Influence of Hydrogen on Fatigue Strength of Austenitic Steels

Hydrogen as a climate-neutral energy carrier provides a promising alternative to fossil fuels. In addition to the exposure to mechanical loads, components and facilities for generation, storage and use of hydrogen are exposed to the deteriorating influence of hydrogen. Apart from the experimental suitability test of the components used, it is necessary to determine the mechanical and technological material properties for the computational design of components. Within the framework of a FVV research project No. 1163 funded by BMWi, at the University of Stuttgart materials were investigated under cyclic load. All investigated materials, for example an austenitic steel, are relevant for practical applications in mechanical and plant engineering.

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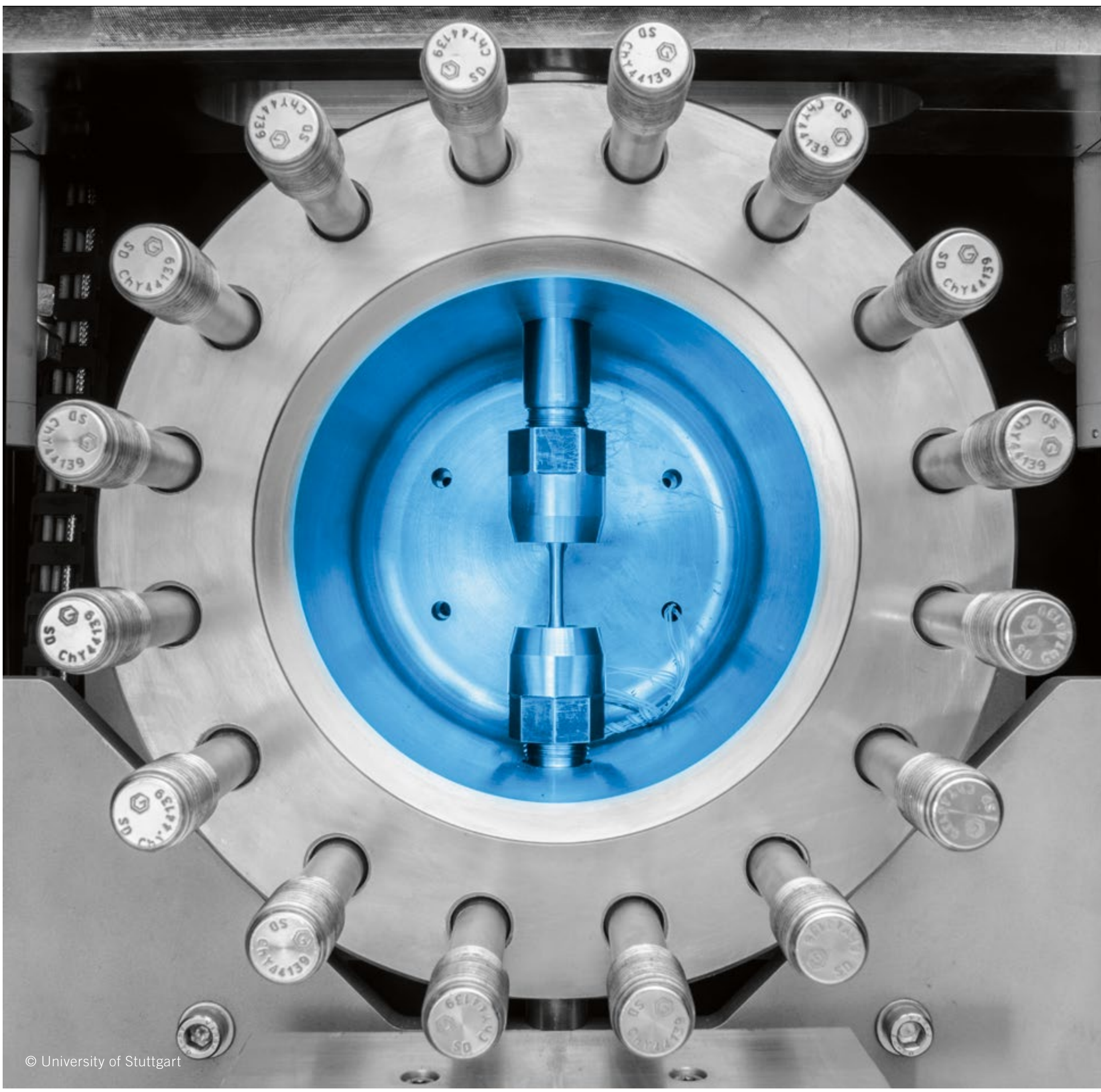

1 MOTIVATION

Several standards and regulations are available for the approval of safety-relevant components for use in hydrogen or hydrogenous gases, for example the Canadian Standard CSA CHMC 1-2014 [1], the API Standard 617 [2] and the AD 2000 Code [3]. Depending on the respective field of application for the component, either safety factors or positive lists are available for applicable materials or application limitations are set. However, no concrete details regarding the reduction of relevant strength and ductility properties are given. This data is essential for a safe and cost effective component design. Furthermore, research is still needed on significant influential factors, such as temperature, pressure and load frequency on material behaviour in gaseous compressed hydrogen. In order to close this knowledge gap, tensile, fatigue and crack propagation tests were performed in compressed gaseous hydrogen atmosphere on the austenitic steel X2CrNi19-11. Investigations were performed in order to demonstrate the impact of hydrogen on damage mechanisms.

2 RESULTS

Tensile tests with a constant extension rate of 0.1 mm/min (CERT) were performed on a metastable austenitic material for characterisation of static strength and deformation behaviour. The investigation was of the material X2CrNi19-11 in a modified version with a deliberately increased nickel content in order to enhance the resistance to hydrogen-induced embrittlement [4]. The chemical composition of the material is provided in **TABLE 1**. The tests were performed in hydrogen (purity > 99.999 %, 100 bar) and, for comparative assessment, inert helium (purity > 99.999 %, 10 bar) at room temperature (RT) and T = -50 °C. The stress-strain-diagrams are depicted in **FIGURE 1**.

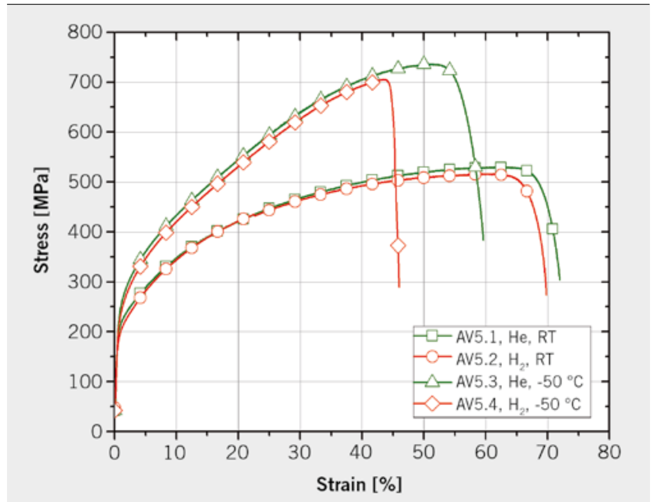

FIGURE 1 CERT tests (RT and T = -50 °C) (© University of Stuttgart)

The stress-strain-diagrams at RT show only minor differences; at -50 °C a significant hydrogen influence is visible. Tensile Strength (TS) and Yield Strength (YS) are reduced in compressed gaseous hydrogen. The deformation properties show clear embrittlement of the material in compressed gaseous hydrogen. This becomes apparent in the reduction of fracture elongation (El) by 30 % furthermore the reduction in area at fracture (RA) for the specimens tested in hydrogen is less than half of that compared to the specimens tested in helium. The RRA value describes the ratio of reduction in area in hydrogen to reduction in area in helium. The technological properties are summarised in **TABLE 2**.

Material behaviour under cyclic load in hydrogen was investigated using stress-controlled fatigue tests on notched specimens. The material was tested both at RT and T = -50 °C. **FIGURE 2** shows that for testing in helium, a higher number of load cycles can be achieved compared to testing in hydrogen. The comparison of both fatigue curves also shows that the degenerative influence of hydro-

C	Si	Mn	P	S	Cr	Mo	Nb	Ni	Ti	N
0.016 %	0.48 %	1.75 %	0.012 %	0.008 %	17.78 %	0.02 %	0.01 %	12.36 %	0.005 %	0.017 %

TABLE 1 Chemical composition of the investigated material X2CrNi19-11 with a modified nickel content (© University of Stuttgart)

Temperature [°C]	Medium	E-modulus [GPa]	YS [MPa]	TS [MPa]	El [%]	RA [%]	RRA [–]
RT	He	201	199	531	78.3	84.3	–
	H_2	201	193	514	76.3	82.9	0.98
-50 °C	He	204	229	736	62.1	84.2	–
	H_2	204	213	709	43.7	40.5	0.48

TABLE 2 Technological properties from CERT test (© University of Stuttgart)

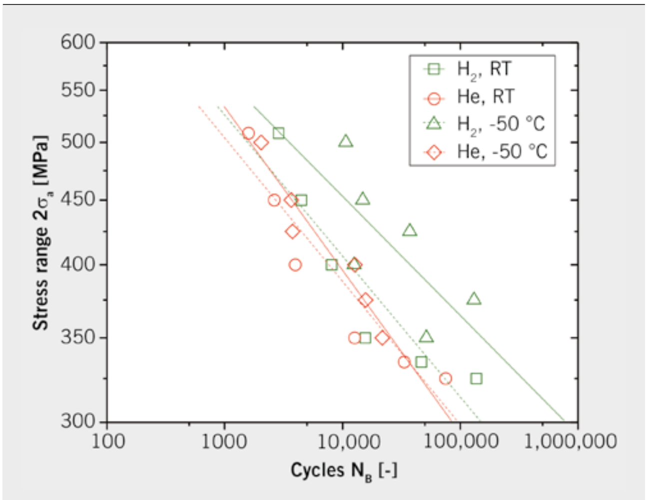

FIGURE 2 Fatigue tests (f = 1 Hz) (© University of Stuttgart)

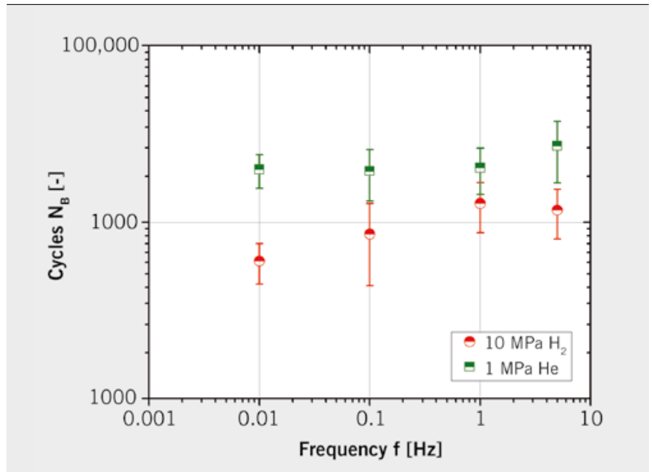

FIGURE 3 Influence of load frequency on the allowable number of load cycles (© University of Stuttgart)

gen on allowable load cycles is higher at lower temperatures. The fatigue curves in hydrogen at RT and at -50 °C are congruent within the scattering of the material.

The focus of the investigations was, in addition to the influence of hydrogen itself, the influence of load frequency. For the experimental investigation, fatigue tests were run at frequencies of 0.01, 0.1, 1 and 5 Hz; each test series was performed using four specimen. The stress amplitude was set to $2\sigma_a$ = 400 MPa, and the stress ratio was set to R = 0.1. The evaluation of the tests is depicted in **FIGURE 3**.

The average values of hydrogen tests show a falling tendency for decreasing frequencies. Due to the overlapping scattering bands, a statistical significance test was additionally performed. The influence of frequency cannot be clearly confirmed statistically, especially due to the small number of test samples. At this point, a higher number of samples or additional methods for verification are required. Therefore, the fracture surface of the samples was investigated by fractographic measures. The X2CrNi19-11 steel is metastable and forms, under plastic deformation, α'-martensite, which can be detected by X-ray diffraction (XRD). The microstructural constituents on the fracture surface are depicted in **FIGURE 4**. The analysis of microstructural constituents shows a statistically significant influence of decreasing frequencies. The content of α'-martensite on the fracture surface decreases from approximately 80 % at 5 Hz to 60 % at 0.01 Hz.

In order to complete the data on fatigue behaviour, cyclic crack growth tests were performed at T = -50 °C. These tests were performed in hydrogen at 100 bar and in helium at 10 bar; load ratio was R = 0.1. The focus of investigations was in the range of stabilised crack growth (Paris-Erdogan-Range). **FIGURE 5** shows, that cyclic crack growth (da/dN) proceeds by a factor of 10 faster in hydrogen as compared to inert helium. Additionally, a significantly higher gradient of the crack growth curve can be observed in hydrogen.

The fracture surfaces of selected specimens were investigated by means of a Scanning Electron Microscope (SEM). **FIGURE 6**

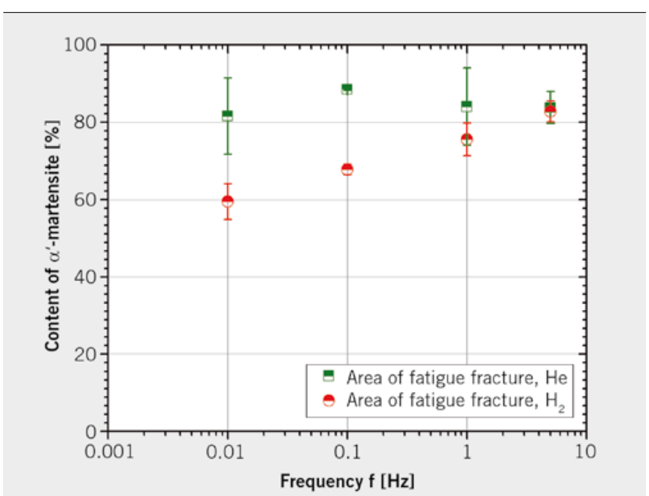

FIGURE 4 XRD measurements of microstructural constituents (© University of Stuttgart)

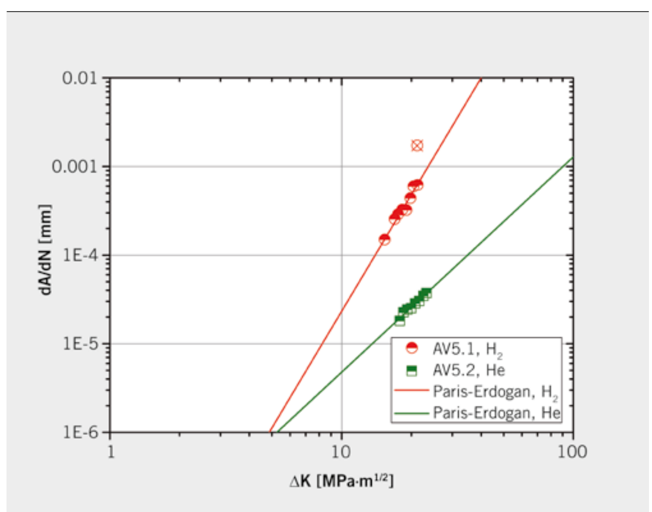

FIGURE 5 Crack growth curve (T = -50 °C) (© University of Stuttgart)

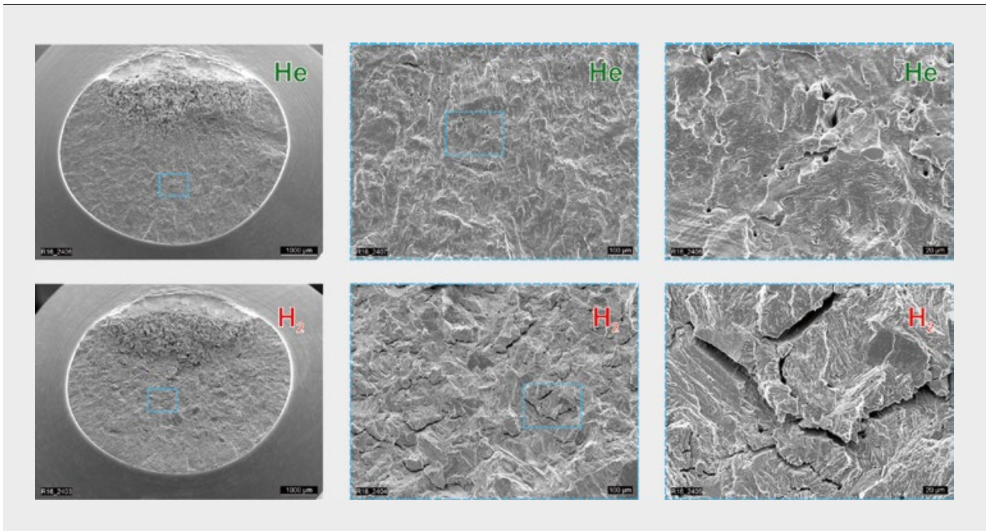

FIGURE 6 Fractographic investigations (SEM) (© University of Stuttgart)

shows the fracture surfaces of two broken fatigue specimens (hydrogen and helium). The fracture surface of the specimen tested in helium shows a smooth surface with some cavities. The specimen tested in hydrogen shows a jagged fracture surface. Instead of cavities, scaled structures can be observed on the fracture surface. Additionally, secondary cracks perpendicular to the surface are present.

3 SUMMARY AND OUTLOOK

In tensile tests in hydrogen at low temperatures, the metastable austenitic material X2CrNi19-11 with increased nickel content shows a reduction in deformability compared to testing in helium. At RT an embrittlement of the material in tensile tests cannot be observed. In fatigue tests the degenerating effect of hydrogen can be confirmed. The load cycles until fracture were significantly reduced in hydrogen at T = -50 °C compared to those in helium. In addition to the classical materials characterisation, the influence of load frequency was of particular interest. Therefore, fatigue tests at different frequencies were performed. The analysis of load cycles until fracture yielded an influence of frequency. This could be confirmed using XRD measurements of fracture surfaces. The metastable austenitic material forms deformation martensite under plastic deformation. The determination of microstructural constituents showed a statistically significant influence of load frequency on the formation of martensite. At decreasing frequencies the content of α‘-martensite decreases in hydrogen, whereas the content in helium is unaffected. Additional cyclical crack growth tests were performed. Crack growth is by a factor of ten higher in hydrogen compared to the reference test in helium. In fractographic investigations a significantly different appearance of the fatigue crack surface could be observed.

The influence of hydrogen with regard to temperature and frequency could be demonstrated in the research procedure. Some questions remain open with regard to the damage mechanisms in effect. More extensive microstructural investigations of the processes that accompany the microstructural transformation could help to enhance the understanding of hydrogen-enhanced material embrittlement.

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