TDS EVALUATION OF THE HYDROGEN TRAPPING CAPACITY OF NbC PRECIPITATES

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ABSTRACT
In this work, ferritic steel containing NbC precipitates was investigated. The materials were subjected to various heat treatments, giving rise to different precipitate size distributions as determined by TEM (Transmission Electron Microscopy). The steels were hydrogen charged both electrochemically and from a gaseous phase, followed by multiple TDS (Thermal Desorption Spectroscopy) measurements. Electrochemical charging gives rise to a low temperature peak (80-120°C), originating from the hydrogen trapped near grain boundaries and at NbC precipitates, having activation energy ranging between 24 and 44 kJ/mol. Gaseous charging leads to a high temperature TDS peak (450-550°C), which indicates that hydrogen is trapped by incoherent NbC precipitates, with activation energy ranging between 62 and 71 kJ/mol.

INTRODUCTION
Although the first detrimental effects of hydrogen on the mechanical properties of iron and steels were described by Johnson in 1875, many features of the involved mechanisms are still poorly understood and are the subject of debate [1]. As a result of the rising demand for high strength steels, since these materials are known to be sensitive to the harmful consequences of hydrogen, an increasing interest for hydrogen embrittlement research arose.

The introduction of carbides as hydrogen trapping sites in steels is an often quoted approach to reduce the amount of diffusible hydrogen in the steels and, as such, reduce susceptibility towards hydrogen damage [2]. Niobium, next to titanium and vanadium, is a carbide forming alloying element [3]. However, the
interaction between the NbC precipitates and hydrogen has rarely been evaluated in detail.

Tsuzaki and co-workers observed the presence of hydrogen near semi-coherent NbC precipitates, having a disc shape with 5 nm length and 2 nm thickness, after electrochemical charging using small-angle neutron scattering (SANS) [4]. Earlier results of Gehrmann et al already claimed, based on hydrogen permeation experiments, that incoherent NbC and NbN precipitates were deep hydrogen traps [5]. NbC precipitates are considered to consist of several hydrogen trapping sites with various activation energies, such as the precipitate-ferrite interface, the coherency strain region surrounding the precipitate (misfit dislocations) and the crystallographic defects inside the precipitate [6]. The hydrogen trapping capacity is argued to be higher than for TiC and VC precipitates [7].

In this work, an alloy containing NbC precipitates in a ferritic matrix was investigated. The samples were subjected to different heat treatments, giving rise to different precipitate size distributions as determined by TEM analysis. The NbC precipitates were hydrogen charged both electrochemically and from gaseous H₂, followed by multiple TDS measurements.

**EXPERIMENTAL**

**Materials**

The composition of the used lab cast material is given in Table 1 and was chosen for stoichoimetric reasons to promote the formation of NbC precipitates. This material was produced in a Pfeiffer VSG100 vacuum melt and cast unit, operated under a protective argon gas atmosphere. The samples were processed by hot and cold rolling the cast blocks to sheets with 1.7 mm thickness.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Nb</th>
<th>Ti</th>
<th>N</th>
<th>Others</th>
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<tbody>
<tr>
<td>CO80 (Nb+C)</td>
<td>0.013</td>
<td>0.0049</td>
<td>0.0054</td>
<td>0.1</td>
<td>0.0092</td>
<td>0.0007</td>
<td>P, S, Al</td>
</tr>
</tbody>
</table>

Table 1: Chemical composition of the material used (weight percent).

In order to promote the formation of different precipitate size distributions, the material was subjected to three different heat treatments, as summarized in Figure 1. Two materials, CO80-1 and CO80-2, were treated at 1200°C for 30 minutes and at 800°C for 10 and 120 minutes, respectively. The third material, CO80-H₂, was heat treated under H₂ atmosphere at 800°C for 58 hours. After the heat treatment, disc-shaped samples with a diameter of 20 mm were punched and ground to a thickness of 1 mm. Figure 1 also shows the optical micrographs of the three materials. All three consist of a ferritic matrix, in the CO80-1 and CO80-2 materials grain growth is clearly observed. On the contrary, due to the lower temperature used in the heat treatment of CO80-H₂, grain growth in this material was limited as the present NbC precipitates did not dissolve and as such prevented grain growth.
In order to verify the presence of NbC precipitates in the steel matrix, STEM (Scanning Transmission Electron Microscopy) analysis, using a JEM-2200FS, as well as EDX (Energy Dispersive X-Ray) spectroscopy was performed. The thin foil samples were prepared by grinding and polishing the samples to a thickness below 100 µm. Afterwards, they were electro-polished, using a TenuPol-5 electro-polishing unit of Struers, in a 10% perchloric acid and 90% acetic acid solution.

The CO80-1 and CO80-2 samples were electrochemically charged for one hour, using a 0.5 M sulfuric acid aqueous solution containing 1 g/L thiourea and with a current density of 0.8 mA/cm². These parameters are based on results of a previous study [8]. The CO80-H₂ samples were already hydrogen charged during the heat treatment. This charging procedure already demonstrated its effectiveness for TiC precipitates as was shown by Pérez Escobar et al [9].

The charged samples were cleaned with distilled water and isopropanol and then inserted in the TDS chamber. The vacuum pump is subsequently initiated.

Figure 1: Temperature-time graphs and optical microscope pictures of the three materials used.

STEM measurements, hydrogen charging and TDS measurements

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and after 1 h the vacuum level is low enough (< 0.35x10^{-8} Pa) to be able to start the test. Similarly to our previous work, the activation energy was determined by performing TDS tests using four different heating rates, namely 3.33, 6.66, 13.33 and 20 °C/min [10]. Subsequently, a deconvolution was applied and the Lee et al method was used to correlate peak temperatures with activation energies [11-13]. Equation 1 is a simplification of the original formula of Kissinger [14].

\[
\frac{d \ln(\phi / T_{\text{max}}^2)}{d(1/T_{\text{max}})} = -\frac{E_A}{R}
\]

Where \(\phi\) is the heating rate (K/s), \(T_{\text{max}}\) (K) the TDS peak temperature, \(E_A\) (J/mol) is the activation energy for hydrogen desorption of the specific trap associated with \(T_{\text{max}}\) and \(R\) (J.K^{-1}.mol^{-1}) is the universal gas constant.

RESULTS AND DISCUSSION

CO80-1

The NbC precipitates present in the CO80-1 material have a length of about 10 nm (see Figure 2). They were found to be round, rectangular or ellipsoidal.

![Bright field STEM image of CO80-1 thin foil.](image)

The TDS spectrum is deconvoluted into three separate peaks (see Figure 3). The activation energies for the three peaks are 27±5, 24±5 and 24±5 kJ/mol, respectively. The first hydrogen desorption peak is believed to be attributable to hydrogen trapped at grain boundaries. This value is well within the known range of desorption energies for grain boundaries, 18 to 59 kJ/mol [15-17]. It also makes up the largest part of the total hydrogen desorption. Hydrogen trapping at dislocations is more unlikely in the present case, as was demonstrated by Pérez Escobar et al [18]. The latter two peaks have similar activation energies and are assumed to be produced by the hydrogen trapped at the NbC precipitates. As was argued by Wei et al, the hydrogen is trapped in the core of the misfit
dislocations surrounding the broad interface of the small NbC precipitates [6-7, 19]

The TEM images of the CO80-2 material show two types of precipitates, smaller ones with a length of about 10 nm and larger ones with a length between 85 and 195 nm (see Figure 4).

![Figure 4: Bright field STEM image of CO80-2 thin foil.](image)

The corresponding TDS spectrum is deconvoluted into four separate peaks (see Figure 5). The activation energies for these peaks are $30 \pm 0.4$, $33 \pm 2$, $40 \pm 3$ and $44 \pm 1$ kJ/mol, respectively. The first peak could again be correlated with hydrogen desorption from grain boundaries. The corresponding activation energy is similar to the one obtained for the CO80-1 material, which has a comparable grain size (see Figure 1). The second peak is probably due to the
hydrogen trapped at the smaller precipitates (10 nm), which are also present in
the CO80-1 material. In this case only one peak is observed, however the
activation energy is in the same range. The other two peaks likely correspond to
NbC precipitates having larger dimensions (85–195 nm). The phase boundary
coherecy is known to decrease with precipitate size. Consequently, an increase
in incoherency and an increase in the corresponding activation energy is
expected as was already stated by Wei et al for TiC precipitates [19]. The
present, higher hydrogen desorption energies, ranging from 40 to 44 kJ/mol,
confirm this statement.

![Figure 5: TDS spectrum of the CO80-2 material after
electrochemical charging, heating rate 6.66 °C/h.](image)

CO80-H$_2$

TEM analysis of the CO80-H$_2$ material shows three types of precipitates:
very small ones of only a few nanometers, precipitates ranging between 50 and
100 nm and precipitates of several hundreds of nanometers (see Figure 6). The
precipitates smaller than 1-3 nm are likely to have a higher degree of coherency,
as was also demonstrated by Wei and Tsuzaki for TiC precipitates [19].

![Figure 6: Bright field STEM image of CO80-H$_2$ thin foil.](image)
The TDS spectra of gaseous charged CO80-H$_2$ samples do not show low temperature peaks, since gaseous charging was performed at temperatures significantly higher than the typical temperature at which the low temperatures peaks occur. Electrochemical charging, which generates the low temperature peak, was not applied after gaseous charging on this material. As such, no desorption energy, for the hydrogen that was trapped in the grain boundaries, could be calculated. A high temperature peak can be clearly observed (see Figure 7). This peak is deconvoluted into two peaks and calculation of the desorption energy gave values of 63 and 71 kJ/mol. The interaction of hydrogen with these precipitates might be similar as for TiC precipitates [19]. Hydrogen is considered to be trapped inside the carbon vacancies present in the incoherent precipitates. Gaseous charging at elevated temperatures is required to supply the necessary energy for the hydrogen to enter this hydrogen trap. It is assumed that the two different desorption peaks can be attributed to the bimodal size distribution of the precipitates that tends to be present in the material.

![Figure 7: TDS spectrum of the CO80-H$_2$ material, heating rate 6.66 °C/h.](image)

**CONCLUSIONS**

TDS measurements were performed on a lab cast material containing NbC precipitates. Electrochemical charging gave rise to a low temperature peak (80-120°C), originating from the hydrogen trapped near grain boundaries, with activation energy ranging between 27 and 30 kJ/mol, and at NbC precipitates, 24 - 44 kJ/mol. Charging in a gaseous environment gave rise to a high temperature TDS peak (450-550°C), which was attributed to the presence of incoherent NbC precipitates, the activation energy ranged between 62 and 71 kJ/mol. Gaseous charging is considered to be necessary in order to provide the required energy to trap the hydrogen in the C vacancies of the precipitates. No low temperature peak is observed, since no electrochemical charging was performed.
ACKNOWLEDGEMENTS

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