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HYDROGEN EMBRITTLEMENT OF FERRITIC STEEL 1.4104

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Abstract:
The primary goal of this study was to investigate laboratory techniques for hydrogenating selected steels and to examine the hydrogen embrittlement of steel 1.4104. These processes, which involve hydrogenation and subsequent mechanical testing, are rarely performed in laboratories due to the need for precise, costly equipment and the inherent risks associated with hydrogen's highly reactive and explosive nature.
Various theories have been proposed to explain the mechanisms behind hydrogen embrittlement in steels. These theories attribute material degradation to hydrogen’s interaction with the steel microstructure. However, their applicability is often limited, as they are developed for specific conditions and may not fully describe the phenomenon under different scenarios.
This work focused on hydrogenating steel 1.4104 using two distinct methods: immersion and cathodic. The aim was to induce embrittlement and compare the resulting fracture surfaces, particularly after conducting Charpy impact tests, to evaluate the effects of each hydrogenation method.
Keywords: hydrogen embrittlement, cathodic hydrogen saturation, ferritic steel

1. INTRODUCTION

The increased presence of hydrogen in structural materials leads to many changes in the material properties of all structural metallic materials. In most cases there is a reduction in mechanical properties. The presence of hydrogen in the material structure also leads to a deterioration of the material's resistance to brittle failure due to a change in the failure mechanism. Atomic hydrogen can induce hydrogen embrittlement in the material. Hydrogen embrittlement of the material is manifested at normal and low temperatures, but also at high temperatures, when dissolved hydrogen can react with carbon or other elements and induce hydrogen embrittlement in the material (Sojka, 2012; Kreibich, 2016). Due to its very small size, atomic hydrogen can diffuse intensively into the surface layers of the material. Even in very small amounts, hydrogen can cause damage to the material. The negative effect is already visible at a concentration of 0.0001 wt.% hydrogen in the material, when it is able to initiate cracks (Kreibich, 2016; Cambell, 2012). Hydrogen diffusion is affected by many factors, including temperature, hydrogen concentration in the material, and hydrostatic stress. The rate of hydrogen movement in a material can also be increased by dislocations. This can happen if hydrogen is located in the center of a dislocation or is generally in the vicinity of the dislocations. The movement of dislocations is very dangerous when hydrogen moves through a grain to a grain boundary. In this case, intercrystalline cracks occur. The rate of hydrogen diffusion is increased by the fact that it occurs near grain boundaries. In this case, the diffusion rate is higher than in interstitial diffusion (Lynch 2011). If molecular hydrogen forms and accumulates in structural defects such as pores, inclusions or grain boundaries, the material becomes brittle and starts to crack. Hydrogen atoms in the material combine to form the H_2 molecule, creating pressures on the order of 10,000 MPa (Kreibich, 2016), (Janovec, 2004). Ferritic stainless steels are Fe-Cr-C type alloys. They are characterized by chromium content ranging from 10.5 to 30%, ensuring their corrosion resistance. The content of other elements (Si, Mo, Al) makes them incapable of heat treatment via the allotropic $\gamma \rightarrow \alpha$ transformation. This is because these elements contribute to the formation of ferrite while suppressing the γ region. During the processing of ferritic steels, it is important to take note of three possible types of embrittlement. The first type of embrittlement can occur during heat treatment in the high temperature region from about 900 °C, but mainly above 1000 °C, the other type is embrittlement by deposition of the σ phase (at temperatures around 700 °C), in addition also in the temperature region around 475 °C. Independently of the temperatures, these steels are also susceptible to hydrogen embrittlement (Ocele, 2020; Martáková, 2021).

While decades of research have advanced the understanding of hydrogen embrittlement in ferritic steels (Martin 2020; Kim 2012), the interplay between hydrogen and microstructure remains poorly understood in many scenarios. Bridging this gap requires combining advanced experimental techniques with refined models to probe hydrogen behavior at multiple scales. Developing testing methodologies that replicate real-world conditions is also essential for designing hydrogen-resistant materials and ensuring the safe implementation of hydrogen infrastructure.

The aim of this paper was to experimentally investigate the susceptibility of ferritic stainless steel 1.4104 to hydrogen embrittlement. The main objective of this work is to determine the effect of hydrogen on the properties of the selected steel, introduced by two different methods. The steel used in this research is used for the production of pressure valve bodies. These components have sharp edges, threads and other peripherals that are often stress concentrators. In combination with hydrogen absorption and continuous stressing of the component, it is necessary to conduct experiments to determine the susceptibility of the steel to hydrogen embrittlement.

2. HYDROGEN EMBRITTLEMENT AND ITS SOURCES

Hydrogen embrittlement typically occurs through a 3-step process:

Hydrogen absorption: At room temperature, hydrogen atoms can be absorbed by carbon steel alloys during various processes, such as manufacturing processes related to acid cleaning, electroplating, or exposure to hydrogen-containing environments.

Diffusion: The absorbed hydrogen atoms are highly mobile and can diffuse to the areas of the highest stress, such as grain boundaries, dislocations, and inclusions, The hydrogen forms voids at the metal grain boundaries. The result of hydrogen diffusion into the material is a loss of ductility, making it more brittle and more susceptible to cracking.

Embrittlement: Given enough time, when the material is exposed to high tensile stress, these voids exert additional pressure on the metal grains, forming initial cracks that grow along weakened grain boundaries until the material finally breaks. This process is known as intergranular cracking (Celo screw industry, 2023).

During the production of a material, there is a number of factors that affect the volume of hydrogen introduced into the material. This depends on the raw materials used, the manufacturing process, the heat treatment methods, as well as the furnace atmosphere used. The type and quality of the material determines how the hydrogen content of the material will ultimately manifest itself (Sojka, 2007). The main source of hydrogen embrittlement in steels is electroplating and other surface treatments such as electrochemical cleaning or pickling. During electrolysis, or when the material reacts with an aqueous environment, hydrogen atoms are present on the surface (Fig.1).

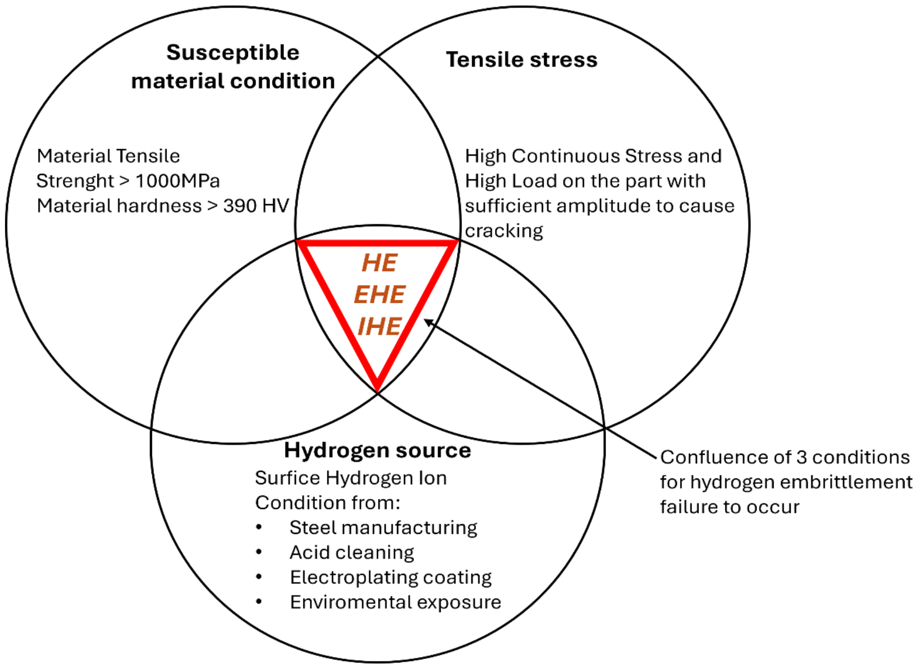

Fig. 1. Cause hydrogen embrittlement failure (Celo screw industry 2023)

These atoms almost immediately begin to aggregate into molecules. In addition to the neutral water molecules H_2O, hydroxide ions H_3O+ are also present in the solutions. Upon contact with an electron, this ion decays into a H_2O molecule and a hydrogen atom, which usually combines on the surface of the metal with another atom. The joining of the molecules forms bubbles which escape from the solution. Unbonded hydrogen atoms can be retained on the surface and enter the material if the current density is high during surface treatments in a liquid environment, or if the metal surface is contaminated with substances that interfere with its catalytic effect (Fridrich, 1963). Other sources of hydrogen may include the operational processes of equipment or structures that are exposed to a hydrogen environment. In technical practice, these are mainly the chemical, oil and gas industries. Under high pressure, both liquid and gaseous hydrogen is often used in the cosmetic industry (Sojka, 2007), (Cambell, 2012).

3. EXPERIMENTAL MATERIAL AND METHODOLOGY

3.1. Experimental methods and material used

The material under test (steel 1.4104) was supplied in the form of small samples of 10x10x55 mm in 10 pieces. The material was supplied by HYDAC Electronics, which, among other things, uses this type of steel for the manufacture of various components that come into contact with hydrogen in various states. V-shaped indentations were made in the center of these pre-prepared specimens to enable the bending impact test to be carried out.

Chemical analysis of the test material was carried out using a SPECTROMAXx light emission spectrometer with a wavelength range of 140-670 nm. A SpectroSort handheld X-ray spectrometer was also used to verify the accuracy of the results. The standard composition of steel 1.4104 is given in Table 1 and was compared with the measured chemical composition Table 2.

Table 1.
Standard chemical composition of steel 1.4104 [wt.%]

C	Si	Mn	P	S	Cr	Mo	Fe
0.17	1.00	1.50	0.040	0.15-0.35	15.50-17.50	0.20-0.60	rest

Table 2.
Experimentally determined chemical composition of steel 1.4104 [wt.%]

C	Si	Mn	P	S	Cr	Mo	Fe
0.175	0.365	1.32	0.0149	0.294	16.32	0.202	rest

The verification measurement confirmed conformity with material 1.4104. There is an insignificant difference in the carbon content, which exceeds the maximum permissible value prescribed by the standard. The next step necessary to define the initial state of the experimental material was to observe the microstructure. Prior to the microstructure observation, the material was metallographically prepared in five consecutive steps (sampling, preparation, grinding, polishing, etching). KALINGS 2 etchant and an etchant composed of glycerin ($C_3H_8O_3$) + HCl + HNO_3 were used to highlight the structure (Fig. 2a). The samples were observed using a NEOPHOT 32 light microscope. Observation of substructures, details and fractures was carried out using a TESCAN LMU II scanning electron microscope equipped with a Bruker EDX analyzer, which allows the determination of the concentration of chemical elements in the selected region.

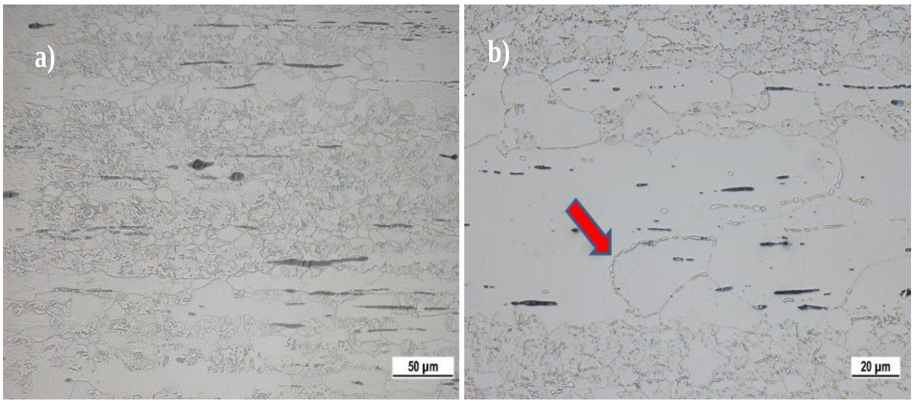

Fig. 2. Structure of steel 1.4104 in the initial state a); particles of tertiary cementite around the grain perimeter b), etch. glycerine + HCl + HNO_3

After etching, ferrite grain boundaries and other structural components were highlighted. The steel structure is formed by slightly deformed ferrite grains with particles of tertiary cementite around the grain perimeter (Fig. 2 b). The cementitious particles are excluded in the volume of the ferritic grains, but also along their boundaries, which significantly affects the brittle fracture properties. In addition, sulfides occur in the structure elongated in the rolling direction of the blank in which cracks are found. The sulfide content is quite large and ranges from 30 μm to 350 μm in length (Drápala 2012).

To analyze the hydrogen embrittlement problem, we have chosen three basic experimental procedures. The saturation of the samples was carried out by two different methods - cathodic and immersion methods (Fig. 3). Subsequently, fracture surfaces were obtained by means of the bending impact test, which were prioritized in terms of assessing embrittlement. The selected hydrogen embrittlement processes correspond to the possible causes of hydrogen embrittlement in practice.

The method of saturating the material by immersion in a suitable medium was chosen based on theoretical knowledge of hydrogen embrittlement, according to which during this process the amount of hydrogen adsorbed to the material is sufficient to induce embrittlement. This procedure is also more practical than cathodic induction. Tagaki S. and Toji Y. report that the use of ammonium thiocyanate is the most suitable choice for immersion hydrogenation. Its advantage is, among other things, that the loss of materials in g/cm^2 is practically zero regardless of the immersion time. A 20% NH_4SCN solution in distilled water was used as the working medium, which, according to the authors Tagaki S. and Toji Y., sufficiently saturates the material within 50 hours. The solution was prepared by mixing 500 g of ammonium thiocyanate with 2 liters of distilled water. The beakers used had to be of such a size that the samples in solution could be placed in them. Immersion saturation of the samples with hydrogen was carried out in a fume hood for 50 hours (Fig. 3b) (Tagaki and Toji, 2012).

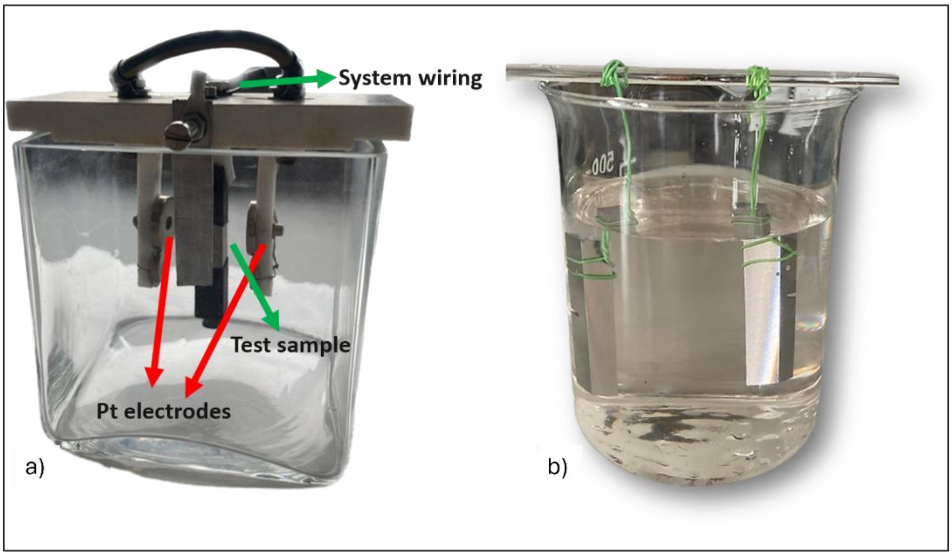

Fig. 3. Methods of saturating samples with hydrogen a) electrolytic saturation b) immersion saturation

The method of electrolytic saturation is conditioned by the moment when the source creates a potential difference and initiates positive hydrogen ions that move from the electrolyte to the experimental material - the cathode. The flow of charged particles forms a layer of hydrogen on the surface of the test sample. An experimental set-up was constructed for this method (Fig. 3 a)). The process is based on the principle of electrolysis and involves a cathode, represented by experimental material, and a platinum anode. A zinc anode was also used to simulate the electroplating, which later proved to be irrelevant. The cathodes did not have standardized dimensions. The direct current supplied to the electrolyte initiates decomposition accompanied by the formation of hydrogen ions - specifically hydrogen protons. A 0.5 M H_2SO_4 solution with the addition of 0.28 g of thiourea NH_2CSNH_2 per 0.5 L of solution was used as the electrolyte (Tagaki and Toji, 2012). Insulating shrinkage strips were put on the samples to reduce the saturated area per notch area. The parameters used are shown in Table 3.

Table 3
Parameters used in saturation by electrolysis.

Current density (mA/cm^2)	Set parameters		Temperature °C	Time (hour)
	Current (A)	Voltage (V)		
100	1.7	3.0	23	24

4. EXPERIMENTAL RESULTS AND DISCUSSION

4.1. Results prior to saturation with hydrogen

The tested sample was characterized by a cleavage fracture with both intercrystalline and transcrystalline failure. The proportion of facial failure was very low. The overall view of the fracture surface (Fig. 4a) shows several large cracks, which indicate an inappropriate state of the structure. Using a Bruker probe, mapping analysis revealed that the sulfides MnS. Fig 4b) shows details of mixed fracture with a small proportion of ductile failure.

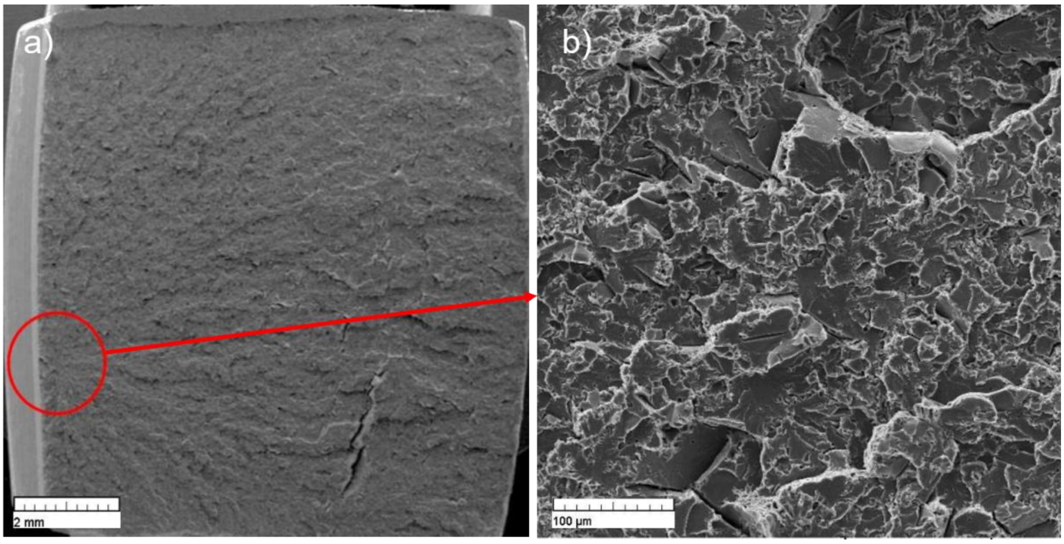

Fig. 4. General view of the fracture surface with its initiation site a); mixed fracture with a small proportion of ductile failure b)

4.2. Results after saturation with hydrogen

Submerged hydrogen saturation produced a large secondary fracture in the center of the fracture surface (Fig. 5a), probably on the segregation belt.

As a result, two primary fracture initiation sites (above and below this fracture (Fig. 5a) were formed. We can observe a significant increase in the number of secondary cracks in the final fracture area. Furthermore, a large variability of the structure after saturation can be seen. There are visible changes in the structure or character of the fractures, which are thought to be caused by possible internal stress from recombination processes of hydrogen atoms. Secondary cracks are mainly oriented perpendicular or parallel to the direction of the main crack, this is related to the deformation texture of the material. In Fig. 5b), transcrystalline cleavage failure combined with transcrystalline ductile failure with a distinct morphology of pits can be observed, which was produced by a dislocation slip mechanism.

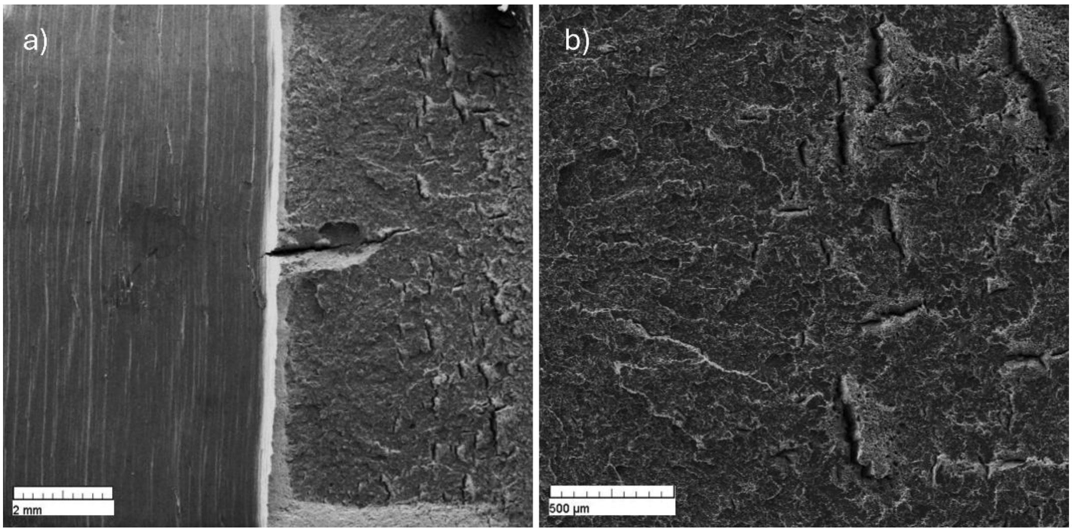

Fig. 5. General view of the fracture surface a); transcrystalline cleavage fault with a small presence of ductile faulting with pitted morphology b)

After this saturation, the number of secondary fractures increased significantly, and the fracture surface appeared more brittle. It can be assumed that hydrogen embrittlement of the material due to internal stresses is behind these changes.
After cathodic saturation, the fracture surfaces of 1.4104 steel were characterized by a mixed failure mechanism, where cleavage failure without plastic deformation was dominant, with a crevice morphology. In addition, there were also areas of ductile failure with a dimple morphology, which are typical of the pearlitic region. As after immersion saturation, the fracture was characterized by a large number of secondary cracks, which were differently oriented, some of them formed at the ferrite-perlite interface. The failure mechanisms and fracture characteristics after saturation are shown in Fig. 6a and Fig. 6b. There are several places where large secondary cracks are visible. The state of stress in the fracture zone has not changed because plastic deformation has not occurred here, or has occurred partially, as indicated by the areas of ductile failure. Such brittle fracture propagates at high speed and is not influenced by the nature of the structure.
From the comparison with the initial state, we can state that observable embrittlement appeared after immersion hydrogenation. The number of secondary cracks increased significantly compared to the initial material. Cleavage failure with small locations of ductile failure prevailed again. Cracks at the phase interface and grain boundaries, which are typical of hydrogen embrittlement, were also more pronounced.
After cathodic hydrogen saturation, the number of secondary cracks increased significantly and cleavage failure with small areas of ductile failure again prevailed. As with the immersion method, cracks were also present at the phase interface and grain boundaries. These cracks are typical of hydrogen embrittlement.

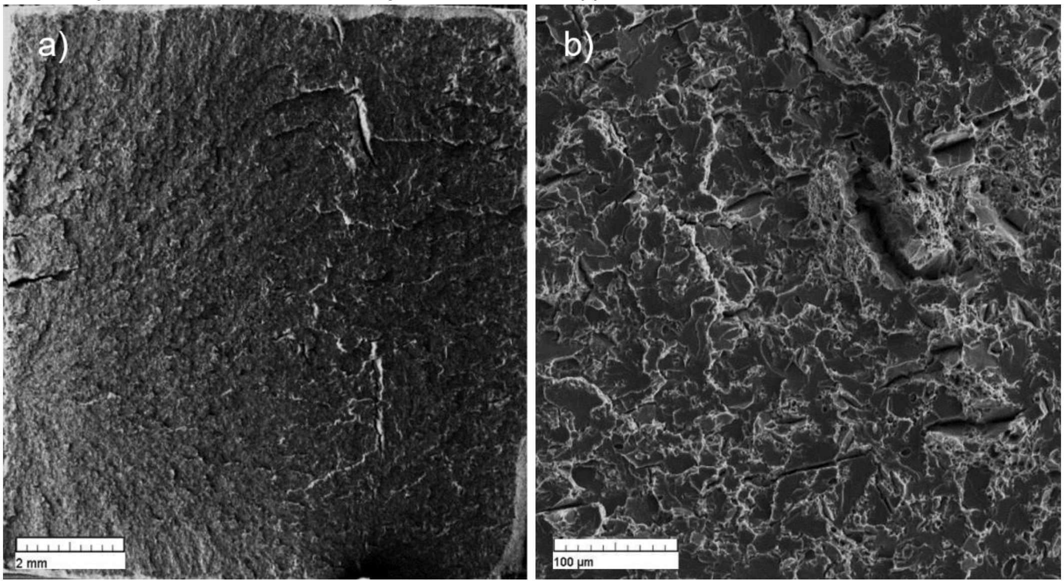

Fig. 6. General view of the fracture area a); mixed fracture with numerous secondary cracks b)

5. CONCLUSION

The material used in this work was selected based on its use in shape-complex threaded components. Such products have applications in hydraulic systems - stationary or mobile, which may be exposed to atomic but especially molecular hydrogen.

The experimental part of the work focused on investigating the effect of hydrogen saturation of steels by two methods: immersion and cathodic. To determine the effect of hydrogen on the properties of materials, it was necessary to define their initial state. After metallographic preparation, the chemical composition and structures of the investigated steel were analyzed. Steel 1.4104 had slightly deformed ferrite grains with sulfides arranged in the rolling direction. After defining the initial state, we found that MnS sulfides are potential hydrogen traps and can contribute to hydrogen embrittlement based on study (Dwivedi 2018). The key experiment was the impact test in bending, performed before saturation. Steel 1.4104 showed low toughness and its fracture surface had a predominantly cleavage character with the occurrence of secondary cracks. After hydrogen saturation by the immersion method, the number of secondary cracks. In the case of 1.4104 steel, the cleavage fracture pattern was dominant, with hydrogen causing more pronounced embrittlement compared to the initial state. For immersion methods, we followed and compared the results with the article (Takagi S. and Toji Y. 2012) Cathodic saturation yielded similar results, but the embrittlement intensity was higher, especially in the central part of the fracture surfaces. Hydrogen atoms diffused deeper into the material, probably leading to a greater impact on toughness. The conclusion is that hydrogen significantly reduces the toughness of the investigated steel due to its interaction with microstructural features such as sulfides, grain boundaries and cementite based on and compared with (Kreibich 1992, Campbell 2012). These sites act as hydrogen traps, which increases the risk of hydrogen embrittlement.

The results from the research indicate that manganese sulfide is not the main cause of hydrogen embrittlement of 1.4104 steel. Its effect is attributed to hydrogen trapping, which induced high stresses causing it to separate from the matrix. The main cause of hydrogen embrittlement in steel 1.4104 appears to be the blocking of the dislocation transition due to the presence of hydrogen in the structure. It is difficult to determine which method is more suitable for experimental purposes, but from a practical and economic point of view, submerged hydrogenation is preferable. However, the results seem to indicate a higher probability of hydrogenation with cathodic hydrogenation.

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