

Influence of cold deformation on hydrogen embrittlement by determining the critical hydrogen concentration in high strength steel for wire applications

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Abstract

The resistance of steel wires to hydrogen embrittlement is very difficult to define and is therefore rarely investigated in literature. In this work a C65 steel wire was tested in hot rolled condition and after cold working. Both material states were first cathodically charged in sodium chloride (NaCl) with addition of thiourea ($\text{CH}_4\text{N}_2\text{S}$) at different current densities to determine the hydrogen content of each charging condition. In the next step mechanical properties and susceptibility to hydrogen induced stress corrosion cracking (HISCC) were determined in Slow Strain Rate Tests (SSRT). To prevent hydrogen effusion during experiments, samples were additionally further charged during the SSRT. Critical hydrogen concentrations for initiation of HISCC of both material states have been determined, whereas the critical hydrogen concentration is lower in the hot rolled state.

INTRODUCTION

The threshold hydrogen content of a material regarding hydrogen embrittlement plays an increasingly important role in corrosion research. This value indicates the hydrogen content to which the material can be used without failure. However, when determining the threshold hydrogen content, different test methods, different analysis methods and different interpretations of the results come together. This paper is intended to provide a guideline for the determination of the critical hydrogen concentration of high strength steel wire samples.

A compilation of critical hydrogen contents in the literature were summarized by Trautmann et al.¹. A clear trend can be seen in the literature that the critical hydrogen content decreases with increasing strength^{1, 2}. However, the methods used to obtain the different data often differ fundamentally.

In order to set a certain hydrogen content, cathodic charging or high pressure charging is commonly used. In electrochemical hydrogen charging, hydrogen is generated cathodically on the sample surface by applying a voltage. In pressurized hydrogen charging, hydrogen molecules are separated into absorbable atoms by dissociation. The most commonly used methods of determining limit values require a determination of the mechanical properties as well as the analysis of the hydrogen content after hydrogen charging. Possible methods to determine the mechanical properties of charged materials are the use of slow strain rate tests, constant load tests, bending tests or fracture mechanics tests³⁻⁷. Possible hydrogen analysis methods are the carrier gas melt extraction, carrier gas hot extraction, thermal desorption analysis or the hydrogen collecting analysis⁸⁻¹⁰. Looking at methods that specifically produce failures, such as slow strain rate tests or crack growth measurements, there can be seen a variation of the criteria to assess a critical hydrogen content of a material. One common method is to determine the hydrogen environment embrittlement index according to ASTM-G129¹¹:

$$\text{Reduction in Area Ratio RRA} = \text{RA}_e / \text{RA}_c \quad (1)$$

Where $\text{RA}_e / \text{RA}_c$ is the ratio of reduction in area between the test environment RA_e and the control environment RA_c .

$$\text{Elongation Ratio RE} = E_e / E_c \quad (2)$$

Where E_e / E_c is the elongation ratio between the test environment E_e and the control environment E_c .

Another possibility of determining material resistances is provided by constant load tests, in which the failure criterion is often characterized by whether failure occurs within a given time or whether the material resists. In practice, this method provides a good representation of the stress situation, but does not always lead to the possibility of determining a critical hydrogen concentration.

Basically, modern steels are designed with regard to their resistance to hydrogen embrittlement in such a way that crack initiating impurities such as inclusions, pores or large precipitates are purposefully avoided, while fine precipitates, fine grains or fine lamellar spacings are produced specifically to trap the hydrogen and thus suppress embrittlement¹². Another possibility to improve the resistance to hydrogen embrittlement is summarized in the term "Grain Boundary Engineering". Here, one attempts to avoid high angle grain boundaries, since these act as diffusion highways for hydrogen¹². Another important role is played by the dislocation density, since increased dislocation density due to a forming process results in increased susceptibility to hydrogen embrittlement. Hydrogen atoms attach themselves to dislocation nuclei and are rapidly moved through the material by the dislocation motion when a mechanical stress is applied¹². When using hydrogen traps in the design of high-strength steels it must be noted, that traps cannot completely prevent hydrogen damage. If the hydrogen absorption is limited, traps provide an effective tool, whereas if the hydrogen absorption is unlimited, the traps will be completely filled up and thus only delay the material damage.

In the case of pearlitic steel wires in the hot rolled and in the cold worked condition, especially dislocations, grain boundaries and phase boundaries between the different lamellas play some important roles. A fine lamellar structure also provides additional strength, while at the same time improves the resistance to HISSC.^{13, 14}

EXPERIMENTAL PROCEDURE

Materials

C65 steel with a sample dimension of 30 x 6 x 6 mm (1.18 x 0.24 x 0.24 in) in the form of a cuboid for hydrogen charging and small tensile samples with a gauge diameter of 3 mm and a gauge length of 25 mm was used as test material. The samples were eroded from the wire material. Material testing was carried out on the hot rolled condition and the cold worked condition. The surface finish was as machined for all specimens. The chemical composition of the investigated material is shown in Table 1.

Table 1: Chemical composition of the investigated material

Material	C [wt.%]	Mn [wt.%]	Si [wt.%]	P [wt.%]	S [wt.%]	Cr [wt.%]	Ni [wt.%]
C65	0.66	0.63	0.22	0.01	0.0068	0.016	0.018

Figure 1 shows the microstructure of the two different material conditions. In the cold worked state, grains stretched in the longitudinal direction can be recognized. The microstructure is mainly pearlitic with some ferrite grains and the average grain size is about 30 μm for both conditions.

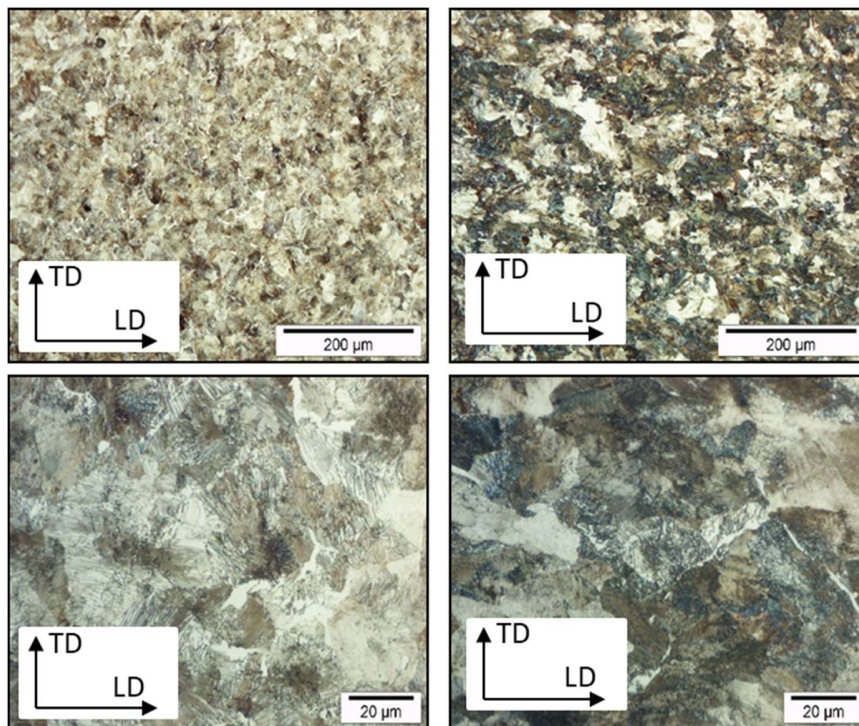


Figure 1: Microstructure of the examined material states in longitudinal direction (LD), on the left side hot rolled with a magnification of 200 and 1000 times and on the right side cold worked with the same magnifications as mentioned for the hot rolled

The mechanical properties of the investigated materials are listed in Table 2.

Table 2: Values of the measured Yield Strength (YS) and the Ultimate Tensile Stress (UTS) of the investigated material states

Material	YS		UTS	
	[MPa]	[ksi]	[MPa]	[ksi]
Hot rolled	491.5	71.29	875.9	127.03
Cold worked	860.5	124.80	1022	148.23

Hydrogen charging

The basis of the testing procedure is the hydrogen charging. Different electrolytic charging methods were applied to find a charging technique with a good control in hydrogen uptake and corrosion rate. In our case we used the electrolytic charging technique with thiourea as hydrogen poison, which not only acts as a recombination inhibitor during hydrogen absorption, but also as a corrosion inhibitor. The electrolytic charging method at open circuit potential (OCP) was a simple immersion test. For the cathodic charging, cathodic polarization starts immediately after immersion of the sample in the test solution. A platinum mesh was used as counter electrode. All tests were carried out at room temperature ($23 \pm 2^\circ\text{C}$) in the charging conditions shown below (Table 3). None of the solutions was deaerated.

Table 3: Hydrogen charging conditions

Medium	Current density	Temperature
		[°C]
3.5 % NaCl + 1 g/L $\text{CH}_4\text{N}_2\text{S}$	1 mA/cm ²	23 ± 2
3.5 % NaCl + 1 g/L $\text{CH}_4\text{N}_2\text{S}$	10 mA/cm ²	23 ± 2
3.5 % NaCl + 1 g/L $\text{CH}_4\text{N}_2\text{S}$	OCP	23 ± 2

For the hydrogen charging, the following general conditions were applied:

1. Cleaning each sample for 3 minutes first in used acetone, then in fresh acetone in an ultrasonic bath;
2. Drying the sample with a paper towel;
3. Test procedure according to the hydrogen charging conditions;
4. Immediate cooling in liquid nitrogen after removing the sample from the test container;
5. Wet grinding of the sample with 120 grit abrasive paper without defrosting of the sample;
6. Carrying out the hydrogen analysis by hot carrier gas extraction at 950°C (1742°F) (cleaning the sample with acetone - blow-drying - weighing - placing the sample in the hydrogen analyzer);

Carrier gas hot extraction took place by an ELTRA H-500 Hydrogen Analyzer™, with previous He gas calibration and use of steel calibration standards.

SSRT

Slow Strain Rate Tests (SSRTs) were performed to determine the mechanical properties under the influence of hydrogen charging. The test procedure is as follows:

1. Cleaning each sample for 3 minutes first in used acetone, then in fresh acetone in an ultrasonic bath;
2. Drying the sample with a paper towel;
3. Hydrogen pre charging in the test cell;