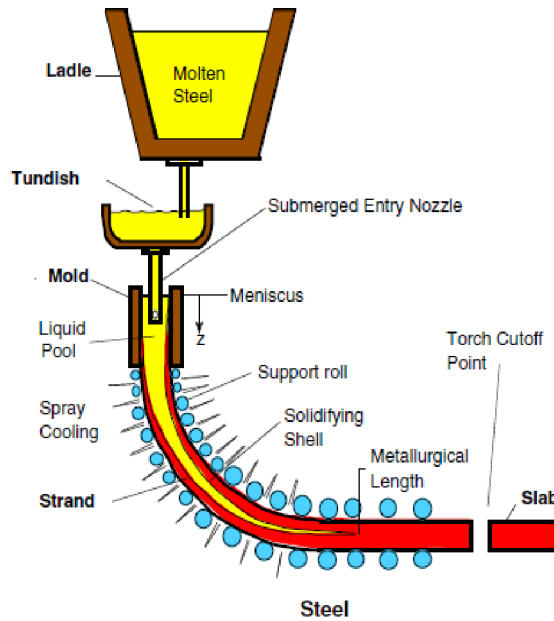


Fig. 1. Schematic of steel continuous casting process [17]

The macrographic examination was conducted using Baumann print method. From each block, three samples were taken: from the ends (denoted by 1 and 3) and middle (denoted 2) (they are represented with blue in Fig. 2). Samples sizes were: width of 200 mm (width of the photo paper) and thickness of 20 mm.

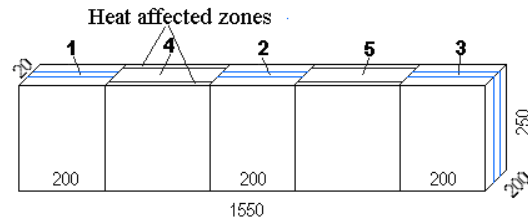


Fig. 2. The position of the sample for Baumann test

Figure 3 shows the Baumann prints of a slab. Examining the prints, it results that the slab has a central segregation zone, visible, in particular, on the sample 2, which could accumulate hydrogen to generate cracks.

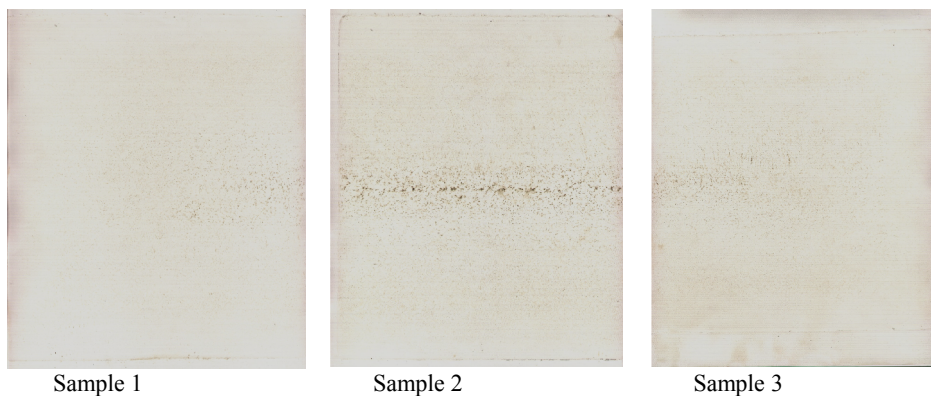


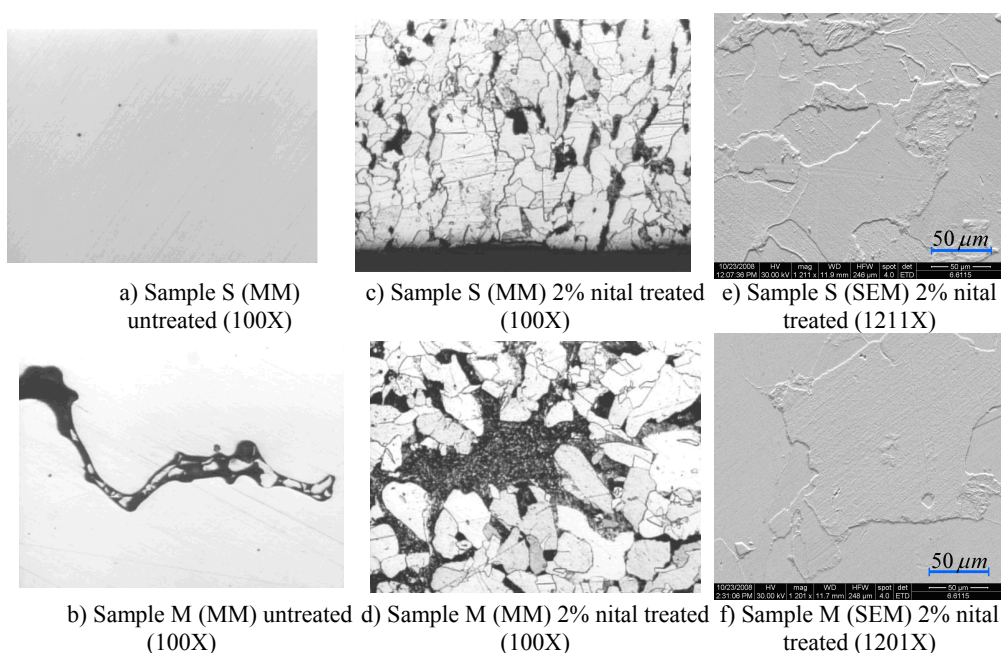
Fig. 3. Example of a Baumann prints

The micrographic examination was performed on samples taken from samples 2 used for Baumann prints. Samples size was 25 mm x 35 mm x 20 mm. Samples were taken

from the middle (denoted M) and from the surface of the slabs (denoted S). The samples M contains a part of the segregation zone that appears in Fig. 3.

After metallographic surface processing, nonmetallic inclusions were determined and, then, after attacking the samples with 2% nital solution, analysis of microstructures was done. The analyses were performed using a metallographic microscope (MM) and a scanning electron microscope (SEM).

Figure 4 presents some images obtained from the examination of the S sample (taken from the surface of a slab) and M sample (taken from the middle of the same slab).



**Fig. 4.** Metallographic and scanning electron microscopy images for S and M samples

The analysis of nonmetallic inclusions shows few fine nonmetallic inclusions, especially oxides (Fig. 4a) on the S samples. Analysis of M samples highlights, mainly in central segregation zone, specific casting holes and nonmetallic inclusions (oxides, sulphides and nitrides like) (Fig. 4b).

The microstructure analysis on S samples (to the very slab surface) shows a ferrite-pearlite structure with fine grains (Fig. 4c). Inside the slab, grain size and heterogeneity increase. The M samples have a structure with large and inhomogeneous grains (Fig. 4d). Same aspects of the above discussion can be seen on SEM images (Figs. 4e and f). The nonmetallic inclusions associated with holes in the middle of the slab look like a network (Fig. 4b). The structure is characteristic of the central segregation zone and contains many traps for hydrogen. Outside the central segregation, there are many places without structural defects (Fig. 4f).

As a conclusion, the structure of slab is inhomogeneous. Its surface structure is more homogenous and the gains size is smaller than that characterizing the middle. This structure is a typical one for the continuous casting slabs.

The sample treatment was made under similar conditions of the test HIC (NACE Standard TM 0284 [11]), using a saline solution, acidified, in which  $H_2S$  was bubbled. The hydrogen sulphide is prepared in a Kipp bows from sodium sulphide and sulphuric acid, according to the reaction:



According to the NACE Standard, the treatment into hydrogen sulphide environment is usually made for 96 hours. Several sets of samples cut off from the same area of the slab were prepared for tests. In this research, the samples were nonhydrogenated and hydrogenated for 96 and 192 hours, respectively.



Fig. 5 The samples shape for alternating plane bending tests (nonhydrogenated – gloss and hydrogenated – mat)

Alternating plane bending tests were made on samples cut off from zone 4 corresponding to each batches (see Fig. 2). Samples were taken from surface of the slabs and from the middle of it. For the tests, rectangular specimens with 288 mm x 45 mm x 10 mm were used and their shape is shown in Fig. 5. Calibrated area with a radius of 80 mm is 25 mm wide. The sample surfaces were polished to 0.002 mm value of roughness Ra.

Following hydrogenation, the roughness changed to 0.0023 mm average value for Ra.

The Charpy impact tests were performed on samples cut also from zone 4 of the slab (see Fig. 2). Samples dimensions are 55 mm x 10 mm x 10 mm, notch in V,  $\alpha$  being 45°, h of 2 mm, notch radius of 0.25 mm. Figure 6 shows samples before tests. The nonhydrogenated samples show a glossy surface and the hydrogenated a mate one.

### 3. TESTS RESULTS AND DISCUSSION

#### Alternating plane bending tests results

Most components of machines, installations, pipelines, bridges, etc. are subject to loads that are not constant over time. It was found that the materials resist less to variable loads than the static ones, as a result of structural changes, progressive and permanent in their nature, and which may culminate with the emergence of cracks or complete break after a sufficient number of load fluctuations. Usually, the initiation process takes place after the emergence of a number of microcracks, which can increase until one of them becomes dominant in coalescence with other microcracks [19, 20].

Flat steel plate samples (Fig. 5) were tested in alternating plane bending conditions with an oscillation frequency of 750/min. At each test, the cycle number is recorded until the final fracture of the specimen. Tests were performed at a single stress level (450 MPa), in the calibrated area of sample.

The average values of the number of cycles to fracture breaking are presented in Fig. 7. It finds the following:

- the number of cycles for hydrogenated samples until breaking is much smaller that that for the nonhydrogenated ones;

- the number of cycles to fracture is lower for specimens taken from the middle of the slab than those taken from surface of the slab;

- the number of cycle to fracture decrease with the increasing of the hydrogenation duration.

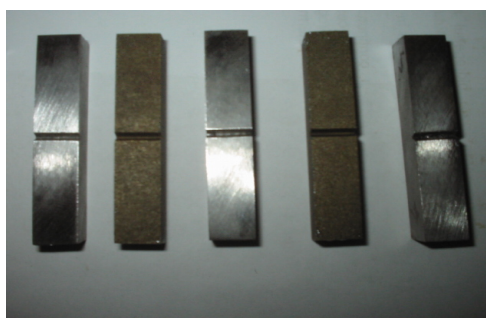


Fig. 6. Samples for the Charpy impact test: nonhydrogenated (glossy) one and hydrogenated (mate)

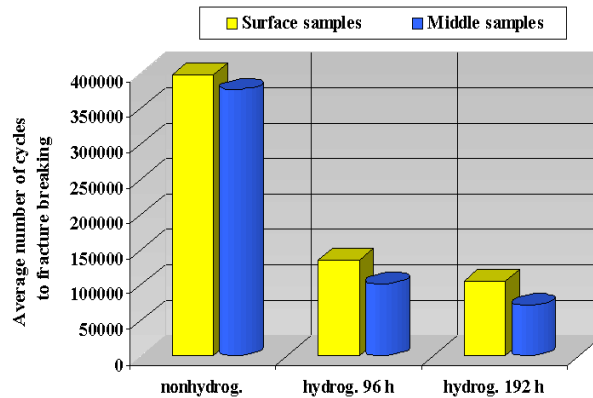


Fig. 7. The averages values for the alternating plane bending tests

The SEM images of the breaking areas for alternating plane bending tests and samples from surface and middle (Fig. 8.) show a fragile breaking for the hydrogenated specimens.

Thus, it appears that the hydrogen embrittlement influences the fatigue mechanical tests. Degradation process in fatigue and crack development mainly rely on a blocking mechanism and the evolution of dislocations, thus, a discontinuous and lasting process. The released hydrogen accumulates in these areas, increasing rupture and crack propagation.

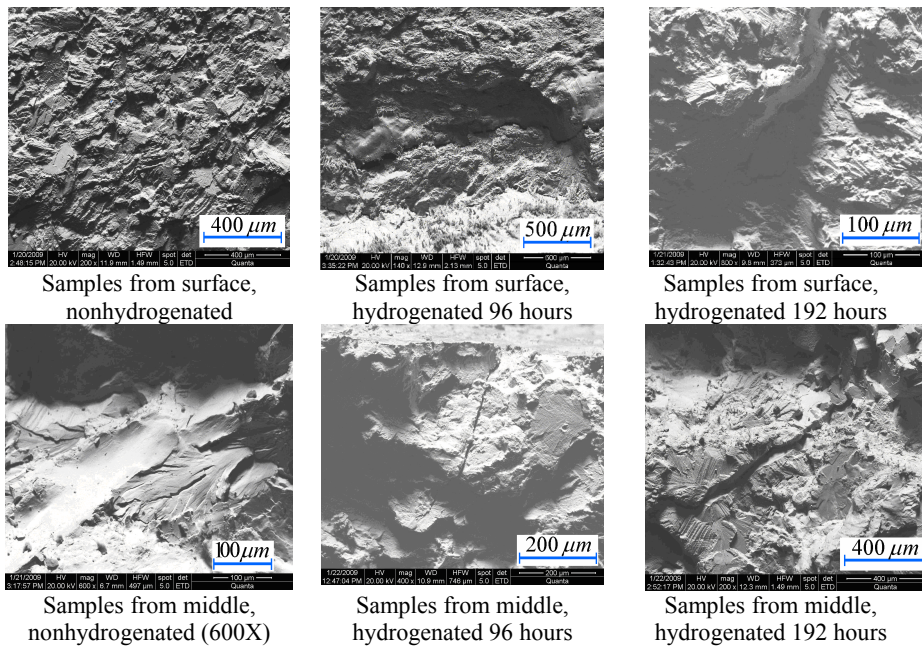


Fig. 8. SEM images of the breaking areas for the alternating plane bending tests

**Charpy impact tests results.** The Charpy impact test has provided valuable indications on the impact properties of the tested materials. It revealed the brittle ductile transition of ferritic steels [21]. The Charpy impact tests results, performed at temperature of 0°C, are presented in Fig. 9.

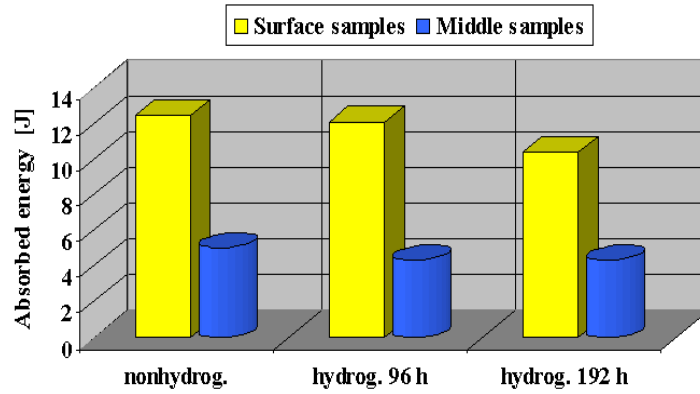


Fig. 9. Charpy impact test data

Tests lead to the following conclusions:

- the absorbed energy is much smaller in the middle of the slab than at the surface, as a result of the structure heterogeneity;
- the absorbed energy for the hydrogenated specimens is slightly smaller than that for the nonhydrogenated ones;
- the increase of hydrogenation duration leads to a lower absorbed energy.

It was observed that the breaking occurred without separation of the fragments for nonhydrogenated samples. It was also found a semi-ductile aspect of fracture. In contrast, for the hydrogenated samples, the breaking occurred with separation of fragments, with a fragile appearance.

For the Charpy impact test, although there is enough energy in metal parts, there are also enough stress concentrators as potential cracks, the accumulated hydrogen cannot show its evolutionary effect. So, the absorbed energy is not significantly influenced by the hydrogen embrittlement. In general, such a test does not allowed for the characterization of the hydrogen embrittlement influence.

**Evaluation of the hydrogen embrittlement degree and the structural heterogeneity degree.** The hydrogen embrittlement action can be expressed by a parameter calculating the embrittlement degree ( $\Delta D$ ) due of hydrogen [12]:

$$\Delta D = 100 \cdot (D - D_H) / D \quad (3)$$

where  $D_H$  is a value obtained for a particular type of test on a hydrogenated sample,  $D$  is the same value obtained in identical conditions, on a nonhydrogenated sample.

The slab structure inhomogeneity study was done using a similar parameter like that defined by relation (3). The parameter was defined as the heterogeneity degree of the slab structure ( $\Delta H_{SM}$ ).

$$\Delta H_{SM} = 100 \cdot (H_S - H_M) / H_S \quad (4)$$

where  $H_S$  is the value obtained for a particular type of determination on a sample from the surface of the slab,  $H_M$  is the value obtained for a determination in identical conditions, on a sample from the middle of the slab.

In order to compare the results obtained from alternating plane bending tests and Charpy impact tests, results were calculated using equations (3) and (4). The results are presented in Fig. 10 for the embrittlement degree and in Fig. 11 for the heterogeneity degree.

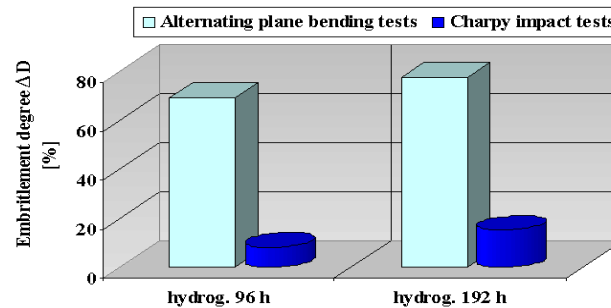


Fig. 10. The embrittlement degree

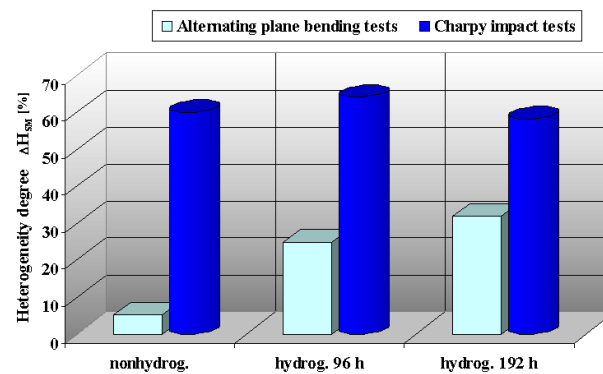


Fig. 11. The structural heterogeneity degree

Experimental data on the embrittlement degree shows:

- the embrittlement degree values in alternating plane bending tests are very high (up to 80.98%), as compared to the values of embrittlement degree in Charpy impact tests, with much lower values (max. 16.93%);
- the embrittlement degree in alternating plane bending tests increases with the duration of hydrogenation; similar results are obtained in Charpy impact tests.

As concerning the structural heterogeneity degree, it was found:

- the heterogeneity degree under variable loading increases with the hydrogenation duration, while, under impact tests, this influence is greatly diminished;
- lasting tests, like alternating plane bending ones, shows a structural heterogeneity degree smaller than those resulting from Charpy impact tests.

#### 4. CONCLUSIONS

The examination of macrostructure and microstructure shows that the slabs obtained by continuous casting are inhomogeneous. The structural heterogeneity is higher in the middle than on the surface of the slabs. The hydrogen embrittlement occurs more intensely in areas with a higher structural heterogeneity.

For highlighting the hydrogen embrittlement degree and structural heterogeneity degree, two different mechanical tests were performed: alternating plane bending test and Charpy impact test.

Hydrogen presence leads to a high embrittlement degree under alternating plane bending tests with consequences of a decrease of the durability.

Hydrogen presence influences in a high measure the structural heterogeneity degree under variable loading. Under shock impact loading, this influence is low.



The embrittlement degree results from hydrogen presence are much higher in variable loading than in impact tests.

The slabs obtained by continuous casting technology, in the presence of the hydrogen, have a high sensibility to variable loadings and less sensibility to impact tests.

Impact tests reveal more structural heterogeneity than variable loading tests, regardless of hydrogenation duration.

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