Project 18-489

Final report

An experimental study on the problem of hydrogen embrittlement in hydrogen driven transport in energy technology

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1. Introduction

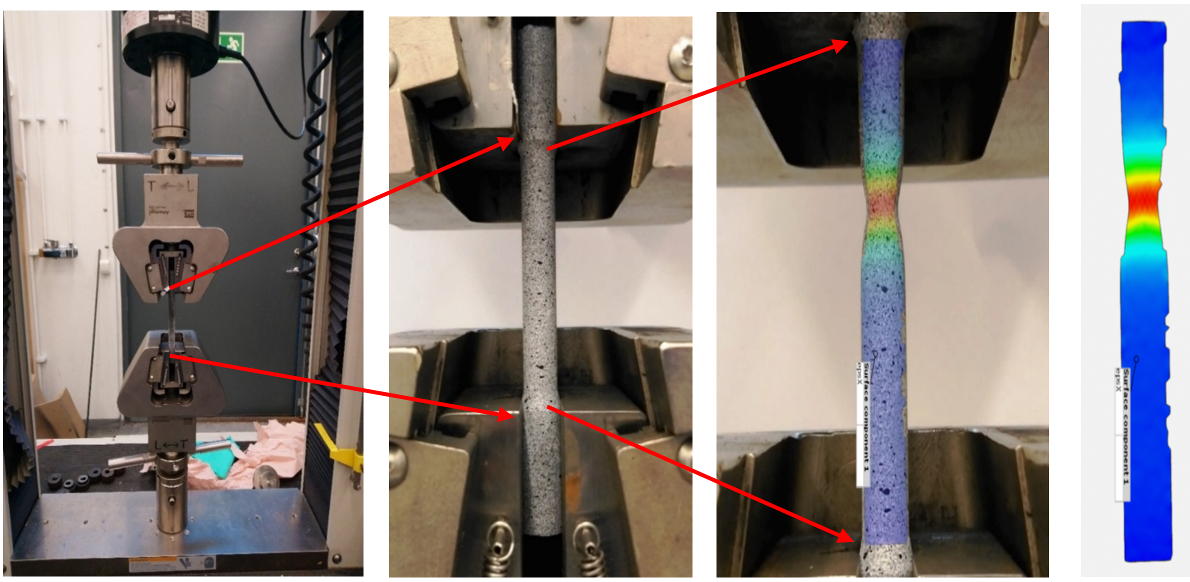
The purpose of the proposed project has been to investigate the influence of hydrogen on the mechanical properties of metals which are used for hydrogen driven transport in energy technology. The study involves intensive experimental studies and continued implementation of the theoretical framework proposed in the applicants doctoral thesis.

2. Experimental methods and materials

The experimental methods consist of a series of tensile tests, digital image correlation (DIC), and hydrogen charging to see the influence of hydrogen on mechanical prosperities of metal samples.

2.1 Tensile testing and DIC

The available tensile test machine we have in our lab has a maximum load capacity of 100kN. First the material is thoroughly examined before it is exposed to hydrogen charging. For this, tensile tests are performed for without charged samples, and during the test a DIC method is used to correctly map the strain field of deformation profile. The DIC images are also used to follow the end displacements, for that the strains are integrated to get the displacements of the specimen ends. The results are then compared to secure the accuracy of the result. Grip displacements was tested but could not be used because of considerable slipping of the grips. Figure 1 shows the MTS tensile test machine set up and DIC test.

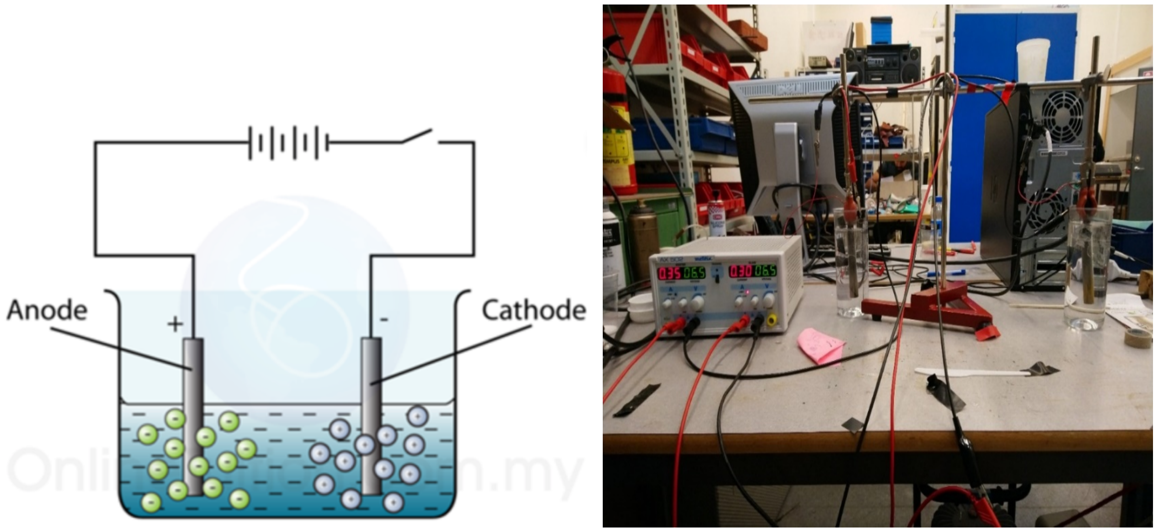


a) b) c) d)

Fig 1. Tensile test of an ASTM cylindrical sample and strain mapping from DIC. From left to right are, a) the grips, b) a typical test specimen with random speckles mounted in the machine, c) a progressive necking with the semi-transparent DIC results, and d) the DIC strain result with red to blue for the highest to the lowest strains.

2.2 Hydrogen charging

For the hydrogen (H2) charging a cathodic charging method is used, as is shown in Fig 2. It is basically an electrolytic cell, where our metal sample acts as a cathode and a platinum wire acts as an anode and also catalyst. The platinum wire is a 0.4mm thick in diameter and of 99.8% pure platinum metal, and imported from Japan during the project. It is a very good catalyst that accelerates the process 2000 times more as compare to normal process without the catalyst. For the solution of electrolytic cell a complex solution which is a combination of two different types of chemical components (NaCl with 99.9% purity and NH_4SCN) and de-ionized water were used.



a) b)

Fig 2. Cathodic charging set up, a) schematic view b) the real setup in the Lab

2.3 Test objectives and materials

The original intension of this project was investigate three types of metals which is aluminum, steel and titanium with intension to shift our focus according to initial trial results. There are certain discrepancies in the nature of hydrogen transport in aluminum. The fact that the diffusion of hydrogen in aluminum is very small at room temperature makes it difficult to rationalize the effect of hydrogen on various properties which need a faster movement of hydrogen atoms. In some earlier literature it is reported that the effect is more visible in a slow strain rate during charging [1]. Also the increased temperature influence the process of embrittlement [1]. In general embrittlement was found to be dependent on temperature, strain rate and microstructure. However, the attempts for thin samples were much more challenging than we expected and were not successful due to the lab facilities. The Lab facility we have are not proper for slow strain rate testing while we are charging the sample, thus pre-charging and fast strain test were performed and we skipped aluminum. However, throughout the project the idea of building a prototype of small instrument to charge the sample with hydrogen while during were developed, and the initial implementation is successful. Thus, implementation of this and considering the influence of temperature planed for implementation during next for the next step.

Hight strength steels are great interest for many industries, in terms of hydrogen embrittlement, for the industrial applications where components are exposed to hydrogen which is used as a fuel as a green energy source. We got a lot of encouragements and interesting questions from many experts from industries like Siemens in Finspång, SSAB and a couple of others during the project. This gave us new angles of the problem and we decided to deepen the focus to the probably most important types of steels. Thus, we studied structural steels and high strength stainless steels of 316L, 304, 321 and duplex is partially studied. Steel under normal conditions are not expected to form hydrides. It is known that steel is affected by the presence of hydrogen by enhanced dislocation mobility. Further, as far as we understand it is unknown if the hydrogen reacts with the alloying elements to form hydrides or compounds in which the hydrogen plays a role. It is presently unknown if there are direct chemical reactions with the steel through synergetic interaction with the alloying elements or chemical reactions, or with the alloying elements only. Thus, the influence of hydrogen to different types of steels are studied in this project.

3. Achieved results

We have approached the challenges in this project from multiple angles. Throughout the project we worked on both formulation of theoretical framework and performing experimental investigation performed simultaneously.

3.1 Theoretical studies and achievements

The theoretical formulation concerns with hydride forming metals proposed in applicant's PhD thesis. For this, the formation of hydride precipitates in front of a crack tip, the role of anisotropy, and interface instability between metal-precipitate interface were studied in the following papers.

The first paper [2] is a pilot study of precipitates growing in front of a crack tip. The material is subjected to mechanical stress with consideration of a sharp interface between metal and precipitate. The equations are put on non-dimensional form. It is then discovered that the problem only has one single length scale, therefore, the growth occurs under self-similar conditions. It is also found that the anisotropy of the expansion strongly affects the precipitate shape. Also the precipitate, once initiated, grows without remote load for expansion strains above a critical value. During the work this work, I realized that the initiation of the hydride could not be understood by the sharp interface theory. Also I learned that corrosion and other phenomena with moving boundaries develop a waviness, a morphology, when there is a competition of release of elastic versus release interfacial energy. Therefore, I wrote second paper which take the interfacial energy into account.

The second study [3], is an analytical study about the evolution of morphological patterns that arise on the interface of bi-material due to the instability of the interfaces between precipitate and metal matrix. For that, first a wavy interface perturbation introduced to examine the spontaneous variations that occur and how they grow or decay depending on the relation between the elastic energy and the interface energy. Cerruti's solution is utilized to compute the perturbed stress field surrounding the interface [4]. The results shows that a virtually flat interface with very small perturbations subjected to tension is in general unstable. The amplitude of sinusoidal perturbations decays for short wave lengths and grow for longer wave lengths.

The third pilot study [5] is about on the role of anisotropic expansion that uses a Landau-Lifshitz phase field model to study the growth of a precipitate originating from a crack tip [6]. In the model, the influence of strain energy, gradient energy and chemical potential energy is included and the influence of interface energy consisting of gradient and potential energies becomes considered implicitly. The crack tip shielding caused by both precipitation and plastic yielding is examined using the J integral. The materials are assumed to be elastic-plastic with linear strain hardening. The results show that the precipitate shape is influenced very strongly by the anisotropic expansion. A wedge like shape of precipitates is achieved for anisotropic materials. The resulting shapes for the anisotropic cases are in line with observations of internal crack tip hydrides in zirconium, see Fig 3.

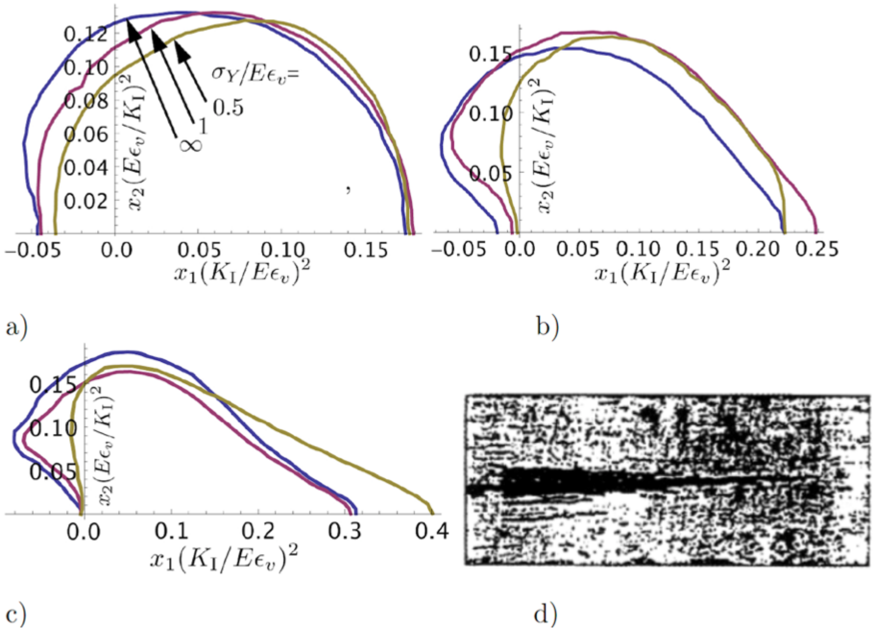


Fig 3. The shape of precipitates for different yield stresses, a) isotropic q = 0 and anisotropic Cases, b) for anisotropy factor q = 0.4, c) for q = 1, and d) is a neutron beam scan of a zirconium hydride obtained by Metzger and Sauve [7]. Colour coding is the same in all graphs

A forth publication is an extended abstract [8]. It is a practical application of the Landau-Lifshitz theory to study the formation of hydrides at a stress concentration caused by a notch. The model has proven its ability to calculate hydride growth in irregular geometries and should be useful for many industrial applications. The outcome of this study is presented at the international conference.

3.2 Experimental studies and achievements

The experimental part has been very rewording experience with many trials, errors, and learn from mistakes.

The procedures of the experiments are as follows: a cylindrical specimen is pre charged for 24 hours with a current of 0.02A and a voltage of 3V. Depending on if it has an effect on the tensile test result or not, we adjust available variable voltage during charging. Our experiments focuses on yield stress, tensile strength, and fracture. After many attempt of unsuccessful test, where the charged and without charged samples showed literally no difference if the transfer time (from remove from charging to mount it to the grip) more than 15minutes, we learned that the diffusion of hydrogen in steel to air is very fast must be handed faster. As it is shown from Fig 4, the results from exactly same set up with 24h charging and testing shows different result as one sample has longer air exposer time or transfer time, the dashed curve is 1 minutes transfer time before test and 8 minutes for dashed.

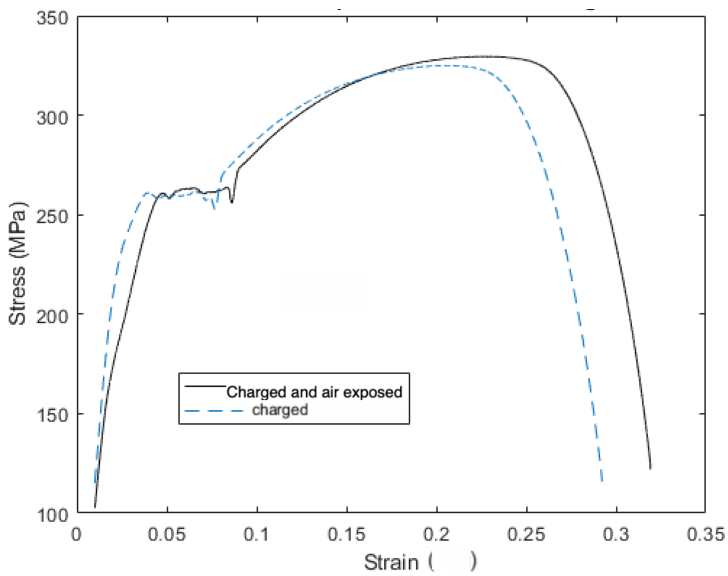


Fig 4. Specimens from structural steel with different transfer time, solid curved is air exposed 8 minutes.

Therefore, here is a need to have a shorter transfer times. To avoid escape of hydrogen from the sample, they are handled fast. It takes around a 40-50 seconds to take the specimen out of the charger, mount it to tensile test machine and start the tensile test. Also, the strain rate is selected to be rather high and always less than 12min/min. Generally a strain rate of 10mm/min is used for both unchanged and charged samples. The results show a slight increase of the yield stress for all samples and even in some cases the fracture strength also increased for structural type of steel. However, for all cases there was a noticeable decrease of the elongation at rupture after hydrogen after charging 48h.

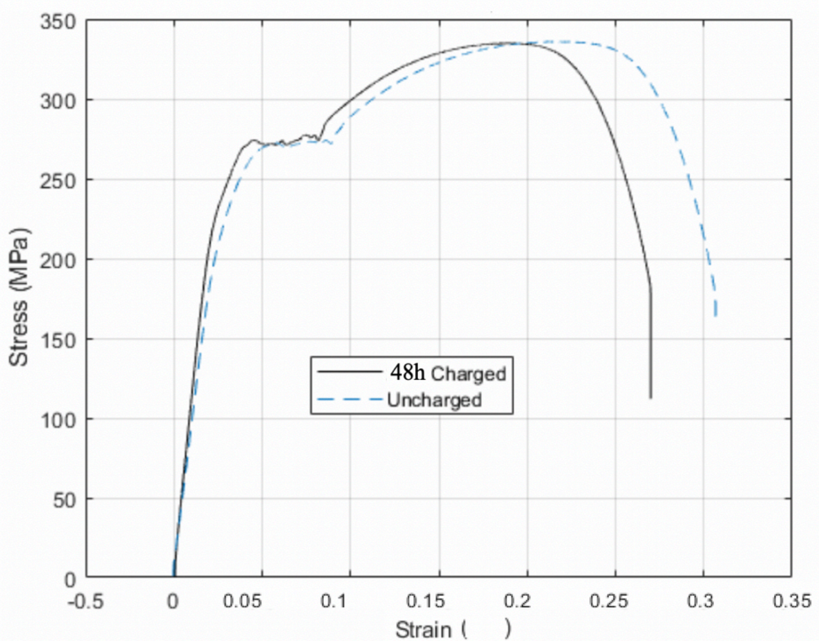


Fig 5. Structural steel specimens with 48h charging time in solid line, and without charged dashed line.

For each case 3- 5 tests were performed. The charging time varied from 24 hours to 144 hours with 24 hours increment for each cases. Therefore, in total more than 50 tests were performed. Since, we can only charge one sample at a time and for longer charge it took 6 days so it is quite time consuming and the process is slow. Since the sample is 12 mm think in dimensions, the charging time which is less than 12 hours did not made any difference, also for longer charging time the oxide layer put some barrier to hydrogen get inside metals and also in some samples there is a sever corrosion and they take over takes over the diffusion. So we hesitated to make any conclusion that the longer the charging time the sever the influence is. Thus, the results are very much depends on the different manufacturing process of the material, different alloying elements and the test conditions .ect.

Structural steels are cheap and highly corrosive, in this project it is mainly used for pre study case for the application of rivets and bridges. Besides this, a high strength stainless steels (SS) are also studied as they are used in a critical applications in the industries for gas turbine, rocket engines and fuel tanks when hydrogen used as a a green energy instead of fossil fuels. For this first tensile tests were performed for H2 charged specimens. All tests without H2 charged are very repeatable. As it can be seen from Fig 6, the results are highly repeatable, see the solid lines for two tests. For the case of little bit scatter more tests are performed. However, the scatter is very little. The slippage of grip was been very problematic no matter how much one can tight the grip. Thus, displacements are extracted from DIC measurements. Fig6, shows the comparison of stress-strain curves of results from tensile test machine versus results of DIC, solid vs dashed lines for SS304.

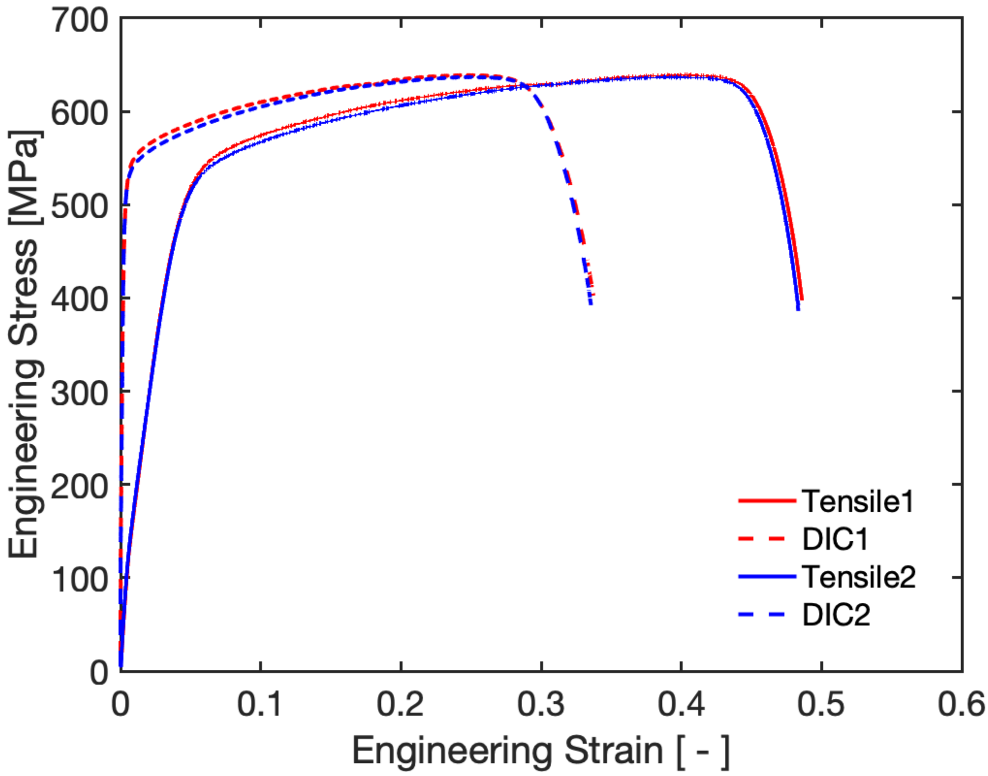


Fig 6. Stress-strain curves of SS304 comparison of results from tensile test measurement vs Correction of strains with DIC measurement

Similar approaches are also performed for H2 charged specimens that after each test strains are corrected with DIC results, H2 pre charging mainly performed for 48 hours. For H2 charged case, tests were performed for 3-5 specimens, results are averaged over total number of specimens and compared the corrected results of without charged ones. Fig 7, shows the comparison of results from without charged and H2 charged tests for 304. It is shown there is an influenced of hydrogen for SS304 on both stress and strains, and the influence is rather small over. However, the fracture surface showed a clear differences between charged and uncharged.

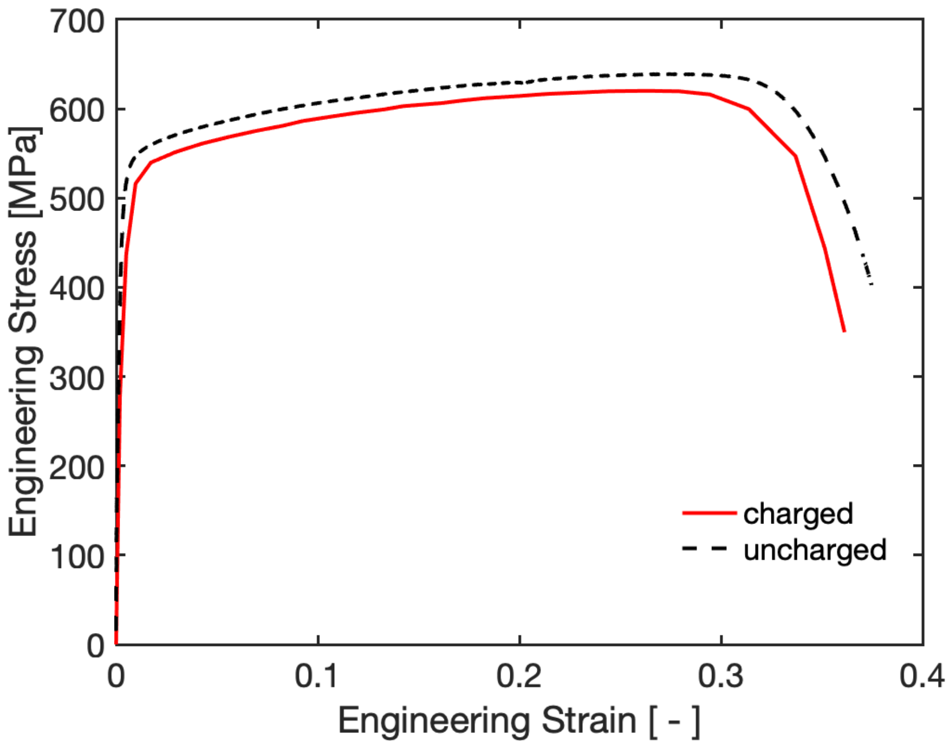
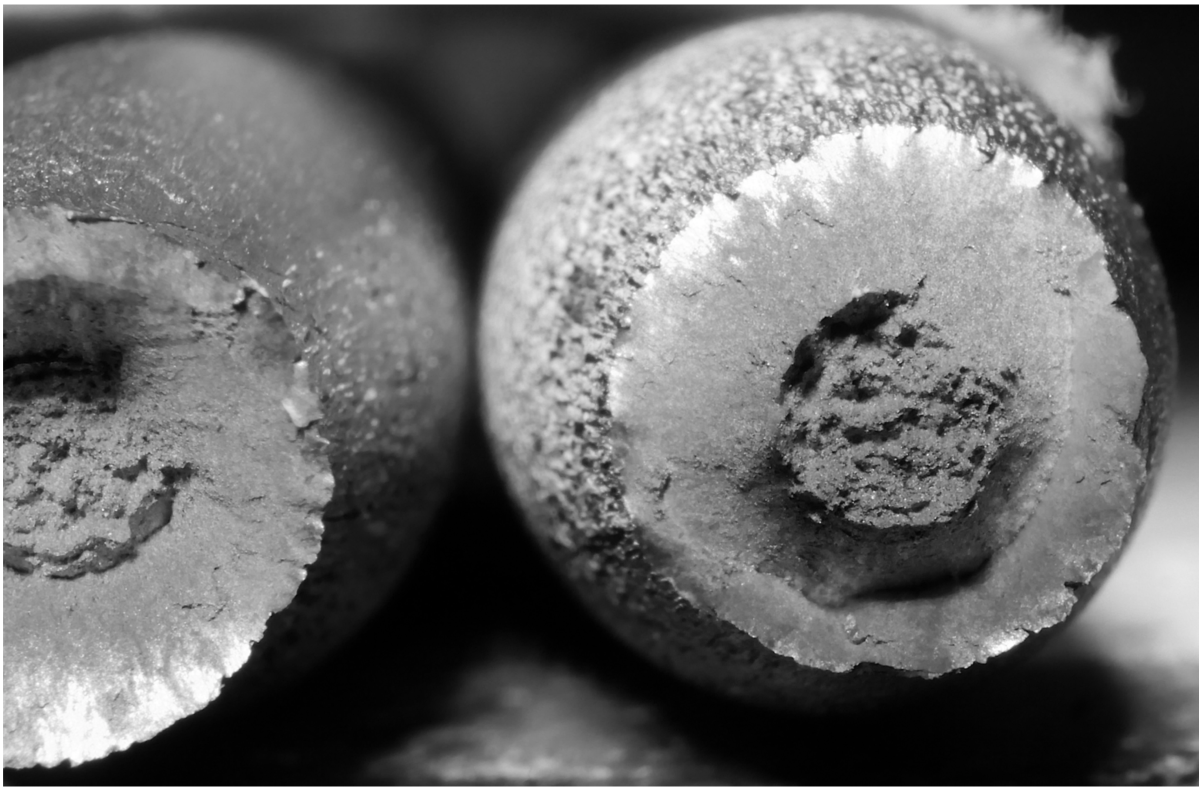


Fig 7. Stress-strain curves of SS304 comparison of results with H2 charged and without charged specimens

Fig 8 show the comparison of fractures surface of SS 304 of H2 charged and without charged specimens. As one can see, the sample without any H2 charge shows a smooth elongation of necking surface, however the H2 charged one showed a wavy patterns fracture at the necking. This comparison is very visible from side views of fracture surface, which is shown in Fig 8 c) and d).



a)

b)

Fig 8 The comparison of fractures surface of SS 304 a) without charged , b) with H2 charged

a)

b)

Fig 8 Side view of fracture surface of SS304 c) without charged , d) with H2 charged

Similar tests were performed for SS316 L also and the results are presented in Fig 9. Similar observations are found for this type of materials as well that there is an influence but rather small. However, there is a noticeable difference in fracture surface that very similar patterns of fracture surfaces are observed as it is from SS304.

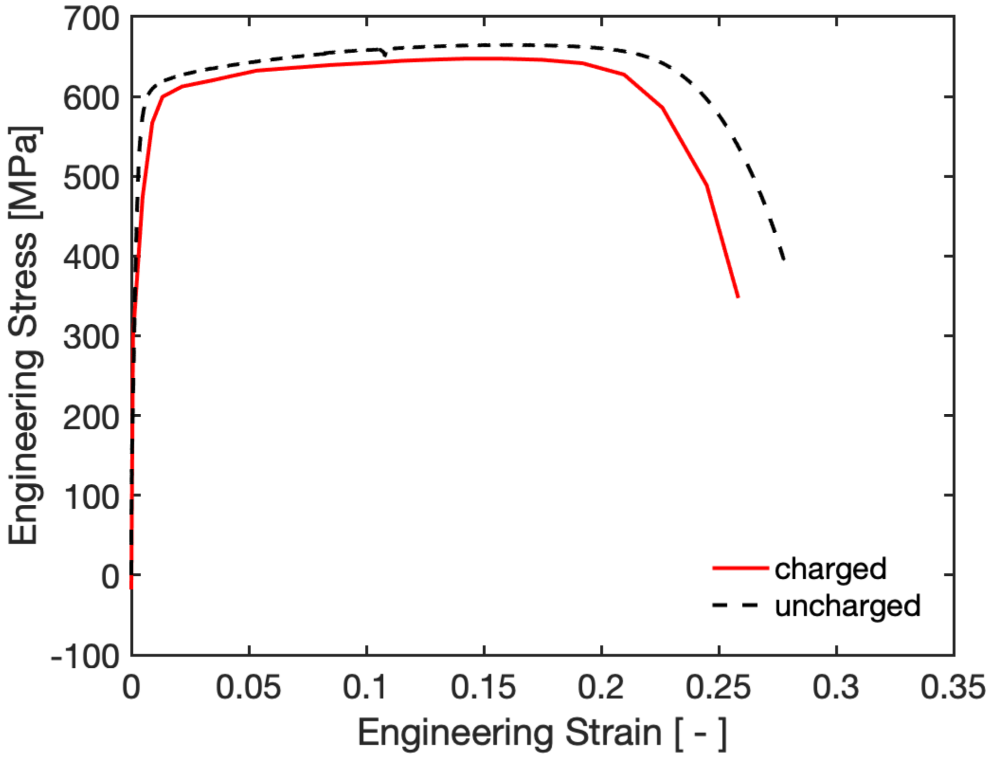


Fig 9. Stress-strain curves of SS316L comparison of results with H2 charged and without charged specimens

Similar tests were performed for SS321, and it is found that there is literally no influence of hydrogen for this type of materials, as it is shown from Fig 10. However, there is a some differences in fracture surface, see Fig 11. The difference is more visible when one zoom in with lenses.

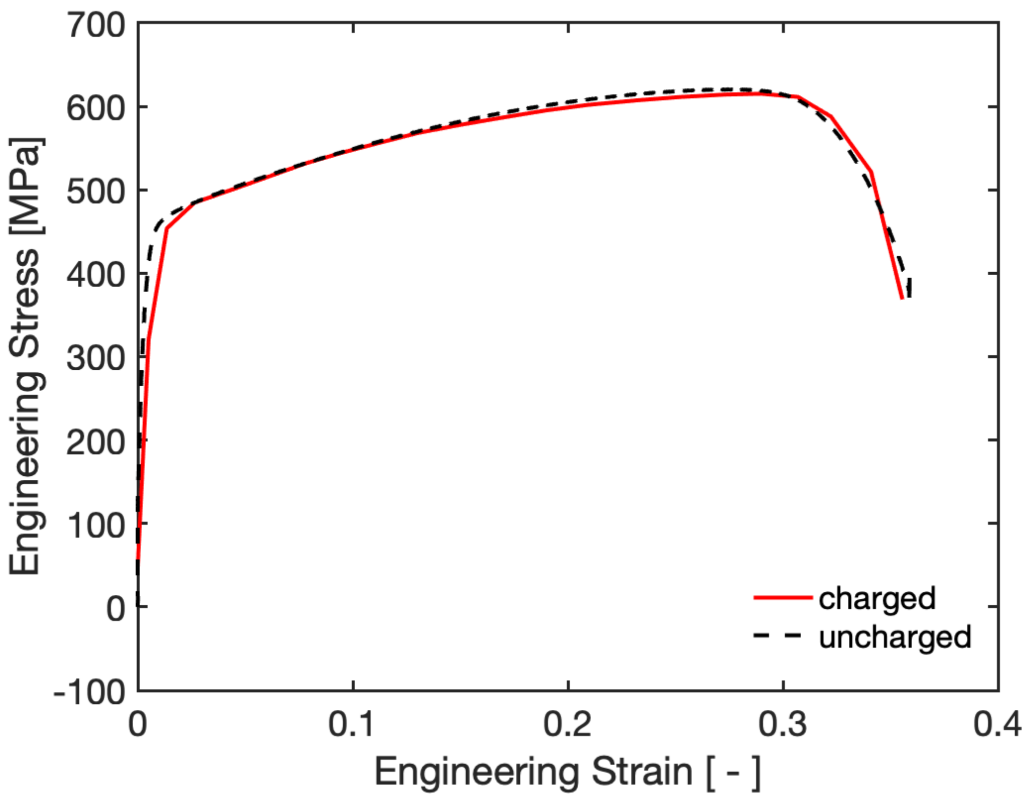


Fig 10. Stress-strain curves of SS321 comparison of results with H2 charged and without charged

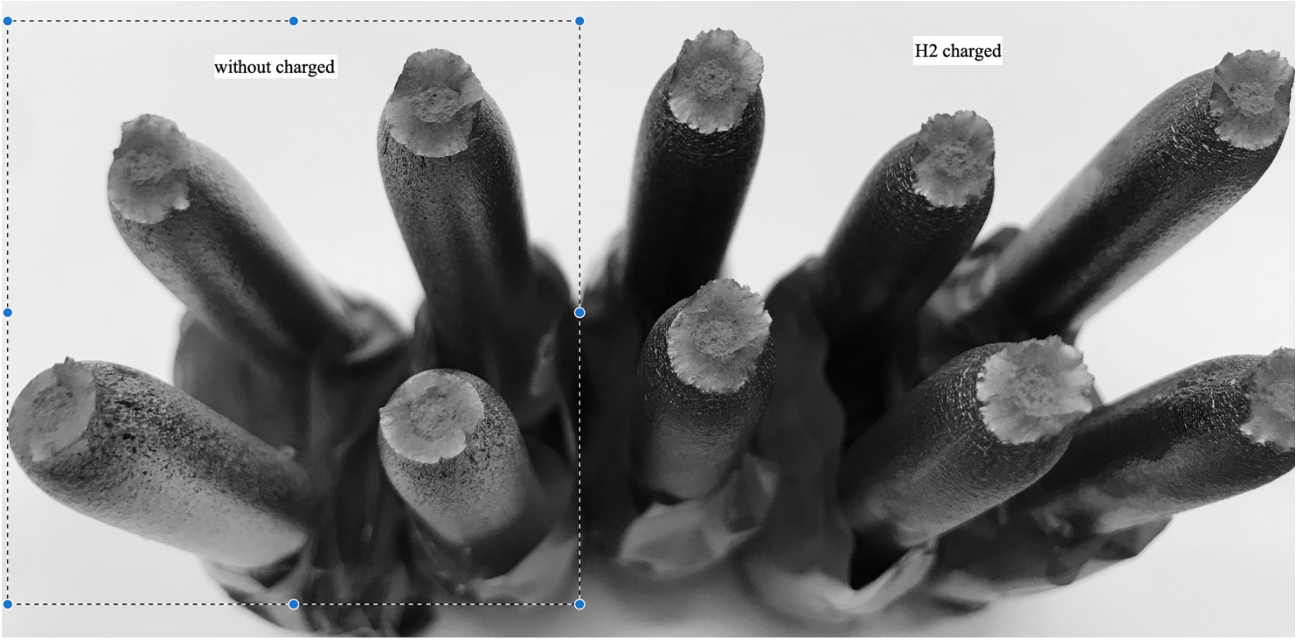


Fig 11 Comparison of fracture surface of SS321, without charged(left, two sets inside frame) and with H2 charged (right, 3 sets)

A prototype device for in-situ charging during slow strain rate test was built during the project, after many failures the initial test is implemented successfully at the very end of this year. The initial tests is performed for 0.05 mm/min, and the influence of hydrogen is enormous as compared to pre-charged fast strain rate test, see Fig 12. The Fig 8 is taken with system camera with higher pixels and micro lenses, however the Fig 12 is taken with iPhone as we don't have access to that camera when we achieve this results during Christmas time. However, the difference of fracture surface of charged samples of slow and fast strain rates are enormous. The results of this data is not presented here as we don't have enough repeated data yet to confirm, however the comparison of fracture surface is presented in Fig 12. This is very exciting and interesting to many industries.

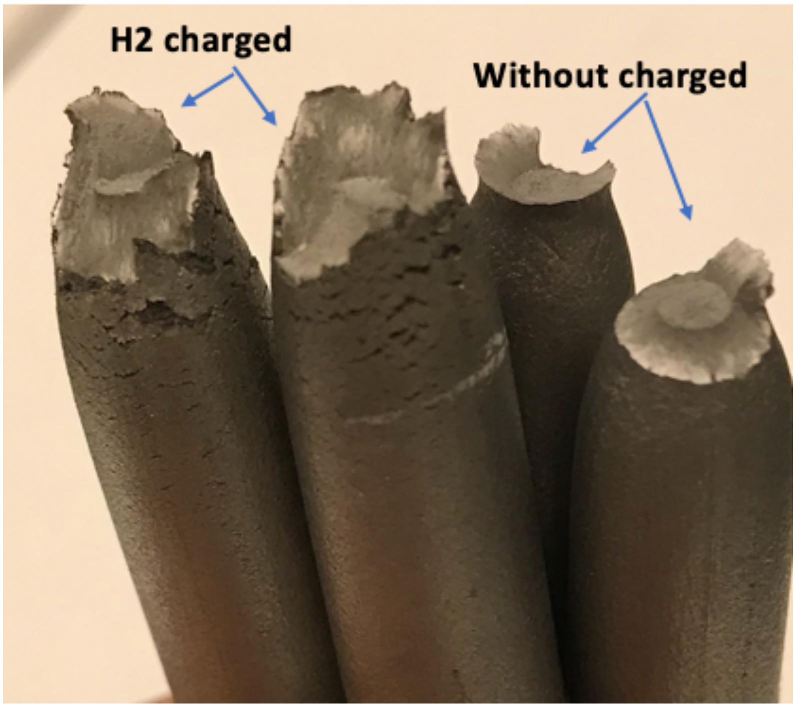
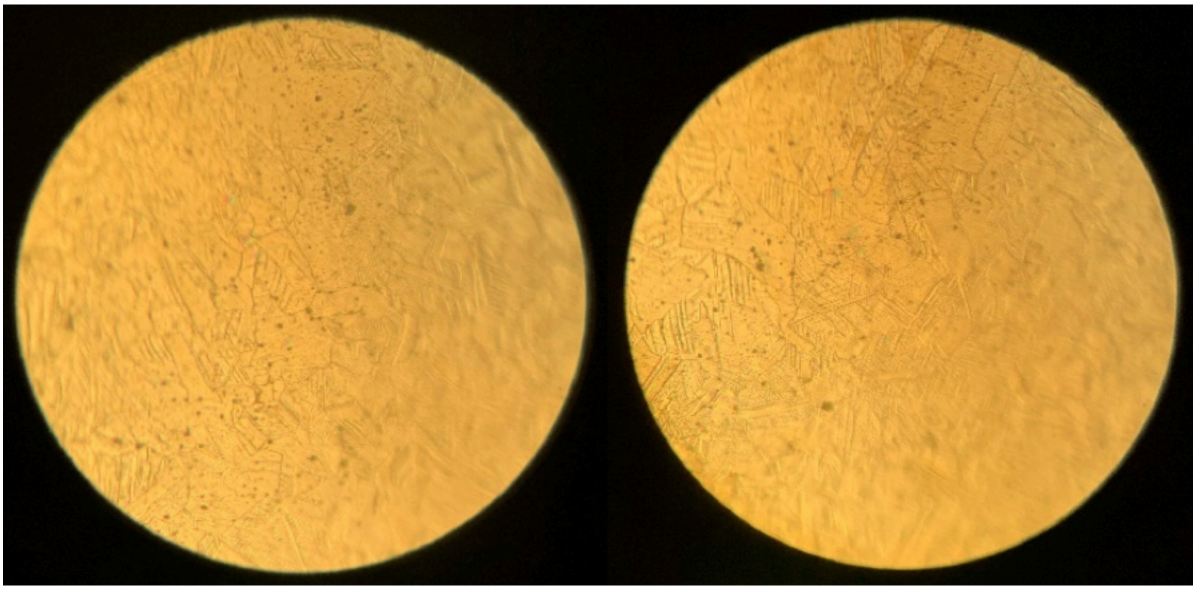


Fig 12 Comparison of fracture surface of SS316L with H2 charged and without charged for slow strain rate (Both tests are performed with slow strain rates, taken with iPhone)

Metallurgical study: Microscopy studies are performed for metallographic study with optical microscopy we have on our lab with 50x magnification. Pictures were taken with low budget camera replacing the eyepiece. Fig 13, show the grain structures charged 48h and uncharged samples for 316L. The small black dots indicate carbides formation. The chrome layer in the alloy prevents metal any further reaction with hydrogen or oxygen. Here with 48 hours of charging showing no effect of any hydrogen embrittlement on grain structure when we compare it with uncharged samples. Similar observations are made for other SS alloys studied here. However, some influences are observed for structural steels that need to be confirmed with advanced microscopy with higher magnifications.



a) b)

Fig 13. Grain structures a) without charged sample, b) with H2 charged sample. Samples are taken close around necking region, all with 50x magnification.

There are more data and results from the tests to compile and analysis, specially the grain structure related studies needs to be done with advanced optical microscope which is booked for January at other universities and SEM studies. Sample preparations for microscopic studies are already done. All results from experiments are compiling for a draft for peer-reviewed international journal publication with an acknowledgment from this ÅForsk project with Ref No: 18-489.

4. Summary of accomplishments

During this project I have achieved a number of valuable accomplishments, in the below list:
Attended 2 international conferences and summer school with the financial support from the present project:

1. The 3rd International Conference on Structural Integrity and Durability, Dubrovnik, Croatia, June 4 - 7 2019.

2. Summer school, Fatigue and Fracture Modeling and Analysis , Dubrovnik, Croatia, June 3rd–4th, 2019.

3. The 3rd International Conference on Structural Integrity, Funchal, Portugal, Sep 2 - 5, 2019

Published 4 papers kindly acknowledging the financial support from ÅForsk with project Ref No: 18-489. Two are peer-reviewed journal papers, one is peer-reviewed Procedia paper from international conferences, one is peer-reviewed conference extended abstract. And one more draft from experimental study for peer-reviewed journal publication is on the way

1. W. Reheman, P. Ståhle, M. Fisk and R. N. Singh. On the Formation of Expanding Crack Tip Precipitates. International journal of fracture, 2019

2. W. Reheman, P. Ståhle, On the Role of Anisotropic Expansion and Yield Stress on Crack Tip Precipitates, Theoretical and Applied Fracture Mechanics, 2019

3. W. Reheman, N. Claudio, M. Fisk, and C. Bjerken, A phase-field modelling of stress-induced hydride formation, 3rd International Conference on Structural Integrity and Durability, Dubrovnik, June 2019

4. W. Reheman, P. Ståhle, S. Kao-Walter, On instabilities of growing bi-material interfaces, Structural Integrity Procedia: The 3rd International Conference on Structural Integrity, Funchal, Portugal, Sep 2019

5. W. Reheman, M. Maqsood, P. Ståhle, and S. Kao-Walter, Influence of Hydrogen on Mechanical and Fracture Properties of 3 different types of stainless steel and metallographic studies, (compiling test results and draft preparing for journal publication)

This project also created two master thesis with an acknowledgement for the financial support from ÅForsk for the necessarily materials for experiments. And few more other thesis are on the way for next spring

1. Mahmoud Sobeih & Moazzam Maqsood, Influence of Hydrogen Charging on Mechanical Properties and Microstructure of Structural Steel & Duplex Stainless Steel 316L, Master thesis, Department of Mechanical Engineering, BTH, Sweden, Autumn 2019

2. Amirali khaliliaa, Influence of Hydrogen on Mechanical and Fracture Properties of duplex stainless steel and metallographic studies, Master thesis, Department of Mechanical Engineering, BTH, Sweden, spring 2020

This project also leaded other cooperation with industry and academy

1. Visited Siemens in Finspång for discussion about Siemens interest in hydrogen embrittlement and discuss my results and established collaborations for further studies of hydrogen embrittlement, also visited their turbine assembly workshop and additive manufactory Lab.

2. Discussion and sharing of the results with academics: Prof. Per Ståhle, Lund University, Assoc. Prof. Martin Fisk, Malmö University, Prof. Alexdra Hartmaier and Dr Mahdi from Ruhr University, Germany.

3. Visited Ruhr University in Germany and discussed my results and established collaborations for 2020.

5. Future plans

While this project has been very rewording and productive, opened new doors for other projects and collaborations, still a number of open ends remain. Most prominently, we are currently in the process of building a prototype for cathodic charging during slow strain rate test (the initial trial is implemented successfully) this allows us to test thinner samples and the influence of thickness for the hydrogen embrittlement. The influence of temperature and heat treatment is another ambition that arouse during this project. For these aspects, we are initiating a thesis project at present. The cathodic charging test for fast strain rate test is now established in our lab and it is working well. Hopefully, we will continue with fracture mechanical studies about hydrogen embrittlement and further advancement of our testing set up remains to be our driving force. For continuing the research in this direction we have applied funding from the knowledge foundation in collaboration with industry partners in Sweden.

6. Reference

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