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Improvement of hydrogen induced stress corrosion cracking resistance of ultra-high strength steel screws and fasteners

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Abstract

Among different forms of environmentally assisted cracking (EAC), hydrogen embrittlement (HE), or more specifically, hydrogen induced stress corrosion cracking (HISCC) is the most critical form while dealing with high strength steel used for manufacturing of screws and fasteners[(1)]. The downsizing trend of steel structures for mobility applications to increase the efficiency and decrease CO_2 emissions faces this problem, as it is well known that increasing the steel strength also increases its susceptibility to HISCC. Thus, the screw strength class 10.9 (900 MPa yield and 1000 MPa tensile strength) is specified as the maximum for safety-related HISCC resistance[(2)]. The main project goal is to establish a controllable method for HISCC testing, which should lead to a better understanding of the embrittlement mechanisms and to evaluate different microstructures, which are tempered martensite, bainite and pearlite by applying different heat treatments to achieve a tensile strength of 1400 MPa or higher. The HISCC testing procedure is performed as the Incremental Step Load Test (ISLT) according to standard ASTM F 1624[(3)] with in situ hydrogen charging by cathodic polarization and corrosion measurements.

Introduction

Production of wire rod. voestalpine Wire Rod recently built up the most advanced wire rod rolling mill worldwide. The billets coming from steel mill are heated to a rolling temperature in a walking beam furnace powered by natural gas (step 3). This is followed by high-pressure water descaling, and then the continuous rolling process on a 2- strand wire rolling line (forming stages) until the required cross section has been reached (steps 4 and 5). An outstanding competence of the new rolling mill is the ability to perform thermomechanical treatments over the entire diameter regime of the wire rod, guaranteeing a good combination of strength and ductility. A major amount goes into the fastener industry in the form of cold heading wire.

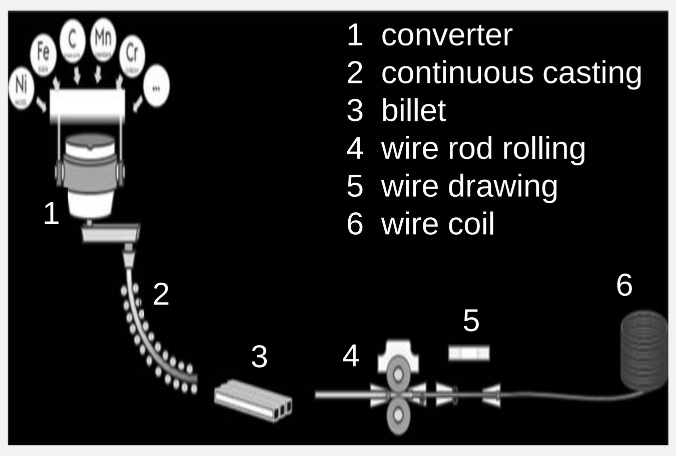

Fig. 1 Schematic for wire rod production

HISCC is described as loss of ductility in a metal or alloy caused by atomic H in combination with load-induced and residual tensile stresses that can lead to brittle fracture after a certain time.[(1)] Sources of H in steel could be internal from processing, which is controllable and can be eliminated by soaking in order to make H diffusing out and/or external H, which enters into steel during service due to corrosion or cathodic protection. This process is incontrollable and can cause delayed fracture.

Material susceptibility depends on two factors. The main factor is the strength. If it increases the crack toughness decreases and the steel becomes more susceptible to HE. Fig. 2 represents the relation between hardness and Notched Fracture Strength percentage during cathodic polarization at 1.2V ($NFS_{1.2V}$%). The secondary factor are phases, inclusions and H traps, which effect the susceptibility.[(2)]

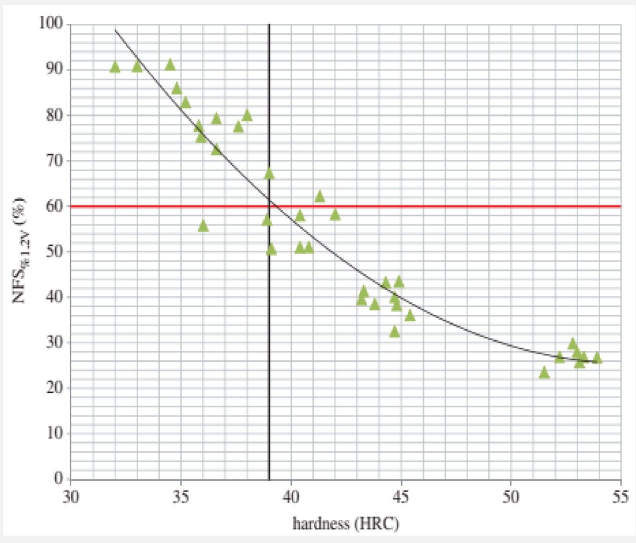

Fig. 2 $NFS_{1.2V}$% decreases with increasing hardness. The 60% line represents the limit of acceptability for fasteners.[(2)]

Hydrogen has a very low solubility in bcc lattice interstitial sites. Thus the majority of H atoms are attracted to so called traps, which can be vacancies, solute atoms, dislocations, grain or phase boundaries, voids and nonmetallic inclusions.[(1)] There exist **reversible traps**, where the binding energy of H atoms is relatively low, thus H is free to escape and enter anytime, as well as **irreversible traps** where its binding energy is higher and H cannot leave the trap at ambient temperature.

Class	Trap type	Binding energy E_b (kJ/mol)	Comment	Technique (material)
Precip.	Mo_2C	22–28	Peak aged	EP
	Mo_2C	21–29	Fine precip.	EP
	VC	17	Coherent	EP
	V_4C_3	30	Coherent	TDA (LCS)
	Fe_3C	21–29	...	EP
	Fe_3C	84	Incoherent	LR (MCS)
	Epsilon carbide	13	...	TDA
	AlN	65	...	LR
	AlN	> 83.94	...	LR
	TiC	94	Incoherent	LR
	TiC	77-95	Semi-coherent	LR
	TiC	87	Incoherent	TDA (MCS)
Phases	Retained austenite	45		TDA (MCS)
	Retained austenite	55		(DPS)
Defects	Dislocations	26–29	5–15 atoms/nm	TDA + EP
	Grain boundary	17		(PI)
	Grain boundary	53–59	High angle	LR
	Voids	21		LR

Fig. 3 H traps and their binding energies.[(4)]

Methods of investigation

Many mechanical methods were employed to investigate HISCC.

- Constant (sustained) load tests for very long time and change in conditions.
- Controlled strain or loading rate tests: Slow Strain Rate Test (SSRT), Linearly Increasing Stress Test (LIST), Rising Load Test (RLT) and Incremental Step Load Test (ISLT).

In this project the ISLT will be used with in situ H charging by cathodic polarization in a special electrochemical cell. It consists of double wall (1) for temperature control of the 3.5% NaCl solution, tensile sample (2), adaptors (3), isolation kits (4), Pt counter electrode (5) and the reference electrode (6).

According to ASTM 1624 the ISLT can be used to evaluate the HE threshold stress of steel samples or screws in air, in cathodic H charging conditions in solution as well as in simulating environmental anodic corrosion attack controlled by the 3-electrode set up (reference-working-counter electrode).

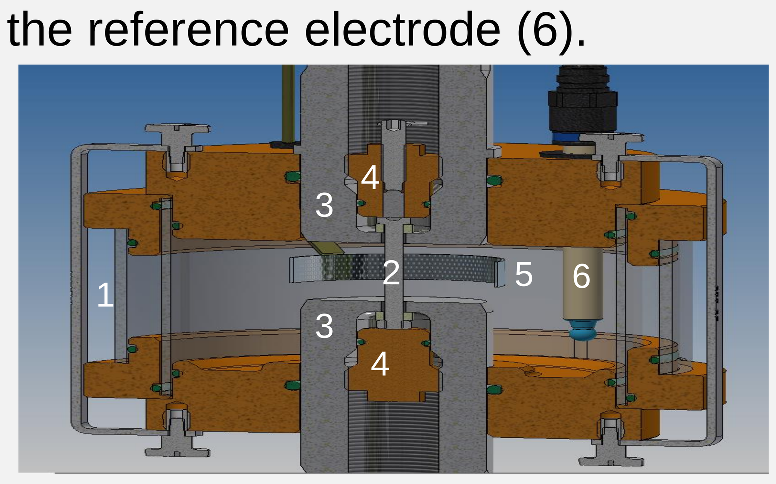
Fig. 4. Assembly of ISLT electrochemical cell.

Hydrogen concentration measurement in tensile samples is of great importance in order to investigate the relation between HISCC susceptibility and amount of diffusible and trapped hydrogen charged at certain conditions.

Electrochemical hydrogen permeation test. According to the Devanathan-Stachurski method, H is cathodically charged on the entry side of a metallic membrane and the permeated H is fully oxidized at the exit side under a constant positive potential, see Fig. 5. In this way the H diffusion coefficient and amount of diffusible hydrogen at certain parameters can be calculated.[(5)]

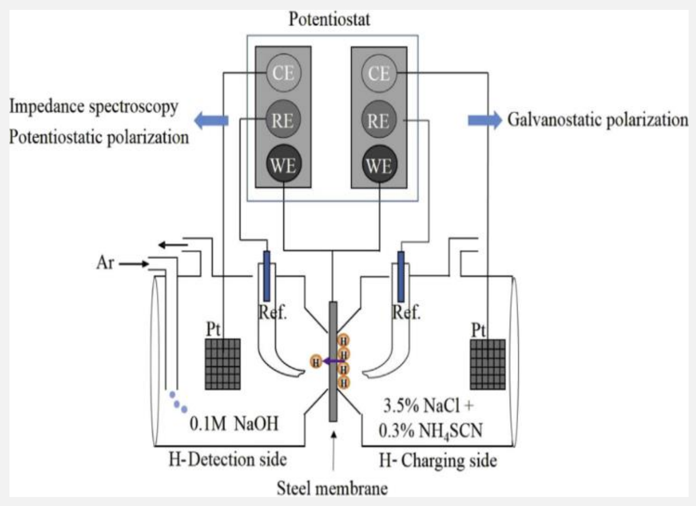

Fig 5. Schematic illustration of an electro-chemical permeation cell [(5)]

Thermal desorption analysis (TDA)
Is the standard method to measure the H content (diffusible and trapped) in the sample after ISLT by heating the sample up to 800°C.

MatCalc software simulation should support the evaluation of the proper heat treatment as appropriate tool for calculating the precipitation kinetics to evaluate the number density, distribution and size of precipitates in high strength steels to investigate the effect of these precipitates as strong H traps on HE susceptibility.

Heat treatments and materials characterization

Three different alloys 42CrMo4, C82 and a V micro-alloyed steel are investigated, Fig. 6. In a first step the martensitic start temperature by use of dilatometry was determined to do proper heat treatments, which are oil quenching and tempering (QT) to produce tempered martensite (TM) as well as isothermal transformation (IT) in salt baths for bainitic microstructure, Fig. 7. Results of hardness and tensile testing of these different microstructures are shown in Fig. 8.

Alloy	EN material No.	C	Mn	Si	Cr	Mo	Ø (mm)
42CrMo4	1.7225	0.38-0.45	0.60-0.90	0.40 max	0.90-1.20	0.15-0.30	22
C82	1.1262	0.80-0.84	0.50-0.70	0.10-0.30	0.10 max	---	9.65

Fig. 6 Chemical composition range (wt.%) of two investigated steels and produced wire rod diameter.

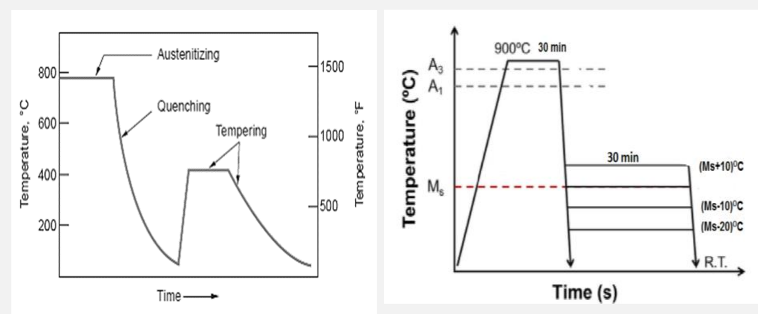

Fig. 7 Heat treatments schematically. Quenching and Tempering (QT), left / Isothermal Transformation (IT), right.

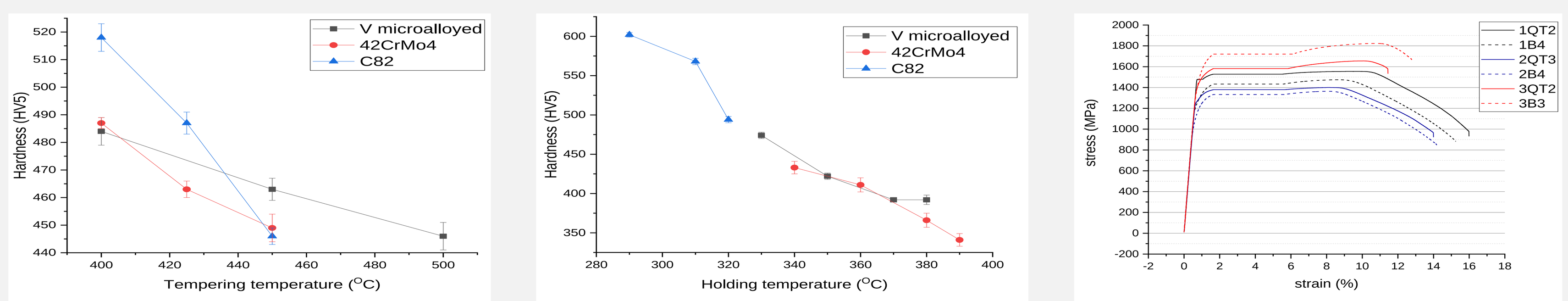

Fig. 8a. Vickers hardness HV5 measurements of QT samples (left), IT samples (middle) and tensile test results (right).

For the phase characterization **Scanning Electron Microscopy** (SEM) was applied on etched metallographic cross sections. Thus tempered martensite, lower and upper bainite as well as carbide precipitates can be analyzed in the heat treated steels of comparable high strength in excess of 1400 MPa.

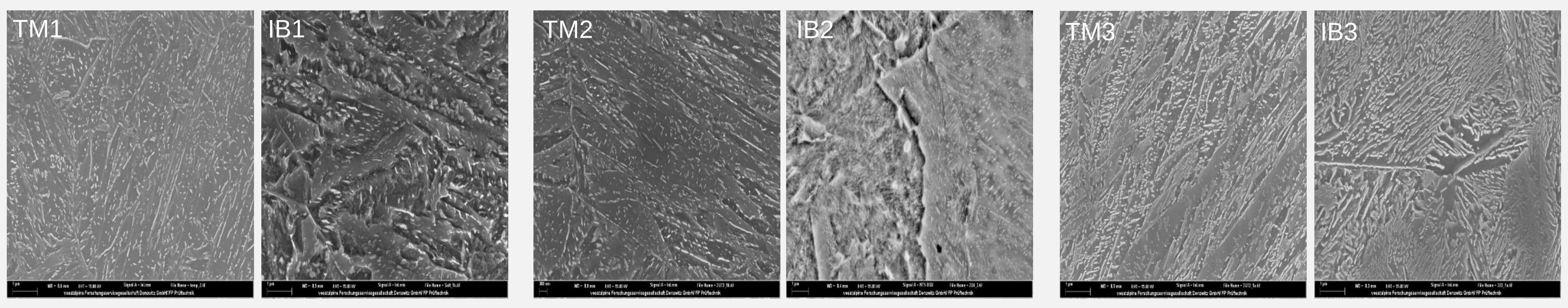

Fig. 9 Tempered Martensite (TM) and Isothermal Bainite (IB) of V micro-alloyed (1), 42CrMo4 (2) and C82 (3) steel.

Conclusion

In order to investigate HISCC susceptibility of three different high strength steels this project will apply a special electrochemical cell for hydrogen charging and corrosion testing during the Incremental Step Load Test. For the optimization of the steel microstructure by heat treatment to gain strong hydrogen trapping, high resolution microscopy, MatCalc simulations, mechanical and corrosion testing will be used as well as hydrogen permeation and thermal desorption analyses. These measures should enable the production of screws strength class 12.9 or higher.

References

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