CHARACTERIZATION OF MATERIALS IN PRESSURIZED HYDROGEN UNDER CYCLIC LOADING AT SERVICE CONDITIONS IN HYDROGEN POWERED ENGINES

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ABSTRACT

A new testing device for cyclic loading of specimens with a novel shape design is presented. The device was applied for investigations of fatigue of metallic specimens under pressurized hydrogen up to 300 bar at temperatures up to 200 °C. Main advantage of the specimen design is the very small amount of medium, here hydrogen, used for testing. This allows experiments with hazardous substances at lower safety level. Additionally no gasket for the load transmission is required. Woehler curves which show the influence of hydrogen on the fatigue behavior of austenitic steel specimens at relevant service conditions in hydrogen powered engines are presented. Material and test conditions are in agreement with the cooperating industry.

1.0 INTRODUCTION

1.1 Hydrogen in cars

Alternative fuel and drive train solutions represent one of the biggest challenges for the vehicle of the future. In response to the greenhouse effect, increasing costs and limited sources of fossil fuels, new options of clean and renewable fuels are under investigation. Hydrogen is an answer to environmental pollution, greenhouse effects, energy efficiency and security of supply.

The liquid hydrogen fuel tank, as shown in figure 1, consists of double-wall cylindrical vessels that hold a hydrogen storage mass of about 9 kg. The preferred shell material is stainless steel, since it is very resistant against hydrogen brittleness and shows negligible hydrogen permeation. The space between the inner and outer vessel is mainly used for the thermal insulation, composed of reflective aluminium foils separated by glass fibre spacers and vacuum.

The auxiliary system box is connected to the fuel tank. It contains all components used to condition the hydrogen mass flow and temperature. Herein, all valves and sensors are housed in valve blocks made of stainless steel. During operation the valve blocks are exposed to very low temperatures down to 20 K at a pressure up to 0.8 MPa. The thermal stress must not lead to leakage or cracks in the material.

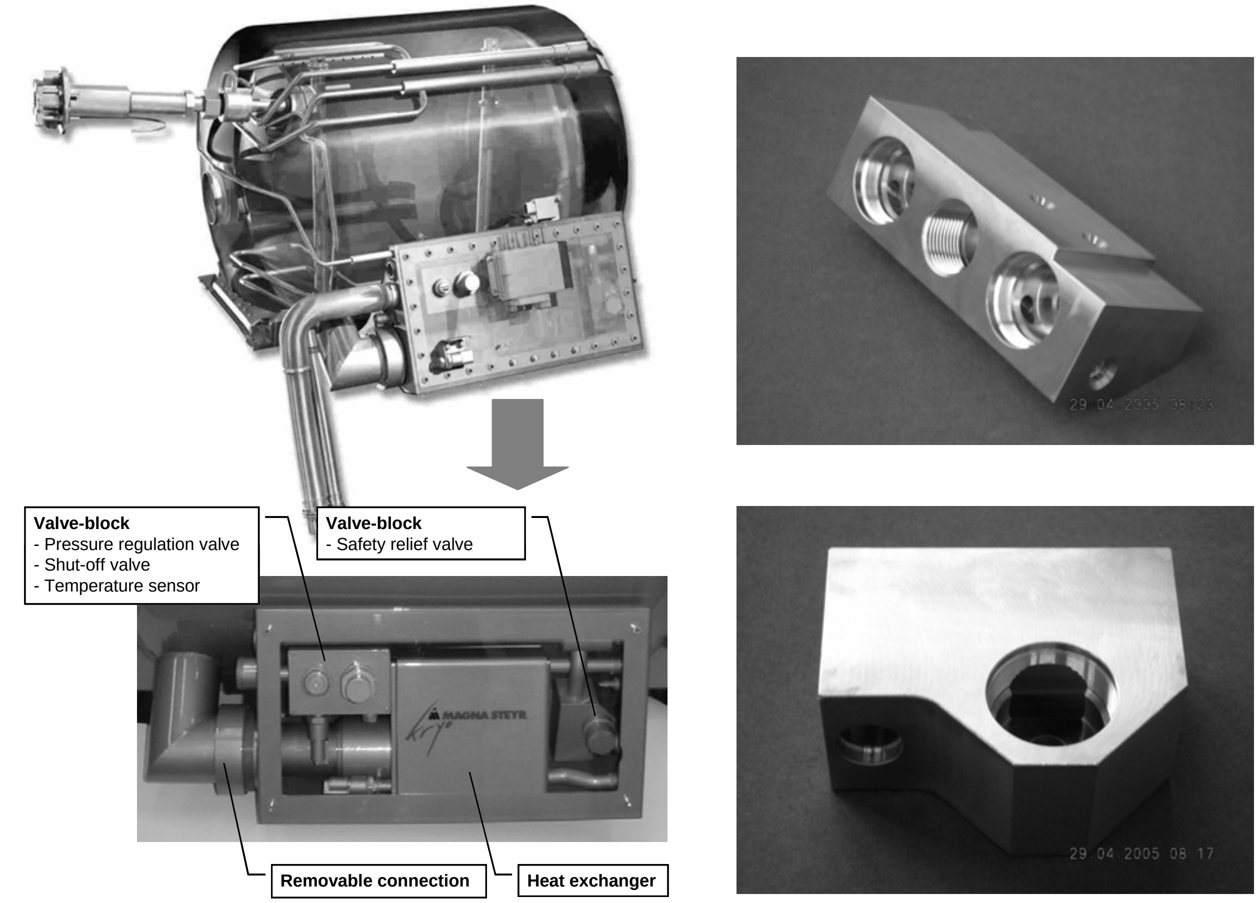


Figure 1. Liquid hydrogen fuel tank system (upper left: fuel tank; lower left: auxiliary system box; upper right: sensor block; lower right: valve block)

1.2 Fatigue testing of metallic specimens

Hydrogen as an energy carrier of future transportation gives new challenges for component design. The new tasks may not be more complicated than the ones solved for conventional fuel, but in order to reach the state of the art in transportation in terms of safety and reliability new techniques and data bases for new fatigue design and testing have to be created.

Structural durability compiles the strength of a component under service loading; including overloading, buckling, creep and cyclic loading as well as relevant environment such as temperature, corrosive media and atmospheres. The fatigue strength is partitioned in low cycle fatigue ($N < 5*10^4$ cycles), finite cycles regime ($5*10^4 < N < 2*10^6$ cycles), high cycle fatigue ($N > 2*10^6$ cycles) and variable amplitudes fatigue.

The investigation of material behaviour under overloads which exceed the yield point is accomplished best by determination of cyclic stress-strain curves and strain controlled Woehler curves (S-N curves). Comparison of the cyclic stress-strain curve with the monotonic curve shows cyclic hardening or softening behaviour of the material. Furthermore those curves can be used for determination of stresses in notched areas [1, 2].

Depending on the design criterion strain controlled Woehler curves, load controlled Woehler curves or crack propagation laws are employed.

1.3 Design concepts

For designing a component data for loading, shape, material and manufacturing technique are required. Material, geometry, manufacturing technique and environment determine the strength of a component; loading and geometry determine global and local stresses. Fatigue assessment is accomplished by the following approaches [2 - 7]:

Nominal stress approach: This approach compares fatigue critical cross sections of a component part with respect to notch stresses with a Woehler curve which was measured under comparable characteristic circumstances (stress concentration factor, size, material, loading mode, manufacturing technique, environment). Basic Woehler curves considering different stress concentrations are published e.g. in [8 - 13]. Characteristics (like different notch stresses, stress ratio in cyclic testing R) which are not considered in the basic Woehler curves must be estimated by experience. The approach is not applicable for complex components which don't permit the determination of a nominal stress nor the stress concentration factor.

Local stress/strain approach (notch stress related approach): The drawback of the nominal stress approach is the negligence of the consideration of the local stresses which lead to failure. Due to crack initiation by those local strains/stresses a calculation by finite-element-analysis or a local measurement by strain gauges with small gauge length allows the estimation of the local stress conditions. The maximum local strain/stress is compared with a Woehler curve determined with un-notched specimens under axial loading in a strain controlled experiment.

Local stress/strain approach under consideration of the strain/stress gradient and the highly stressed material volume: The consideration of the maximum local stress or strain to assess endurance of a component is not always sufficient. The stress gradient and with this the highly stressed material volume determine the endurance properties of the construction [2, 3, 7]. The influence of the highly stressed material volume has to be considered for comparing the maximum local stress with a Woehler curve. This influence is determined by systematic examination of local strains/stresses for different high stressed material volumes [2, 7]. Best practice in automotive design is the determination of characteristic material data by cyclic loading of components or specimens similar to the final components.

1.4 Equivalent stress, allowable stress and fatigue life estimation

Stresses in critical zones in components are mostly multi-axial. In order to make an assessment they have to be transformed in an equivalent stress by an appropriate strength hypothesis [14 - 16]. Differences of phase in the stress-time hysteresis have to be considered.

An assessment of the allowable stresses is commonly based on material data for a probability of failure of 50 %. The allowable stresses are based on the scatter of stresses in service as well as the scatter in manufacturing and fatigue. Depending on the safety level of the component a higher probability of failure or a higher safety factor has to be used for design. Routine inspections can allow the use a lower safety factor.

The fatigue life estimation in case of variable amplitude loading requires the application of a damage accumulation hypothesis, e.g. Palmgren-Miner with modification according to Haibach [4, 5].

1.5 Fatigue testing of Hydrogen charged specimen

In automotive applications hydrogen can be used in the form of high pressure gas (high pressure tank system), liquid gas (liquid gas tank system, at cryogenic temperature), low pressure gas at medium temperatures (delivery tube system) or as low pressure gas at high temperatures (hydrogen fired spark-ignition engine). According to the statement in chapter 1.3 a measurement of fatigue data is performed best at an environment comparable to the latter service conditions (hydrogen pressure, temperature). Behind the tank system the hydrogen is transported at ambient temperature and a pressure between 2 and 10 bar.

Two main alternative ways to charge materials with hydrogen are used: electrolytic charging and charging at elevated hydrogen pressure. In order to stick to the rules from chapter 1.3 we prefer charging at elevated pressure in service conditions in terms of cyclic loading (due to the difficulties in estimating the hydrogen absorption and the diffusion rate under cyclic strain).

For design reasons a basic knowledge of material data from which most assessments for different approaches can be derived is the most valuable. The basic material data for the assessment of fatigue strength is a local design curve which is derived from tests with notched specimens, charted in the nominal stress system, figure 2, curve 1. From this curve, the local SN- curve, curve 2, is calculated by knowledge of the stress-concentration factor. (This can be also derived from a finite-element calculation, see chapter 2.0). This curve is in relation to a given highly stressed material volume, determined by knowledge of the stress gradient in the notch, figure 3 right. The results in the local system are calculated for a probability of survival of 50 % which is much too small for design reasons. A third curve, the local design curve, is derived from the curve charted in the local system (figure 2, curve 2) taking into account the safety factor and a reasonable probability of failure of the parts (10 ppm in figure 2). If the critical area of a component has a different highly stressed material volume, than the volume for which curve 3 in figure 2 was derived, curve 3 can be shifted according figure 3, left, for considering the actual highly stressed volume.

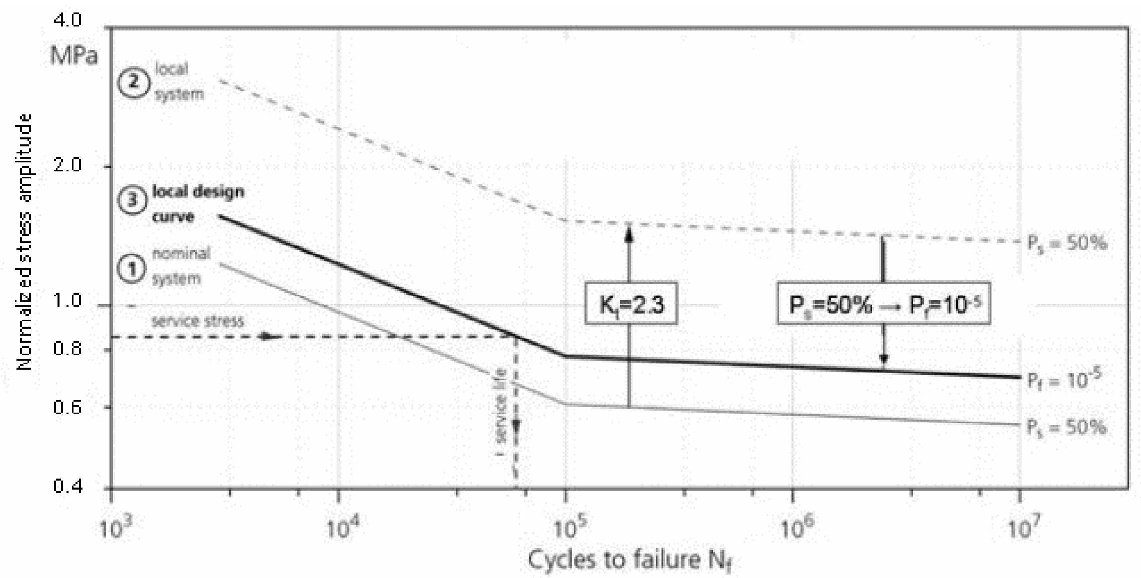
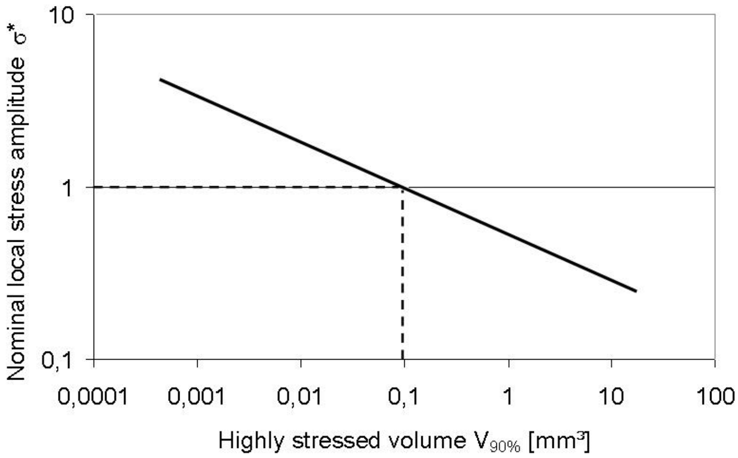


Figure 2. Woehler curve with local- and nominal stress/strain system, notch factor K_t = 2.3, probability of failure P_s = 50%, probability of survival for design P_f = 10 ppm.



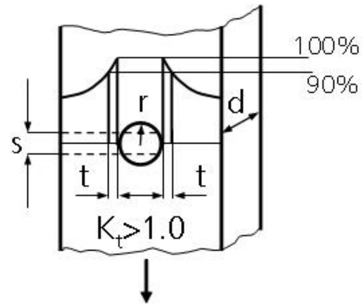


Figure 3. Left: Local stressed amplitude vs. highly stressed volume $V_{90\%}$. Right: Highly stressed volume $V_{90\%}$ in a notched tension specimen.

In order to perform experiments under relevant conditions a new specimen which allows fatigue tests under pressurized hydrogen with small amounts of hydrogen was designed for running the experiments on a low safety level (at low costs).

2.0 EXPERIMENTAL SETUP

Specimens from austenitic steel (Mat. No. 1.4306), used for the delivery tube system, were tested under pressurized hydrogen (10 bar, pureness 99.999 %) at room temperature. This is conforming to the conditions in the hydrogen delivery system behind the tank. The chemical composition is given in table 1; the steel was solution annealed at 1050 °C and water quenched.

Table 1. Chemical composition of the specimens.

	C	Si	Mn	P	S	Cr	Ni	B	N	Co
[%]	0.023	0.35	1.60	0.035	0.002	18.36	10.18	<0.0005	0.0263	0.15

A servo-hydraulic testing device with a maximum load of 63 kN at maximal 20 Hz was used. The testing device is equipped with a tempered safety chamber which can be Nitrogen floated, if needed, figure 4 left. The temperature range is up to 200 °C in this setup.

The picture on the left in figure 4 shows the new specimen for cyclic testing. In order to perform tests with pressurized hydrogen under the given safety settings the specimen mentioned in chapter 1.5 was designed to allow the measurement of cyclic fatigue properties with very small amounts of hydrogen. In this specimen the hydrogen is put into a cavity in the specimen (also under pressure, if needed) and on the outside atmospheric pressure is present, figure 4, right. The specimen has a defined internal notch in order to examine the results according to the rules from chapter 1.5. With this the charging of the material with hydrogen under load in the highly stressed material volume is equal to the loaded volumes in latter components.

New in the design of the specimen is first: the small amount of hydrogen which allows testing in common workshops without special safety equipment. If the specimen fails the amount of hydrogen is dissolving under a not combustible concentration. Still self-evident safety precautions like no open flames are appropriate. Second advantage is the load transmission without a gasket in the hydrogen chamber. If the hydrogen is applied from the outside of the specimen a chamber with the hydrogen is needed. The sealing at high pressure is a challenge for constructions with a moving part like the load transmission. In this specimen design any medium can be applied without a sealing to a moving part without expensive safety equipment (legal requirements have to be considered) and still relevant load conditions (relating to the highly stressed volume) and relevant environment (hydrogen inside, air outside) is applied.

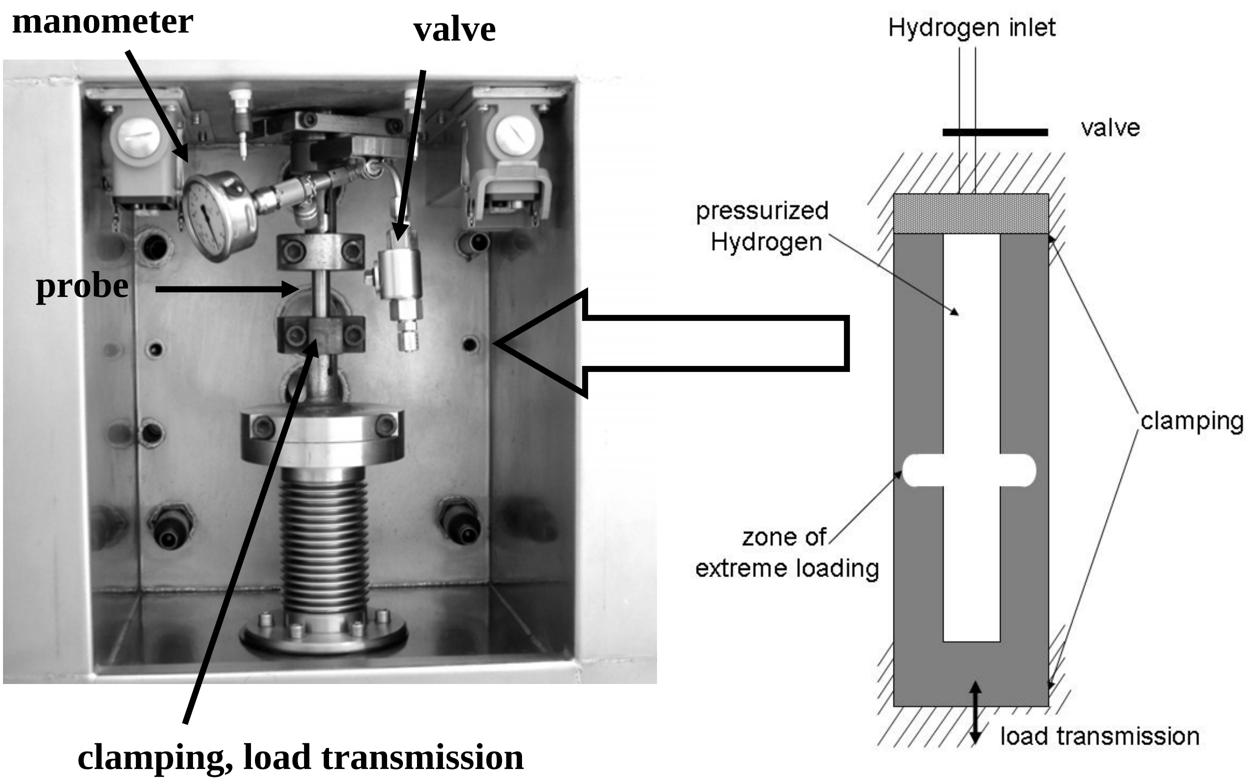


Figure 4. Left: Servo-hydraulic testing device with Nitrogen floated safety chamber. Right: New designed specimen for measurements with small hydrogen volume.

Figure 5 shows the design of the specimen with the internal notch in the cavity. Due to the symmetry only a quarter of the specimen was modeled and meshed with tetra-elements with mid-side nodes. Internal pressure of 10 bar is applied while the specimen is axially loaded. On the left in figure 5 the area with highest stresses is calculated in order to examine the zone of failure. On the right the element-volume (V_{ges}) with a von-Mises stress level from 90 to 100 % is calculated. According to chapter 1.5 this volume is needed to shift the local design curve to comparable nominal stress amplitudes for given highly stressed volumes in the latter component. The specimen is designed with a notch factor of 2.3 which ensures a failure in the notch.

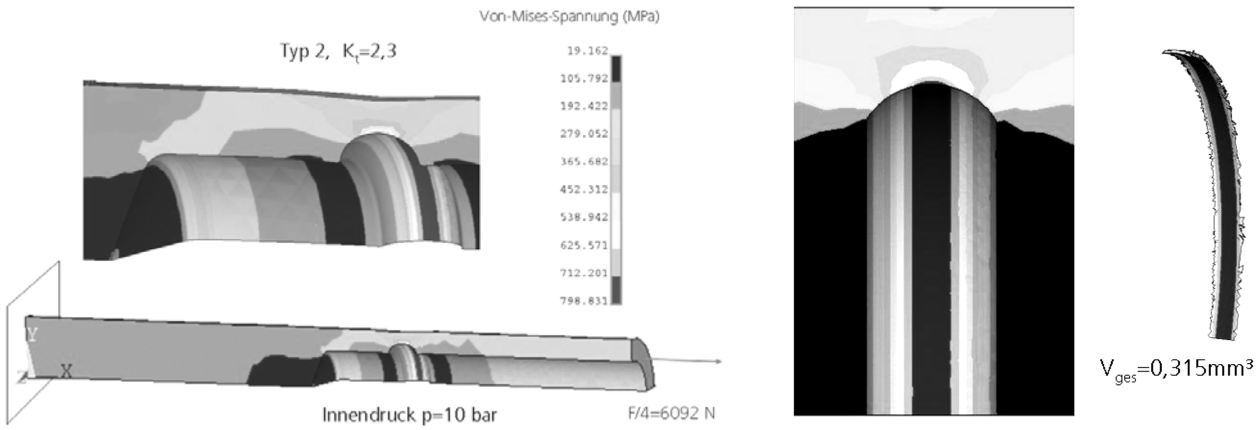


Figure 5. Left: Stress calculation of the new specimen. Right: Calculation of the highly stressed volume.

2.1 Remarks to testing

Three general types of hydrogen embrittlement are distinguished [e.g. 17]: Hydrogen reaction embrittlement, internal hydrogen embrittlement and hydrogen environment embrittlement (also external hydrogen embrittlement). The first type describes the reaction of hydrogen with the material or an alloying element of the material and the formation of embrittling reaction products. The second type describes the influence of hydrogen from the manufacturing process or from welding in terms of diffusion and segregation at internal defects. The last type of hydrogen embrittlement deals with effects appearing during plastic deformation of the material and the interaction of the deformed zone with the gaseous environment and the subsequent transport (diffusion) of the hydrogen to the zone of embrittlement.

Due to the complex processes of hydrogen dissociation, absorption (adsorption, passivation) and diffusion [17 - 19] small changes in the test setup could lead to results which are not comparable with service conditions. Especially the weighting of the different metallurgic effects in slightly different test setups makes derivations from well known effects from hydrogen-free testing difficult. As an example the influence of different heat treatments on the low-cycle fatigue properties of steel in air and in pressurized hydrogen is shown in figure 6 (taken from [17]).

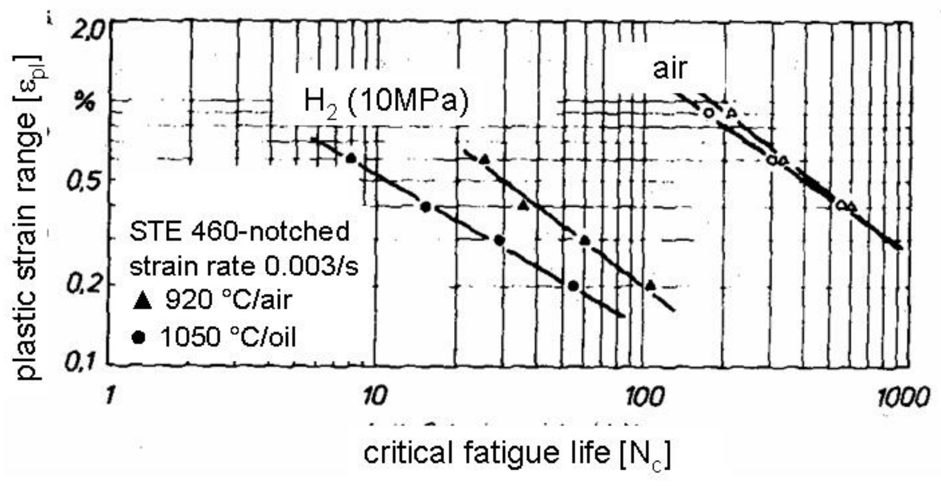


Figure 6. Low-cycle fatigue properties of steel with different heat treatments in air and pressurized hydrogen.

In the presented specimen the highly stressed volume as the area of crack initiation and crack propagation is examined. Due to the test conditions with pressurized hydrogen applied to this highly stressed volume dissociation, absorption and diffusion are comparable to service. The hydrogen gradient in the material, depending on the stressed volume and the stress gradient, is the same as under service conditions. With this results from testing can be transferred to service conditions and be implemented as predictive material models in numerical simulation.

3.0 RESULTS AND DISCUSSION

The material supplied by Magna Steyr was metallographically examined. The steel (mat. no. 1.4306) is austenitic with twins on the grinded surface. Bands of delta-ferrite were found and quantitative analyzed by image analysis. The surface fraction of delta-ferrite in the representative picture in figure 7 is 3.5 %.

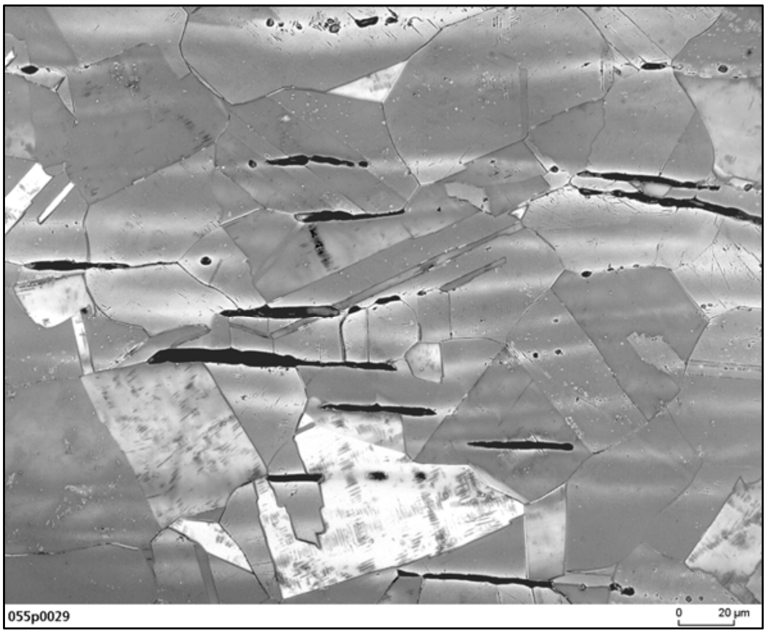


Figure 7. Microstructure of the examined material (mat. no. 1.4306), dark: delta-ferrite, surface fraction of delta-ferrite: 3.5 %.

The specimens manufactured according to the new design were tested for pressure tightness and repeatable failure at the designated zone. Due to the notch factor of 2.3 all tested specimen failed in the notched area, with internal pressure and without pressure as well. Two sets of tests were performed: one in air at 1 bar and one with hydrogen atmosphere of 10 bar in the specimen and air outside of the specimen. These test conditions represent service conditions of delivery tubes from the tank system to the engine.

Figure 8 shows the results on first testing with the new specimen. The tests were performed with a frequency of 15 Hz (exceptions (2 Hz) are mentioned in the diagram) and a stress ratio of R = -1 and R = 0. The stress ratio R is the ratio between minimum and maximum load of one cycle.

The effects caused by hydrogen in low-cycle fatigue are well-known, e.g. see figure 6. According to literature with rising number of load cycles the differences between hydrogen charged material and hydrogen-free material should become smaller [17]. In our tests the difference for high loading is rather small, for higher load cycles the endurable nominal stress amplitude decreases for 15 %. An influence of the load frequency

(15 Hz vs. 2 Hz) for higher load levels was not found. The mean stress sensibility M ($M = \frac{\sigma_a(R=-1)}{\sigma_a(R=0)} - 1$) is found as 0.26.

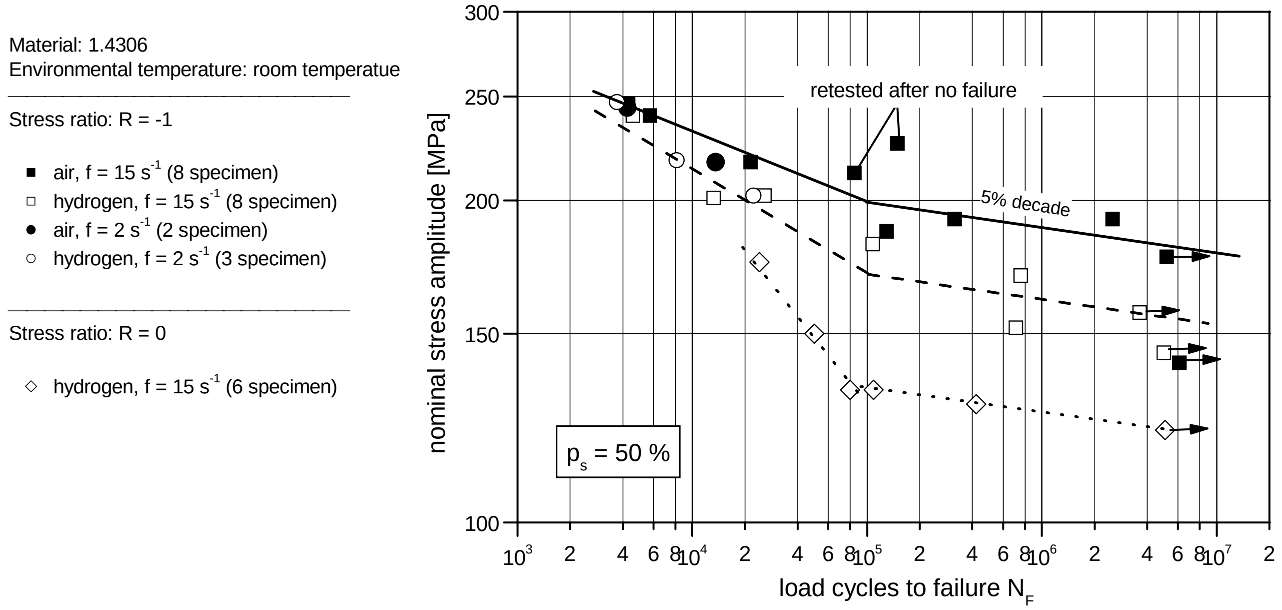


Figure 8. Curve 1: Results for experiments with the specimen design

4.0 CONCLUSIONS AND OUTLOOK

On the example of hydrogen as a hazardous medium endurance testing on austenitic steel was performed. The new specimen design has proven its potentials for safe testing under hazardous medium with low safety equipment in a common workshop.

Besides testing at elevated temperatures testing with variable amplitudes (Gassner curves) is necessary. Further on the influence of the load frequency has to be examined to higher load cycles. In our tests no significant influence for low cycle fatigue was found, but this should be target of further examinations especially at very low frequencies. Combinations of the temperature, load frequency and other environmental influences have to be considered.

5.0 LITERATURE

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