



20th European Conference on Fracture (ECF20)

## Hydrogen embrittlement of low carbon structural steel

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### Abstract

Hydrogen embrittlement (HE) of steels is extremely interesting topic in many industrial applications, while a predictive physical model still does not exist. A number of studies carried out in the world are unambiguous confirmation of that statement. Bearing in mind multiple effects of hydrogen in certain metals, the specific mechanism of hydrogen embrittlement is manifested, depending on the experimental conditions.

In this paper structural, low carbon steel, for pressure purposes, grade 20 - St.20 (GOST 1050-88) was investigated. Numerous tested samples were cut out from the boiler tubes of fossil fuel power plant, damaged due to high temperature hydrogen attack and HE during service, as a result of the development of hydrogen-induced corrosion process. Samples were prepared for the chemical composition analysis, hardness measurement, impact strength testing (on instrumented Charpy machine) and microstructural characterization by optical and scanning electron microscopy - SEM/EDX.

Based on multi-scale special approach, applied in experimental investigations, the results, presented in this paper, indicate the simultaneous action of the hydrogen-enhanced decohesion (HEDE) and hydrogen enhanced localized plasticity (HELP) mechanisms of HE, depending on the local concentration of hydrogen in investigated steel. These results are consistent with some models proposed in literature, about a possible simultaneous action of the HELP and HEDE mechanisms in metallic materials.

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Selection and peer-review under responsibility of the Norwegian University of Science and Technology (NTNU), Department of Structural Engineering

*Keywords: carbon steel; hydrogen embrittlement; mechanisms; impact strength; SEM*

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## 1. Introduction

Hydrogen damages is one of the most complex phenomena of degradation of metallic materials, due to a number of new unknowns in the kinetics of process, compared to the degradation in the absence of hydrogen in the metal. Hydrogen Embrittlement (HE) of steels is extremely important topic in many industrial applications, since a fully developed and practically applicable predictive physical mechanism-model, still does not exist. Most often, a multidisciplinary approach, based on the use of different advanced experimental-laboratory methods, theoretical and quantum mechanical models, modern micro-and nano-research, micro-fracture mechanics, atomistic investigations and solid-state physics, provides conditions for a much better understanding of extremely complex, multiple and simultaneously active mechanisms of HE [Teter at al., 2001; Serebrinsky at al., 2004; Barnoush and Vehoff, 2010; Lynch, 2012].

In numerous non hydride-forming metals, contemporary research has recognized hydrogen-enhanced decohesion (HEDE) and hydrogen enhanced localized plasticity (HELP) as a two mechanisms responsible for the embrittlement of steel [Katz at al., 2001; Birnbaum, 2003; Dadfarnia at al., 2010]. Coexistence of different HE mechanisms, and their simultaneous effects in metallic materials, including steels, is still not well documented, while recognition of the dominant mechanism (one or more), is an extremely challenging and crucial problem [Gerberich at al., 2009; Novak at al., 2010; Taketomi at al., 2013]. These two seemingly opposing mechanisms of hydrogen embrittlement (HEDE and HELP) are extremely difficult to detect at the same time. Activation of the particular mechanism of hydrogen embrittlement, and the extent of its influence on the fracture process, is primarily caused by the successive processes at the micro and nano levels in the fracture process zone at the crack tip [Katz at al., 2001; Djukic, 2012]. However, the overview of the hydrogen embrittlement in steels, under various conditions, is still unclear.

Typically, research of the hydrogen damage mechanisms, conducted in the world, was carried out using previous uniform enrichment of metallic materials with hydrogen throughout the volume of the samples. Therefore, the critical experiment, that would allow realistic simulation of the kinetics of the development of certain hydrogen embrittlement mechanisms., that is in a full compliance with the actual kinetics in the components of industrial plants exposed to hydrogen during service, is very difficult to conduct [Djukic at al., 2012a].

In this paper structural carbon steel, grade 20 - St.20 (GOST 1050-88) was investigated. Numerous tested samples were cut out from the boiler tubes of fossil fuel power plant, damaged by the High Temperature Hydrogen Attack (HTHA) and HE during service, resulting from the development of hydrogen-induced corrosion process [Djukic and Sijacki Zeravcic, 2004; Djukic at al., 2010]. Based on multi-scale approach, applied in experimental investigations, the results, presented in this paper, depending on the local concentration of hydrogen in investigated steel, indicate the simultaneous action of the HELP and HEDE mechanisms of hydrogen embrittlement [Djukic, 2012].

## 2. Background

In the present work hydrogen embrittlement mechanisms were studied in structural carbon steel, for pressure purposes, grade 20 - St.20 (GOST 1050-88). This steel was used to fabricate evaporator boiler tubes (fluid parameters: pressure, 15,5 MPa; temperature, 350 °C) from 210 MW fossil fuel power plant, damaged after 73.000 h operation, due to high temperature hydrogen attack resulting from the development of hydrogen-induced corrosion process. Our previous studies [Djukic and Sijacki Zeravcic, 2004] showed that the simultaneous effect of hydrogen damage mechanisms in evaporator boiler tubes, due to specific metal – hydrogen interaction, must be considered from materials point of view, fluid hydrodynamics in evaporator tubes, hydrogen-induced corrosion process and the complexity of design – exploitation characteristics of thermal power plant boiler unit.

## 3. Experimental concept and details

Most of the research on the mechanisms of hydrogen damage, conducted in the world, was based on the previous uniform enrichment of metallic materials with hydrogen throughout the volume of the samples. On the other hand, during the operation, metallic materials of industrial components are usually very unevenly saturated with hydrogen [Kolachev, 1999; Smiyan at al., 2002].

There is no universal mechanism to simultaneously describe and take into account all forms of HE. Since over a wide range of hydrogen concentration the enhancement in the mobility of dislocations was detected from very low to high, it can be concluded that the HELP mechanism might be active, but in varying degrees, depending on the concentration of hydrogen in metal [Teter et al., 2001]. On the other hand, the prerequisite for the activation of HEDE mechanism, which results in a very sudden and sharp ductile - brittle transition (ductility loss), requires sufficiently high - critical hydrogen concentration in metal [Oriani, 1972; Teter et al., 2001; Gangloff, 2009].

The experiments in this study were performed on the specimens cut from the real boiler tube, unevenly saturated with hydrogen during exploitation due to HTHA. These specimens were systematically tested for viability of potential hydrogen embrittlement mechanisms (HELP or HEDE) and as well as their simultaneous action (HEDE+HELP). Applied special experimental concept is based on the correlation of the macro hardness values with the corresponding parameters obtained by impact toughness testing and scanning electron microscopy - SEM fractography analysis of fracture surfaces that enabled to define the activity and degree of influence of individual mechanism of HE [Djukic, 2012]. Only SEM fractography of fracture surfaces is not sufficient for understanding deformation and fracture mechanisms. Despite the fact that hydrogen concentration was not determined, the results in the present study show that the macro hardness value could be very well correlated with the hydrogen concentration in the metal, and that it is growing with an increase of hydrogen concentration, regardless of which of the embrittlement mechanisms is dominant [Kolachev, 1999].

Numerous tested specimens were cut out from the power plant fossil fuel boiler tubes, damaged due to HTHA and HE during actual service [Djukic, 2012]. The specimens used in this study for impact strength testing at ambient (20 °C) temperature were cut from steel St.20 (GOST 1050-88), machined from real boiler tubes of diameter:  $D = 60$  mm and nominal wall thickness:  $t = 6$  mm, Fig. 1. The non-standard, "Roman Tile" likes geometry [Capelle et al., 2009], Charpy V-1 notched specimens (1mm/45°) were used (dimension: 3x3x44 mm and 3x6x44 mm). These samples were cut out from the locally thinned evaporator tube in the vicinity of the brittle, thick wall, "window" type fracture where the hydrogen damage occurred, Fig. 1. Before testing, specimens were flattened, as necessary, at extremely slow strain rate. The use of this particular specimen geometry for impact strength testing is explained by the impossibility due to low thickness and boiler tube important curvature to machining standard Charpy specimens. Hardness measurement positions on the outer surface of the Charpy specimens are also marked in Fig. 1.

Analysis of chemical composition was performed by mass spectroscopy using an ARL 31000 quantometer, while for the hardness measurement stable Vickers hardness device, type HPO 250, VEB-WPM, Leipzig, was used. The impact testing was performed in accordance with the ASTM E23 on the instrumented machine SCHENCK TREBEL 150J. Specimens for the SEM fractography examination of fracture surfaces of Charpy specimens were prepared in the standard way. Fractography examination was carried out on SEM unit, type JEOL JSM-6460LV at different magnifications, including the high one. In order to identify chemical content, Energy-dispersive X-ray spectroscopy (EDS) analysis of ferrite matrix and characteristic phases were also performed. The chemical composition of low carbon steel, grade 20 - St.20 steel (GOST 1050-88), with ferrite-pearlite microstructure is given in Tab. 1.

Table 1. Chemical composition of St.20 steel (wt.%)

C	Si	Mn	S	P
0.24	0.28	0.48	0.025	0.013

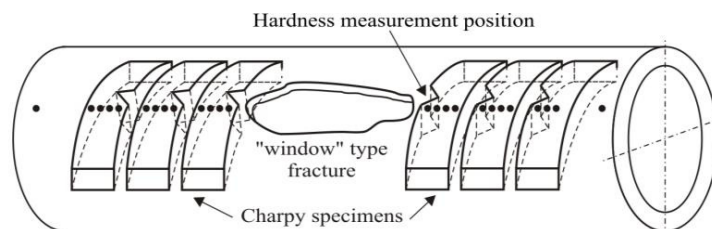


Fig. 1. Position of Charpy specimens and hardness measurements in the vicinity of the "window" type, hydrogen damage fracture

#### 4. Experimental results and discussion

Mechanical characteristics of material in the vicinity of the "window" type, hydrogen damage fracture indicated a noticeable embrittlement of material. Yield strength (398 MPa) was significantly higher than minimum standard value (216 MPa - GOST 1050-88), and it is close to the minimum standard value for tensile strength (min. 420 MPa). Tensile strength was 481 MPa, while deformation characteristic, expressed by elongation ( $A=13.8\%$ ), was much lower than standard recommended one ( $A_{\min}=24\%$ ), which is an indication of a significant increase of material brittleness.

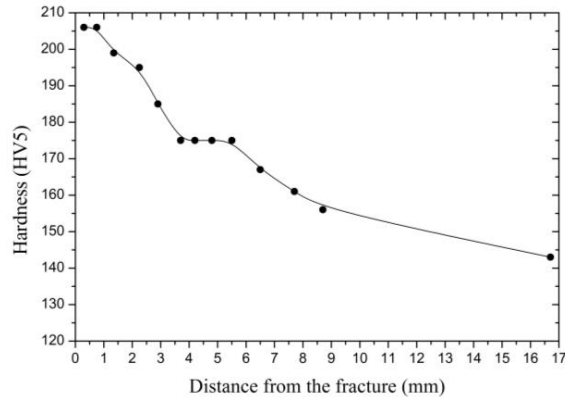


Fig. 2. Variation of the Vickers hardness (HV5) as a function of the distance (x) from the edge of the fracture

Degree of hydrogen embrittlement was evaluated on the basis of decrease in the hardness with increasing distance (x, mm), from the edge of the "window" type hydrogen damage fracture, Fig. 2. Variation of the hardness as a function of the distance from the edge of the fracture (see Fig. 1), clearly indicates a substantial increase in hardness in the vicinity of fracture characterized by very uneven distribution. The hardness value in the vicinity of the opening is high (206HV5), and at a distance of  $\sim 3$  mm from the fracture, it remained significantly higher (185HV5), in comparison to the maximum acceptable standard hardness value (max. 162HV5) for the St.20 steel.

Also, it was observed that in a relatively narrow zone at a distance 3.7 up to 5.5 mm from the fracture, the hardness remains elevated and constant ( $\sim 175$ HV5). Here it can be seen that the slope of the curve changes in the hardness-distance curve before and after plateau. Near the fracture (up to 3.7 mm), the slope of the hardness curve is significantly higher, compared with those, at a distance from the opening higher than 5.5 mm. This hardness trend indicated the change in the dominant mechanism of hydrogen embrittlement, which was confirmed by impact toughness testing and fractographic studies of the fractured surface of specimens [Djukic, 2012]. The abrupt change in mechanical properties is a function of the content of hydrogen in the metal and whereby it appears when it exceeds a critical hydrogen concentration [Kolachev, 1999; Teter et al., 2001; Capelle et al., 2009].

Fracture surfaces can generally be described as "quasi-cleavage" based on surface appearance, Fig. 3(b). The fracture modes reflected by the fracture surfaces are neither intergranular fracture nor cleavage fracture; however they are showing signs of plasticity. Over recent decades "quasi-cleavage" has been used to describe any fracture surface appearance that cannot otherwise be explained as either intergranular, microvoid coalescence (MVC) or true cleavage. Ultimately, the hydrogen-assisted fracture mechanisms which lead to these imprecisely defined fracture surface appearances are still unknown [Nibur et al., 2010]. Based on careful analysis of fracture surfaces with very fine features, two distinctive fracture features can be distinguished: areas of transgranular ("cleavage like") fracture, marked as TG on Fig. 3(c,d), and very fine MVC ( $<2\ \mu\text{m}$ ) with relatively poorly defined dimples, marked as MVC on Fig. 3(c,d). The general fracture appearance is arguably similar to plasticity related hydrogen induced cracking (PRHC) [McMahon Jr. et al., 2009]. Simultaneous action of the HELP and HEDE mechanisms (HELP+HEDE), Fig. 3(b-d), is characterized by a distinctive mixed mode of fracture with the simultaneous presence of brittle transgranular-TG fracture features of ferrite (confirmed by EDS analysis), predominantly by HEDE mechanism, and locally ductile fine MVC fracture feature of pearlitic microconstituent due to HELP mechanism [Djukic, 2012a].

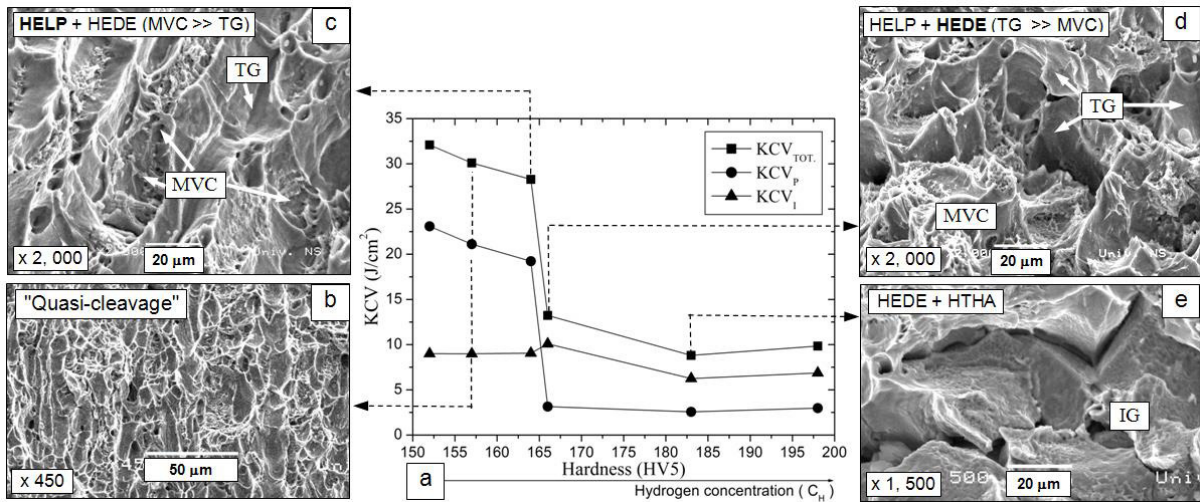


Fig. 3. (a) Variation of the impact strength ( $KCV_{TOT}$ ) and its crack propagation component ( $KCV_P$ ) and crack initiation component ( $KCV_I$ ) of a Charpy specimens, as a function of the specimens hardness (hydrogen concentration); (b-e) SEM fractographs of the fracture surfaces of particular Charpy specimens tested

Simultaneous appearance of HELP and HEDE mechanisms is further supported in a model proposed by Jokl et al. (1989). The initial dominant activity of HELP is followed by a negligible drop in the impact strength ( $KCV_{TOT}$ ) and its component of crack propagation energy ( $KCV_P$ ) and steady value of crack initiation component ( $KCV_I$ ), Fig. 3(a) – hardness: 150-165, and decreases with increasing in hydrogen concentration (hardness). Relatively sudden manifestation of HEDE mechanism, on reaching a critical value of hydrogen concentration, is followed by a sharp ductile–brittle fracture transition, Fig. 3(a). This drop is not only due to cohesive strength decline, which may not be significant, but also due to a noticeable reduction in the appearance of hydrogen-enhanced local plasticity. Expressed observations are consistent with a model of the simultaneous effects of HELP and HEDE [Gerberich et al., 2009].

At the lower hydrogen concentration (lower hardness), HELP mechanism is dominant, which is manifested by an increase in ductile MVC fracture features in "quasi-cleavage" like fracture surface ( $MVC \gg TG$ ), Fig. 3(c). On the other hand, prevailing transgranular fracture features - TG of ferrite, without obvious traces of plasticity ( $TG \gg MVC$ ), Fig. 3(d), followed by a sharp drop in  $KCV_{TOT}$ . (reduced by a factor of two) and especially  $KCV_P$  (reduced by a factor of five), with a negligible increase in the  $KCV_I$ , Fig. 3(a), is a consequence of increased activity of HEDE mechanism, i.e. hydrogen-induced decohesion, with increasing in hydrogen concentration [Djukic, 2012].

Occurrence of the brittle intergranular (IG) area on fracture surface at the high hydrogen concentration (higher hardness), is associated not only with action of HEDE and reduction of the HELP mechanism effects, but also with HTHA mechanism activity (HEDE+HTHA), Fig. 3(e). HTHA failure mechanism initially occurs in the areas where the concentration of individual methane cavity is significantly increased, which is reflected in an additional increase in the brittleness of material. When the HTHA mechanism is dominant, in addition to the formations of the voids, fissures and micro cracks along the ferrite grains (complete degradation of pearlite microconstituent during HTHA), there is also significant additional drop in the both  $KCV_I$  and  $KCV_{TOT}$  (reduced by a factor of two), Fig. 3(a).

The transition from ductile to brittle failure in steels due to hydrogen remains a phenomenon that is still not sufficiently explored and clarified either. In the world literature there are disagreement and polarization of opinions about the inherent nature, trigger mechanism and hydrogen embrittlement mechanisms, responsible for the cleavage and quasi-cleavage fracture due to hydrogen [McMahon Jr. et al., 2009; Nibur et al., 2010; Martin et al., 2011; Lynch, 2012]. The transition from one mode to another is still a matter of debate. It is also important to note, that the emergence of dominant macro brittle fracture (TG and IG) of material enriched with hydrogen, determined by the choice of experimental parameters, usually precludes the possibilities of proper detection of the phenomenon of hydrogen-assisted micro-local plasticity, i.e. simultaneous effects of both HEDE and HELP mechanisms.

## 5. Conclusions

Testing of the samples in this paper, unevenly hydrogen enriched during actual operation of boiler tubes, as well as the selected special experimental concept described above were designed to explore the mechanisms of hydrogen embrittlement in this low carbon structural steel for pressure purposes, St.20. The principal observations are:

- Simultaneous action of the hydrogen-enhanced decohesion (HEDE) and hydrogen enhanced localized plasticity (HELP) mechanisms, were detected, depending on the local concentration of hydrogen in investigated steel.
- A coexistent of HE mechanisms (HELP+HELP) is characterized by a mixed, quasi-cleavage like, mode of fracture, with the simultaneous presence, up to varying degrees, of brittle transgranular-TG fracture features of ferrite, predominantly by HEDE, and locally ductile, fine microvoid coalescence-MVC fracture feature of pearlitic microconstituent due to HELP activity. Simultaneous effect is responsible for the decline in ductility.

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