Thermal desorption spectroscopy study of the hydrogen trapping ability of W based precipitates in a Q&T matrix

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Abstract
The hydrogen trapping efficiency of different types of W based precipitates is considered in three generic Fe–C–W alloys with increasing carbon content and a stoichiometric amount of W. A martensitic microstructure is prepared and two conditions are compared; i.e. an as-quenched (as-Q) state and a quenched and tempered (Q&T) state in which W based carbides are formed. The tempering time and temperature are modified to change the carbide characteristics. Hence, the hydrogen trapping characteristics are evaluated for the different carbides. Melt extraction is done to determine the hydrogen content, whereas thermal desorption spectroscopy (TDS) is performed to verify whether the tempered induced carbides are able to trap hydrogen efficiently. The trapping capacity is found not only to be size dependent, but also reliant on the morphology and type of the carbides, as investigated by transmission electron microscopy. TDS revealed that the tempered induced W2C in the Q&T at 600 °C for 1 h condition do not trap hydrogen due to their rather large size (>20 nm) and hence incoherent nature. Moreover, the hydrogen content is decreased compared to the as-Q condition due to the reduced dislocation density. The tempering time is reduced to 10 min to evaluate the size effect on the carbide trapping ability. As such, smaller W2C (<20 nm) are induced, which trapped a significant amount of hydrogen, as demonstrated by TDS, with a corresponding activation energy of 42–45 kJ/mol. This compensated the reduction in dislocation density, causing a higher hydrogen level. Furthermore, tempering at 700 °C for 1 h results in an increase of hydrogen compared to the Q&T at 600 °C for 1 h condition. This is confirmed by TDS and TEM to be linked to the trapping ability of W23C6, showing a slightly higher activation energy ranging from 47 to 49 kJ/mol.

Introduction
Recently, interest in the hydrogen economy has gained more attention since hydrogen, as a clean energy carrier, is able to generate an energy revolution in renewable energy systems [1]. The increased production and use of hydrogen can support climate change. However, development of a hydrogen based economy has proven to be a challenge due to the required infrastructural investments [2] together with the challenges...
concerning production, storage, transportation and distribution [3]. Nevertheless, hydrogen can have a role in the energy system and it also may be an option for decarbonizing heat, while hydrogen fuel cells are already used to replace batteries in forklift trucks for example [1]. Therefore, hydrogen deserves more attention to assess its place in the future energy system.

In addition, in offshore industry for instance, corrosion is avoided by cathodic protection due to a conversion of all the active anodic sites of the metal to passive cathodic sites. However, when cathodic overprotection occurs, atomic hydrogen absorbs into the steel and a hydrogen concentration is built up. Consequently, the material ductility will be degraded to a certain extent and hydrogen induced cracking is promoted [4].

Also the automotive industry faces the issues concerning the detrimental impact of hydrogen on the material’s mechanical integrity. The use of high strength steels has, for instance, been promoted since they can both guarantee an increased safety together with weight reduction which is required to meet the stringent CO2 emissions regulations. Unfortunately, these steels are considered to be prone to hydrogen induced mechanical degradation and as a result impeding further alloy development [5]. Amongst others, dual phase (DP), transformation induced plasticity (TRIP) and high strength low alloyed (HSLA) steels are common used grades in the automotive industry and were already subject of multiple hydrogen related studies [6–13]. The impact of hydrogen on the mechanical properties of a DP, TRIP and HSLA steel was specifically studied in [14], where the best resistance against hydrogen embrittlement was obtained for the HSLA steel due to the presence of Ti and Nb carbonitrides. The presence of carbides is generally considered to be beneficial since the strength level of the steel is increased and since they are assumed to trap hydrogen efficiently removing the detrimental mobile hydrogen from the microstructure [15–17]. In the specific case of cathodic protection, the beneficial impact of adding suitable trapping sites considering slowing down hydrogen diffusion and possibly crack growth rates.

Di Stefano et al. [18] studied the H interaction with TiC in α-Fe by means of first-principles calculations based on density functional theory. They found a broad range of trapping sites for hydrogen going from different types of interfaces between the particle and matrix and carbon vacancies inside TiC. The latter was considered the most efficient one, although they were assumed to be difficult to activate at room temperature since the energy barrier for H entering the TiC is high. Wei et al. [19] showed that coherent and semi-coherent NbC, TiC and VC were capable of trapping hydrogen during electrochemical charging. Moreover, Takahashi et al. [20] confirmed the presence of hydrogen at the interface of carbide and matrix by atom probe tomography as deuterium atoms were observed at the surfaces of nano-sized TiC. Wallaert et al. [21] showed that electrochemical cathodic charging resulted in hydrogen trapped near grain boundaries and at the interface of small NbC whereas gaseous charging at elevated temperature revealed deep trapping sites corresponding to hydrogen at incoherent NbC, while Pérez Ecobar et al. [22] made similar observations for TiC.

To improve the wear resistance, W is amongst others frequently used in tool steels [23]. At tempering temperatures between 500 °C and 700 °C, W2C carbides are formed which transform into W6C and W23C6 carbides when the temperature rises above 700 °C. Besides, the tempering induced secondary hardening effect is less prominent compared to other carbide forming elements, such as Ti or V. The slow diffusion of W, causing a delay in the W2C nucleation is the dominant factor inducing this limited strengthening effect [24], which was also observed by Kwon et al. [25]. The interaction of hydrogen with W based carbides has only received limited attention so far. Zhoa et al. [26] recently investigated the impact of W on the hydrogen embrittlement in micro-alloyed steels by slow strain rate testing. The addition of W increased the activation energy of hydrogen desorption. However, this was correlated to the changes in microstructure caused by different amounts of W and not by W based carbides [26]. Malitckii [27] studied the effect of hydrogen on ODS-EUROFER and EUROFER97 by tensile testing hydrogen charged samples. Transmission electron microscopy exposed hydrogen induced micro-cracks, clearly initiating at the interface of the chromium and tungsten carbides, which were located at the grain boundaries. This might indicate that hydrogen preferably diffuses to the tungsten carbides and is trapped there. Wang et al. [28] studied the trapping and release of deuterium by means of thermal desorption spectroscopy (TDS) on tungsten carbide coatings prepared by chemical vapor deposition. The spectrum showed complicated features and the broad TDS spectrum was considered as an overlap of three peaks. They concluded that further study was necessary to get a decent understanding of the observed phenomena.

Commercial high strength steels show, however, a multi-phase microstructure, complicating the interpretation of hydrogen related data. Therefore, single phase alloys were processed and have been under investigation as well [18,22,29–35]. Recently, Fe–C–X (X = Ti, Cr, Mo, V and W) alloys were studied in depth to analyze the trapping capacity of tempered induced Ti, Cr, Mo, V and W based carbides and their impact of the hydrogen induced mechanical degradation [36–41]. Two conditions were compared to assess the hydrogen/carbide interaction: firstly, an as quenched state and, secondly, a quenched and tempered state where free carbon is enabled to precipitate with the ternary alloying element during tempering. Tempering was done at the temperature at which the most significant secondary hardening effect due to the generation of carbides occurred. TiC, Cr23C6, Mo2C and V4C3 were confirmed to have a beneficial impact on the hydrogen induced ductility loss and were able to trap a significant amount of hydrogen as determined by TDS [36–39]. W2C precipitates, on the contrary, were not able to trap hydrogen [40]. The size and coherency of the specific carbides were considered to be crucial in terms of hydrogen trapping ability; i.e. the small and coherent TiC and V4C3 precipitates of about 5–20 nm showed the best trapping efficiency, whereas coarser Cr23C6 and Mo2C only trapped a limited amount of hydrogen, as revealed by TDS. W2C particles, which were introduced by tempering at 600 °C for 1 h, were larger than 20 nm and did not trap hydrogen. However, concluding that W based precipitates are not capable to trap hydrogen based on this one investigated tempering condition would be unfair. Therefore, thorough investigation is clearly needed on the trapping capacity of these W carbides and the temper treatment of different
Fe–C–W alloys was modified in this work to identify the role of well-designed tempered induced W based precipitates.

**Experimental procedure**

**Material characterization**

Three generic Fe–C–W alloys with increasing carbon content were lab cast with a stoichiometric amount of the ternary alloying element, W. To avoid the formation of nitrides, Al was added to bind the present nitrogen. The carbon increase allows a reliable estimation of the interaction of hydrogen with W based precipitates in different Fe–C–W alloys. The chemical compositions are given in Table 1.

The materials were processed in a Pfeiffer VSG100 incremental vacuum melting and casting unit under an argon gas atmosphere. Subsequently, hot rolling was performed till 1.5 mm and an appropriate heat treatment was applied to obtain two main conditions. The materials were austenitized at 1250 °C for 10 min to obtain an austenitic microstructure and to dissolve the carbides from the processing procedure. These were then quenched in brine water (7 wt% NaCl) to attain a fully martensitic structure. This condition will further be referred to as as-Q. Next to the as-Q state, a second condition was prepared by tempering the quenched material for 1 h at different temperatures to induce W based carbides. The tempering stage was followed again by brine quenching. This condition will further be referred to as Q&T. A variation to the tempering time was further applied to change the carbide characteristics and subsequently thoroughly analyze the trapping ability of W based carbides. The Vickers hardness (HV) profiles versus applied tempering temperature were obtained by indenting a 2 kg pyramidal diamond cone for 10 s into the samples. An average of 20 different indents was taken to assess the hardness of each material. Scanning transmission electron microscopy (STEM) allowed characterizing the carbides in terms of their size, size distribution and morphology. Diffraction patterns were taken for the identification of the present carbide type. Carbon replicas and thin foils were prepared for this purpose.

**Determination of total hydrogen content**

To determine the total hydrogen content, melt extraction was used at 1600 °C, for which samples were charged electrochemically in 0.5 M H2SO4 and 1 g/l thiourea electrolyte at 0.8 mA/cm2 for 1 h. The conditions were chosen in such a way that a full saturation was guaranteed while no blisters or any internal damage was induced in the microstructure, as was confirmed by a similar procedure as described elsewhere [36]. An average of 10 measurements was taken to determine the hydrogen content. The system includes a pulse furnace in which a pre-weighted sample is heated up directly to the required temperature. The metallic sample releases its hydrogen as gaseous H2 and is dragged along by a nitrogen flow. This mixture (N2–H2) is directed to a thermal conductivity measuring cell. Essentially, the thermal conductivity of the mixture depends on the H2 concentration since the conductivity of H2 and N2 differs significantly. As such, the software can calculate the hydrogen concentration based on the variation in thermal conductivity.

**Determination of hydrogen trapping capacity**

The hydrogen trapping sites and their activation energies were determined by performing TDS analysis. Samples for TDS analysis were discs with a diameter of 20 mm, which were ground till 1 mm thickness to remove surface oxides [42,43]. The samples were hydrogen charged, similarly as described above, and three different heating rates of 200 °C/h, 600 °C/h and 1200 °C/h were used. Three samples were tested for each heating rate. However, the applied experimental procedure required 1 h between the end of hydrogen charging and the start of the TDS measurement as an appropriate vacuum level needs to be created in the analysis chamber before the TDS measurement could start. The hydrogen detection was done by a mass spectrometer. The method based on the work of Lee et al. [44–46] was used to determine the Ea of hydrogen traps related to the peaks observed in the TDS spectra. Equation (1) is a simplification of the original formula of Kissinger [47]:

\[
\frac{d \ln \left( \frac{\Phi}{T_{max}^2} \right)}{d \left( \frac{1}{T_{max}} \right)} = -\frac{E_a}{R}
\]

where \( \Phi \) is the heating rate (K/min), \( T_{max} \) the TDS peak temperature, \( E_a \) (J/mol) the detrapping activation energy for the specific hydrogen trap associated with \( T_{max} \) and \( R \) (JK–mol–1) the universal gas constant. After TDS measurements using different heating rates, deconvolution of these results and determining the corresponding peak temperatures for a trap, plotting \( \ln(\Phi/T_{max}^2) \) vs. \( 1/T_{max} \) allows to obtain the \( E_a \) corresponding to that specific trap.

**Material characterization**

The Vickers hardness level of the different conditions was determined to estimate the temperature at which the secondary hardening effect, due to the carbide formation, was most significant (cf. Fig. 1). After tempering at 600 °C for 1 h, a clear secondary hardening peak was detected, which is associated with the precipitation of W based carbides. The as-Q conditions of the alloys still showed the highest hardness value, which is ascribed to the decreasing dislocation density upon tempering and the slow diffusion of tungsten [24] resulting in a limited secondary hardening [25]. Nevertheless, the differences in HV between the three alloys were fairly constant and related to the increasing carbon content as shown in Table 1. Moreover, all carbon is found to be dissolved in the as-Q conditions for alloy A, B and C by thermo-

<p>| Table 1 – Chemical composition of the used materials in wt.% |
|---------------------------------|----------|----------|-----------|</p>
<table>
<thead>
<tr>
<th>Material/element</th>
<th>C</th>
<th>W</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A</td>
<td>0.096</td>
<td>2.670</td>
<td>150–200 ppm Al</td>
</tr>
<tr>
<td>Alloy B</td>
<td>0.186</td>
<td>6.130</td>
<td></td>
</tr>
<tr>
<td>Alloy C</td>
<td>0.277</td>
<td>8.700</td>
<td></td>
</tr>
</tbody>
</table>
dynamical dissolution equations \cite{40,48}, which clarify the similar HV differences between the alloys. A martensitic (as-Q) and tempered martensitic (Q&T) matrix were obtained as presented in \cite{40} and in-depth TEM analysis was done to characterize the precipitates. Representative results are displayed for alloy C in the Q&T condition at 600 °C for 1 h. A TEM bright field image together with the corresponding relative carbide size distribution map is presented in Fig. 2. Only carbides with sizes above 20 nm were detected. The carbides sizes for Fe–C–W alloy A and B will be slightly larger since these are embedded in a less dense martensitic matrix due to the lower carbon content, which was already demonstrated before in Fe–C–Mo \cite{38} and Fe–C–Cr alloys \cite{37}. Furthermore, a diffraction pattern was taken from a selected area, indicated by the white circle in the TEM bright field image shown in Fig. 3 (a), to determine the carbide type. The selected area diffraction pattern is presented in Fig. 3 (b) and revealed the existence of the W2C crystal structure with a zone axis along [123]. The crystal structure of W2C can be designated as a slightly distorted hexagonal close-packing of W atoms with carbon atoms occupying half of the octahedral interstices. The carbon atoms will be distributed in an ordered manner, the type and degree of ordering depending on temperature \cite{49}. The corresponding directions of the diffraction spots are designated in the diffraction pattern as well.

**Hydrogen uptake and trapping capacity**

The total amount of hydrogen was determined by melt extraction after hydrogen charging as described above. The results for all conditions, i.e. the as-Q and the Q&T samples at different temperatures, are summarized in Fig. 4. The amount of hydrogen increased for alloy A → B → C in both the as-Q and all Q&T conditions. This observation was, in correspondence to the hardness results, linked to the increasing carbon content, which lead to a denser martensitic microstructure, hence increasing the available hydrogen trapping sites. Similar findings were already obtained previously \cite{30,31,50}. In contrast, the hydrogen content in the Q&T condition at 600 °C and 700 °C followed inversely the tendency of the hardness results. The Q&T condition with tempered induced carbides at 600 °C, which resulted in a material strengthening (cf. Fig. 1), showed the lowest amount of hydrogen, while the hydrogen content increased again for the Q&T condition tempered at 700 °C. Moreover, although W2C particles were induced during tempering at 600 °C (cf. Fig. 3), the amount of detected hydrogen was reduced compared to the carbide free as-Q conditions. This remarkable result did not follow the tendencies found for TiC, Mo2C and V4C3 precipitates where the Q&T condition at 600 °C clearly showed a significant higher amount of hydrogen compared to the as-Q condition \cite{36,38,39}. The observed steady decrease when tempered at 500 °C, 550 °C and 600 °C is however consistent for alloy A, B and C, indicating the weak or absent trapping capacity of the induced carbides. The lower amount of hydrogen for Q&T condition at 500 °C, 550 °C and 600 °C compared to the as-Q condition can therefore be linked to the decreasing dislocation density with tempering \cite{37,40,51,52}. TDS analysis is however required for further confirmation on the hydrogen trapping capacity of the induced W2C precipitates. In addition, the increase at 700 °C is remarkable as well and contradictory to the decreasing dislocation density reasoning.

![Fig. 1 – Evolution of the hardness vs. tempering temperature applied for 1 h for the Fe–C–W alloys.](image1)

![Fig. 2 – TEM bright field image together with the corresponding carbide size distribution map of alloy C in the Q&T (600 °C for 1 h) condition.](image2)
Similarly to the TiC precipitates in the Fe–C–Ti alloys [36], this increase can be linked to elastic stress fields surrounding the larger incoherent carbides or to the presence of a different W based carbide which might be capable to trap a significant amount of hydrogen. This will be further analyzed in Section 6.

The Q&T (600 °C for 1 h) condition clearly contained W2C precipitates as confirmed by the hardness profiles and TEM analysis. To verify whether these precipitates were able to trap hydrogen, TDS was performed as presented in Fig. 5 and the corresponding activation energies are summarized in Table 2. Only results on alloy C are considered since similar findings were observed for alloy A and B, for which we would like to refer the reader to other work [40].

Only one trapping site was detected for the as-Q and Q&T (600 °C for 1 h). The induced W2C carbides were hence not able to trap hydrogen. These deconvoluted peaks showed activation energies in the range of 28–32 kJ/mol, which can be mainly correlated to hydrogen trapped at the lath boundaries [53] and possibly to some of the remaining hydrogen trapped by dislocations [19,54,55]. This was concluded since the detection of hydrogen trapped by dislocations has been confirmed to be hardly possible by TDS due to its experimental restrictions [41,56]. During the 1 h needed to establish vacuum in the analysis chamber, hydrogen trapped by dislocations has been demonstrated to be mostly released. The decrease in dislocation density by tempering [51,52] might thus account for the reduction in hydrogen content when the samples were tempered (600 °C for 1 h), as confirmed by melt extraction (cf. Fig. 4). However, the decrease in dislocation density cannot completely account for the decrease in TDS peak for the Q&T (600 °C for 1 h) peak as hydrogen trapped by dislocations is assumed to be mainly undetectable by TDS [36–39].

Definitely, the hydrogen diffusivity plays a significant role as well when interpreting these TDS spectra, i.e. the Q&T condition showed a higher diffusion coefficient compared to the as-Q condition as determined by permeation experiments and discussed in [40]. This higher hydrogen diffusivity was correlated to the lower dislocation density. Besides, the difference between the total hydrogen content (cf. Fig. 4) and amount of hydrogen detected by TDS originates from some residual, strongly irreversibly trapped hydrogen which is absorbed in the material during processing and is only released from the material upon melting.

The incapability of the present carbides to trap hydrogen was associated to their rather large size and hence incoherent nature. This impact on the hydrogen trapping ability was further investigated by applying a modified thermal treatment to induce smaller W based precipitates.

**The effect of carbide size on the hydrogen trapping capacity**

Since the carbide size and coherency mainly determine the hydrogen trapping capacity [36–39], the tempering time was reduced to 10 min instead of 1 h to introduce smaller W2C in the Fe–C–Ti alloys [36]...
the martensitic matrix. A representative STEM bright field image together with the corresponding relative carbide size distribution map is shown in Fig. 6. Smaller disc-shaped precipitates were detected with sizes ranging from a few nm up to 30 nm. These tiny carbides already disappeared when the tempering time was 1 h (cf. Fig. 2).

Melt extraction was performed on the samples tempered for 10 min and results on the as-Q, Q&T (600 °C for 10 min) and Q&T (600 °C for 1 h) materials are presented in Fig. 7. Clearly, an increase in hydrogen content was observed for alloy A, B and C in the Q&T (600 °C for 10 min) condition compared to the as-Q states. Although the dislocation density was decreased when tempered for 10 min, more hydrogen was detected, which indicated that the present smaller carbides of less than 20 nm indeed trapped a substantial amount of hydrogen. The hydrogen trapped by the precipitates compensated the loss of hydrogen trapped by the dislocations. TDS was done again to confirm this hypothesis. When tempering continued for 1 h, the hydrogen content decreased again, which was correlated

### Table 2 – Summary of the corresponding activation energies for the deconvoluted peaks.

<table>
<thead>
<tr>
<th>Activation energy (kJ/mol)</th>
<th>Alloy A</th>
<th>Alloy B</th>
<th>Alloy C</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Q</td>
<td>Peak 1</td>
<td>Peak 2</td>
<td>Peak 1</td>
</tr>
<tr>
<td>Q&amp;T (600 °C for 1 h)</td>
<td>31 / 30</td>
<td>32 /</td>
<td>29 / 28</td>
</tr>
</tbody>
</table>

![Fig. 5](image_url) – TDS curves for alloy C in the as-Q and Q&T (600 °C for 1 h) condition at heating rate of 600 °C/h.

![Fig. 6](image_url) – STEM bright field image together with the corresponding carbide size distribution map of alloy C in the Q&T (600 °C for 10 min) condition.

![Fig. 7](image_url) – The total amount of hydrogen after electrochemical charging for alloy A, B and C in the as-Q, Q&T (600 °C for 10 min) and Q&T (600 °C for 1 h) condition.
to the lack of trapping ability of the larger W2C precipitates (cf. Fig. 5) and a decrease in dislocation density.

The TDS spectra of alloy C in the as-Q and Q&T (600 °C for 10 min) condition are presented in Fig. 8. Alloy A and B showed similar tendencies and the corresponding activation energies for all deconvoluted peaks is summarized in Table 3. The TDS spectrum of the Q&T (600 °C for 10 min) material showed a clear shoulder and was therefore deconvoluted into two peaks. The first one showed an $E_a$ of about 28–31 kJ/mol and was hence linked to hydrogen trapped by the lath boundaries, accordingly to the as-Q and Q&T (600 °C for 1 h) condition (cf. Fig. 5 and Table 2). The second peak showed a higher $E_a$ of about 42–45 kJ/mol and was therefore correlated to hydrogen trapped by the tempered induced precipitates with sizes less than 20 nm. Moreover, hydrogen trapped at W2C is assumed to be trapped at the carbide/matrix interface, since the corresponding peak disappears with increasing tempering time (cf. Fig. 5) due to the decreasing total interfacial area. Similar observations were made in [19,21,36–41,57]. This also confirms the findings of the melt extraction (cf. Fig. 7) and the hydrogen trapping dependence on the carbide size and coherency, as proposed previously for other type of carbides [19,22,36–39,57,58]. Hence, the trapping capacity of a certain type of carbide is hard to assess since the different characteristics of the carbide determines its trapping ability. Therefore, carbides with tailor made characteristics will be required for materials with optimal hydrogen resistance.

### The effect of carbide type on the hydrogen trapping capacity

One remaining issue is the increased hydrogen content when the materials were tempered at 700 °C, as shown in Fig. 4. The hardness measurements gave a lower value, so basically the small W2C precipitates, which strengthened the materials at 600 °C, have grown too large to have a beneficial effect on the strength level. There seems to be a contradiction as more hydrogen was detected, and it was confirmed in the previous section that only the tiny W2C particles, with sizes less than

| Table 3 – Summary of the corresponding activation energies for the deconvoluted peaks. |
|---------------------------------|----------------|---------------|----------------|----------------|
| Activation energy (kJ/mol)      | Alloy A Peak 1 | Alloy A Peak 2 | Alloy B Peak 1 | Alloy B Peak 2 |
| As-Q                            | 31 /           | 30 /          | 32 /           | 31 /           |
| Q&T (600 °C for 10 min)         | 29 42          | 28 44         | 31 45          |

Fig. 8 – TDS curves for alloy C in the as-Q and Q&T (600 °C for 10 min) condition at heating rate of 600 °C/h.

Fig. 9 – TDS curves for alloy C in the as-Q and Q&T (700 °C for 1 h) condition at heating rate of 600 °C/h.
20 nm, were able to trap hydrogen. To clarify this observation, TDS was again performed on alloy A, B and C in the Q&T (700 °C for 1 h) condition. The corresponding spectrum for alloy C is presented in Fig. 9 together with the as-Q condition for sake of comparison, while Table 4 summarizes the corresponding Ea's of the deconvoluted peaks for all alloys. The first deconvoluted peak with Ea of about 31–33 kJ/mol was again attributed to hydrogen trapped at the lath boundaries, similarly for the as-Q and Q&T at 600 °C conditions. When the materials were tempered at 700 °C, an additional peak was present with an Ea of about 47–49 kJ/mol. Due to this increased Ea, this second peak is linked to hydrogen trapped at carbides. This confirms the melt extraction results presented in Fig. 4, but is however, still remarkable, taking into account the previously discussed behavior of larger W2C carbides.

Table 4 – Summary of the corresponding activation energies for the deconvoluted peaks.

<table>
<thead>
<tr>
<th>Activation energy (kJ/mol)</th>
<th>Alloy A</th>
<th>Alloy B</th>
<th>Alloy C</th>
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<tbody>
<tr>
<td>Peak 1</td>
<td>Peak 2</td>
<td>Peak 1</td>
<td>Peak 2</td>
</tr>
<tr>
<td>Q&amp;T (700 °C for 1 h)</td>
<td>32</td>
<td>47</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>48</td>
<td>31</td>
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<tr>
<td></td>
<td>49</td>
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To clarify the additional peak in the TDS spectrum when the material was tempered at 700 °C, a detailed TEM investigation was performed. Fig. 10 shows a STEM image where the precipitates are clearly visualized. A corresponding relative carbide size distribution map is added as well and a broad scale of sizes is detected in this condition. One should take into account that considerably more and larger carbides were detected in the Q&T at 700 °C condition compared to the Q&T at 600 °C condition, which therefore affects the corresponding relative size distribution maps. However, when comparing to

![STEM bright field image and Carbide size distribution](image)

**Fig. 10** – STEM bright field image together with the corresponding carbide size distribution map of alloy C in the Q&T (700 °C for 1 h) condition.

![TEM bright field image and selected area diffraction pattern](image)

**Fig. 11** – TEM bright field image of alloy C in the Q&T (700 °C for 1 h) condition (a), of which a selected area diffraction pattern was taken, indicated by the white circle and presented in (b). The crystal structure of W23C6 is shown in black with a zone axis along [213].
the Q&T at 600 °C condition (cf. Fig. 2), again smaller carbides with sizes less than 20 nm were present. This indicated that a different kind of carbide was induced when tempering at 700 °C.

Diffraction was performed on a selected area as indicated by a white circle in Fig. 11 (a) to determine the morphology of the precipitate. Next to the presence of coarse W2C particles, the existence of W23C6 particles was revealed as well. The selected area diffraction pattern is presented in Fig. 11 (b) and confirmed the existence of the W23C6 crystal structure with a zone axis along [213]. The corresponding directions of the diffraction spots are designated in the diffraction pattern as well. Therefore, the extra TDS peak can be correlated to these newly formed small W23C6 carbides which indeed tend to trap hydrogen.

**Conclusion**

The hydrogen trapping capacity of W based carbides was evaluated by TDS analysis in three lab cast Fe–C–W alloys with increasing carbon content. Two conditions were compared; a martensitic as-Q and a tempered martensitic Q&T condition in which W2C and W23C6 precipitates were generated, depending on the applied heat treatment. The total amount of hydrogen decreased when the tempering was done at 600 °C for 1 h compared to the as-Q condition for alloy A, B and C. The tempering induced W2C precipitates were not able to trap hydrogen as verified by TDS. This was linked to their rather large size (>20 nm). The decrease in hydrogen content determined by melt extraction was correlated with a reduction in dislocation density. When the tempering time was reduced to 10 min at 600 °C to generate smaller W2C particles (<20 nm), a higher hydrogen content and an additional TDS peak was observed. The smaller W2C carbides trapped a significant amount of hydrogen with a corresponding activation energy of about 42–45 kJ/mol. Moreover, the hydrogen content also increased when tempering was applied at 700 °C instead of 600 °C for 1 h. TDS again revealed the presence of a peak correlated to carbides with slightly higher activation energies of about 47–49 kJ/mol. TEM diffraction showed, next to the existence of coarse W2C particles, also the presence of small W23C6 carbides, which accounted for the observed hydrogen peak in the TDS analysis. Therefore, both the size and the type of the carbides play a determinant role to interpret the trapping capacity of W based precipitates.

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