Hydrogen Absorption and Desorption of Steel in the High Strength Bolt Manufacturing

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It is needless to say by now that delayed fracture is an intrinsic issue in high strength bolt steels. Since hydrogen absorption of bolt steels in galvanizing must be taken into account besides the absorption from the environment of bolt usage, baking is integrated within the manufacturing process of galvanized bolts in order to decrease the absorbed hydrogen. But there are processes in bolt manufacturing other than galvanizing in which the hydrogen absorption is assumed to take place. The authors investigated the effect of each manufacturing process on the amount of the absorbed hydrogen in bolt steels.

KEY WORDS: diffusible hydrogen; hydrogen absorption; hydrogen desorption; high strength bolt; heat treatment; quenchant; quench cracking.

1. Introduction

Delayed fracture of steel has been one of top issues in developing high strength bolts and it is by now already well known that hydrogen absorbed from the environment of bolt usage increases the tendency to fracture in bolts. This kind of embrittlement has come to be called as hydrogen embrittlement. The susceptibility of bolts to the hydrogen embrittlement increases as the strength of bolts increases. Such the hydrogen that accounts for the hydrogen embrittlement out of the whole hydrogen which is absorbed in bolts is so called diffusible hydrogen.1) Because hydrogen permeates into bolts from the environment of usage, it is common that high strength bolts are galvanized to prevent the permeation. Baking usually comes after galvanizing in order to lessen the diffusible hydrogen that also possibly derives in galvanizing itself. Therefore, investigations have been conducted on hydrogen absorption and desorption behavior through galvanizing and baking.2,3)

Although galvanizing and baking is supposed to be the final heat treatment before shipment and is to hold the greatest influence on the behavior of the diffusible hydrogen, processes other than galvanizing and baking, such as pickling of wire rods, drawing, spheroidizing annealing and cold heading and threading, can be the source of the diffusible hydrogen in bolts. Such the investigation which specifically studies the absorption and desorption of hydrogen in bolt manufacturing has been conducted on pre-stressed concrete steel bars4) but unprecedented on high strength bolt steels so far.

Our motivation is to reveal absorption and desorption of the diffusible hydrogen in bolt manufacturing processes. The amounts of the diffusible hydrogen were measured and possible sources of the diffusible hydrogen were thoroughly discussed.

2. Experimental Procedures

2.1. Materials Used

The chemical compositions of bolt steels employed in the current study are tabulated in Table 1. JIS SCM435 steel and the steel containing boron are denoted as SCM435 and Boron in this paper, respectively. In order to investigate the amount of the diffusible hydrogen in SCM435 at each manufacturing process, samples were selected as follows. Fig. 1 shows the typical bolt manufacturing process along with steps where sampling was carried out. These processes are denoted with their initials in upper case including Heat Treatment in order to differentiate the heat treatments performed on the bolts from heat treatments referred to in 2.2. Sample ① was taken from As Rolled wire rod, sample ② was from a wire rod after Acid Pickling and Neutralizing, sample ③ after Spheroidizing Annealing, sample ④ after Drawing, and sample ⑤ was a bolt after Cold Heading and Threading.

In order to compare the variation of the amount of the diffusible hydrogen among various bolts with different dimensions, different strengths and different steels, SCM435 and Boron bolts given different Heat Treatment were investigated. These bolt samples are denoted as sample①s hereafter.

<table>
<thead>
<tr>
<th>steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCM435</td>
<td>0.34</td>
<td>0.16</td>
<td>0.80</td>
<td>0.013</td>
<td>0.012</td>
<td>1.15</td>
<td>0.15</td>
<td>–</td>
</tr>
<tr>
<td>Boron</td>
<td>0.22</td>
<td>0.20</td>
<td>0.87</td>
<td>0.018</td>
<td>0.015</td>
<td>0.79</td>
<td>–</td>
<td>0.0022</td>
</tr>
</tbody>
</table>
2.2. Heat Treatment

The effect of heat treatment conditions on the hydrogen absorption was investigated. A polished disc of SCM435 having dimensions of 15 mm in diameter and 10 mm in thickness was employed as a specimen. Specimens were prepared by quenching in either oil kept at 70°C or in water at 25°C after being held in a muffled furnace at 830°C for 20 minutes. The furnace was continuously being purged with N₂ gas during experiment. A number of oil quenched specimens were tempered at various temperatures from 200 to 500°C for 60 minutes followed by water cooling upon tempering. The one of the specimens that was coated with phosphate was given quenching to estimate the effect of the coating on hydrogen absorption during heat treatment. The atmosphere inside a manufacturing furnace during heat treatment is the one experimental parameter that is hard to reproduce in laboratory. The effect of the atmosphere was not investigated. As soon as heat treatment was finished, specimens were gotten rid of oxide scale by polishing with emery papers and stored in a container cooled with liquid nitrogen.

Table 2. Details of sample⑥s.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Class of bolt strength (JIS B 1051)</th>
<th>Bolt size (JIS B 0123)</th>
<th>Heat Treatment conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCM435</td>
<td>10.9 *M20 50 mm length</td>
<td>test-1 860°C-OQ***</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>test-2 860°C-OQ, 520°C temper(WC)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>test-3 QT+Galvanizing&amp;Baking</td>
<td></td>
</tr>
<tr>
<td>Boron</td>
<td>12.9 **M16 50 mm length</td>
<td>test-4 860°C-OQ</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>test-5 860°C-OQ, 490°C temper(WC)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.9 *M16 45 mm length</td>
<td>test-6 860°C-OQ</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>test-7 865°C-WQ</td>
<td></td>
</tr>
</tbody>
</table>

*hexagon head bolt **hexagon socket head bolt ***OQ: oil quenching upon quenching, WQ: water quenching upon quenching, WC: water cooling upon tempering, QT: quenching and tempering

2.3. Thermal Desorption Spectroscopic Analysis

The installation equipped with a silica tubular furnace through which an Ar gas carrier flows to a gas chromatography was chosen to perform the thermal desorption spectroscopic analysis. The heating started from the room temperature up to 600°C with the heating rate of 200°C per hour. A diffusible hydrogen content was calculated by integrating a thermal desorption spectrum from the room temperature up to 300°C.  

3. Results and Discussions

3.1. Diffusible Hydrogen Absorption and Desorption in the Bolt Manufacturing

The amounts of the diffusible hydrogen through sample① to sample④ and their thermal desorption spectra with regard to temperature are plotted in Figs. 2 and 3, respectively. The diffusible hydrogen was detected from sample①, which indicates the absorption of the diffusible hydrogen during Acid Pickling and Neutralizing. This implies that the absorption should also occur in Acid Pickling and Neutralizing and Phosphate Coating after Spheroidizing Annealing, of which the amount of the diffusible hydrogen was not investigated in this paper. The diffusible hydrogen that may have been absorbed in Acid Pickling and Neutralizing and Phosphate Coating must have desorbed out by or during Cold Heading and Threading given that no diffusible hydrogen was detected from sample⑤ nor sample⑥.
3.2. Diffusible Hydrogen Absorption and Desorption in Heat Treatment

The amounts of the diffusible hydrogen in sample ⑥, their thermal desorption spectra of SCM435 and two spectra of Boron are shown in Figs. 4, 5 and 6, respectively. In both the steels, certain amounts of the diffusible hydrogen were detected from the Quenching samples. They are also detected from the Quenching and Tempering samples in SCM435. This is the proof of diffusible hydrogen absorption in both Quenching and Quenching and Tempering. In addition, the Quenching samples always adsorbed more diffusible hydrogen than the Quenching and Tempering samples. It ought to be strongly focused that the temperatures at which the hydrogen desorption curves showed the first peaks were lower in Quenching and Tempering samples (test-2 and test-5) than Quenching samples (test-1 and test-4) in Fig. 5. The first peak of a hydrogen desorption curve of steels usually shifts to the higher temperature after being exposed in the air for a certain period because the diffusible hydrogen detected at the lower temperature tends to desorb preferentially during exposure in the air. This indicates that the diffusible hydrogen observable in Quenching and Tempering samples derived in Tempering rather than in Quenching; the whole diffusible hydrogen that derived in Quenching may have desorbed out of the bolt during Tempering. The computed duration that the content of the diffusible hydrogen decreases from 1 mass ppm to the half in a bar of 20 mm in radius at the tempering temperature of 500°C is 30 s according to the model[5] Suzuki et al. offered. The diffusible hydrogen of no more than 1 mass ppm derived in Quenching should have thoroughly desorbed out of the bolts during Tempering in which the bolts were heat treated at 490°C or 520°C for a certain period that is ordinarily much longer than 30 s in bolt manufacturing.

It is also notable that the amounts of the diffusible hydrogen in Quenching and Tempering and QT plus Galvanizing and Baking bolts in Fig. 4 are so lower than the critical diffusible hydrogen content[6] (Hc) that bolts should not suffer from the diffusible hydrogen they absorbed in Tempering.

The results from the experiment using the disc specimens are summarized in Table 3 and thermal desorption spectra except test-10 are plotted in Fig. 7. The diffusible hydrogen was detected in both the oil quenched specimen and water quenched specimen. The amount of the diffusible hydrogen in the oil quenched specimen (test-8) was greater than that in the water quenched specimen (test-9). The same result

<table>
<thead>
<tr>
<th>test</th>
<th>quenching</th>
<th>tempering</th>
<th>Diffusible hydrogen (mass ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>test-8</td>
<td>830°C-OQ</td>
<td>–</td>
<td>0.017</td>
</tr>
<tr>
<td>test-9</td>
<td>830°C-WQ</td>
<td>–</td>
<td>0.008</td>
</tr>
<tr>
<td>test-10</td>
<td>830°C-OQ</td>
<td>200–500°C×60 min (WC)</td>
<td>0</td>
</tr>
<tr>
<td>*test-11</td>
<td>830°C-OQ</td>
<td>–</td>
<td>0.019</td>
</tr>
</tbody>
</table>

*: test-11: phosphate coated specimen

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**Table 3. Amounts of the diffusible hydrogen in SCM435 with quenching and tempering.**

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**Fig. 4.** Diffusible hydrogen contents of the bolts after Heat Treatment.

**Fig. 5.** Thermal desorption spectra of SCM435 bolts after Heat Treatment.

**Fig. 6.** Thermal desorption spectra of Boron bolts with different Quenching condition.

**Fig. 7.** Thermal desorption spectra of SCM435 with quenching.
was observed in the bolt samples referred to above. No dif-
fusible hydrogen, however, was detected in the tempered
samples.
It has been revealed that hydrogen permeates into the bolt
steels in Heat Treatment. There are three possible sources of
hydrogen; \( \text{① quenchant (oil or water), ② furnace atmosphere and ③ phosphate coating as a lubricant for Cold Heading and Threading. Discussion is going to be made about possible}

sources of the diffusible hydrogen in the next section.

3.2.1. The Effect of the Quenchants
It has been widely accepted that boiling generally transit
the three phases from the film boiling, nucleate boiling to
convection on the surface of a material being cooled. A
thermally decomposed gas generates mainly in the film boil-
ing phase, which consists of hydrocarbons when the quen-
chant is oil and water vapor when it is water. These are
illustrated in Fig. 8. The amount of the gases that generate
upon cooling is proportional to the temperature deficit be-
tween a heated material and a quenchant and to the
dimensional factor which is given by V/S where V repre-
sents a volume and S represents a surface area. This sug-
gests that the larger amount of a thermally decomposed gas
should generate where the temperature of a bolt increases
and where the V/S ratio of it increases. It is unfortunate that
the suggestion concerning the temperature is not arguable
based on the experimental results presented in this paper.
This means that the discussion on the variation of the
amounts of the diffusible hydrogen between the two bolts
(test-2 snd test-5) having different strengths cannot be made
because the strengths simply depend on Tempering temper-
atures.
As for the other suggestion, the dependence of diffusible
hydrogen contents with regard to the V/S ratio is plotted in
Fig. 9. These plots obviously indicate that the bolt steels
having the greater V/S ratio absorb the more diffusible
hydrogen upon cooling in the liquid quenchants. The anal-
ogy between the fact that the more amount of the thermally
decomposed gases generates according to the V/S ratio and
the result that the more diffusible hydrogen is absorbed in
the bolt steels according to the V/S ratio extrapolates that
the dictating phase in which the bolt steels absorb the most
hydrogen is the film boiling where the thermally decom-
posed gases massively generate on the surface of the bolt
steels during cooling in Heat Treatments.
In this study, the more diffusible hydrogen was detected
in Boron bolt (test-6) than in SCM435 bolt (test-4). Komazaki et al. reported the contradicting effect of boron
addition that the prevention of hydrogen adsorption on the
steel surface could be gained by it. This contradiction must
be due to the difference in the experimental condition. The
absorption of hydrogen in cooling and that in cathodic elec-
trolysis in an aqueous solution may not be comparable.
Given that the thermally decomposed gases are the most
decisive media on the hydrogen absorption upon cooling, it
is worth noting that the amount of the diffusible hydrogen
absorbed was greater in the oil quenched bolts and specimen
than in the water quenched bolts and specimen. This should
be because a hydrocarbon gas usually contains more hydrogen
atoms than water vapor does.

3.2.2. The Effect of the Atmosphere and Phosphate Coating
In the industrial bolt manufacturing, \( \text{C}_3\text{H}_8 \) gas is mixed
with the air to one-seventh in volume as a fuel in Quenching
and Tempering which inevitably renders a furnace atmos-
phere deoxidizing. Comparing test-1 with test-4, which are
different in V/S ratio, and test-6 with test-7, which are
quenched in different quenchants, the amounts of the diffus-
able hydrogen vary according to the effects referred to above
even though those bolts were heat treated in the same atmo-
sphere. The fact that the various bolts heat treated in the
same atmosphere have a variety in the amount of the diffus-

![Fig. 8. Schematic diagram of transition of the boiling phases upon cooling and thermally decomposed gases.](image-url)

![Fig. 9. Variation of diffusible hydrogen contents with regard to V/S ratio: (a) quenching, (b) quenching and tempering.](image-url)
ible hydrogen postulates the quite limited influence of the atmosphere on the diffusible hydrogen absorption of the bolts. The amount of the diffusible hydrogen desorbed from the phosphate coated specimen was no different from that of the specimen without the coating as shown in Table 3. This postulates that the coating has the limited influence on the diffusible hydrogen absorption, too.

It has been confirmed that the diffusible hydrogen can be absorbed into the bolt steels not only from the environment of usage but also from the manufacturing processes. The absorption took place in Acid Pickling and Neutralizing, Heat Treatment, and Galvanizing & Baking. The emphasis has to be made especially on that the absorption occurs upon cooling in Quenching and Tempering. The amount of the diffusible hydrogen brought from the coating has the limited influence on the diffusible hydrogen absorption, too.

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3.2.3. Quench Cracking

The special notification has to be made on the phenomenon that steels absorb hydrogen massively upon quenching because this must lead to the association of the hydrogen absorption with the quench cracking. Liu et al. indicated that the quench cracking was a form of hydrogen-induced cracking along with the result that a nickel plating which isolated a steel from water vapor upon quenching prevented cracking. But this indication was only extrapolated from the resemblance in surface features of the quench crack surface to the typical hydrogen induced crack surface. It is proven in this paper that the bolt steels do absorb hydrogen in Heat Treatments, especially massively upon Quenching. This evokes the question if hydrogen induces not only delayed fracture but also quench cracking.

The amount of the diffusible hydrogen absorbed was greater in oil quenching than in water quenching although empirically quench cracking is much less likely to occur in oil quenching than water quenching. This must readily be explained by the difference in the residual stress distribution of steels quenched in oil from in water.

These should be remained for a further investigation.

4. Conclusions

(1) Up to cold heading and threading, the effect of the diffusible hydrogen absorbed into the bolt steels was negligible because diffusible hydrogen was detected neither in the samples after Drawing nor Cold Heading whereas it was detected in the sample after Acid Pickling and Neutralizing.

(2) The diffusible hydrogen was detected in the Quenching and Quenching and Tempering sample's. The dominant source of the diffusible hydrogen is a quenchant. The diffusible hydrogen is mostly absorbed upon cooling. The amount of the diffusible hydrogen absorption increases as the V/S ratio increases. The effects of the furnace atmosphere and the phosphate coating are comparably limited.

(3) The amounts of the diffusible hydrogen in Tempering or QT+Galvanizing & Baking bolts were no deteriorative although it should be taken into consideration that the certain amount of the diffusible hydrogen absorbed in Heat Treatment could be brought into Galvanizing.

(4) It is worth noting that the absorption of hydrogen upon quenching may result in following quench cracking. This should inspire a future study.

REFERENCES