HYDROGEN EMBRITTLEMENT OF DIFFERENT VARIANTS OF TRIP 800 STEELS
VODÍKOVÁ KŘEHKOST ROZDÍLNÝCH VARIANT OCELÍ TRIP 800

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Abstract

The presented paper evaluates the hydrogen embrittlem ent of three TRIP 800 steel variants. The two types of investigated steels are based on C-Mn-Si composition. The first one was made industrially, the second one was prepared in laboratory conditions. The third TRIP 800 steel variant corresponding to C-Mn-Si-Al composition was also prepared in laboratory conditions. All of the mentioned TRIP steels are characterized by yield strength ranging from 420 to 490 MPa and tensile strength between 880 and 950 MPa. The TRIP steels were studied in the form of sheets with thickness of 1.5 mm. Their resistance to hydrogen embrittlement was evaluated using tensile tests. The tensile specimens were electrolytically hydrogen charged in different solutions (with or without “hydrogen poisons”). Duration of electrolytic hydrogen charging varied from 4 to 24 hours. Tensile tests were carried out immediately after hydrogen charging. Hydrogen embrittlement manifested itself by significant decreasing the ductility, and due to this fact, the hydrogen embrittlement index was calculated. Both two heats prepared in laboratory conditions showed higher resistance to hydrogen embrittlement in contrast to the industrially manufactured heat. It is probably thanks to the higher content of retained austenite (11 – 13 %) in the laboratory prepared heats. Concerning the failure mode, transgranular cleavage fracture was mostly observed after hydrogen charging. Special defects, so-called “fish eyes”, were observed only to a limited extent. Exceptionally, the hydrogen charging process itself was responsible for the irreversible damage of the steels.

1. INTRODUCTION

In recent years requirements on properties of steels in many industrial segments were rapidly increasing – namely in automotive industry. The main demands to support the safety-based car body construction and design nowadays are high tensile strength and high fracture toughness as well as high ability to energy absorption during impact. The other necessary properties are good cold-working properties, weldability or ability to hot-dip galvanizing. There is still growing interest in advanced steels that are used for construction of car bodies, so-called advanced high strength steels (AHSS) [1]. The AHSS notation refers to dual phase (DP) steels, complex phase (CP) steels and TRIP steels that are characterized by transformation induced plasticity. TRIP steels are very prospective materials due to their positive ratio between tensile strength and toughness. Moreover the TRIP steels are also well known for their high energy absorption during impact. TRIP steel properties are based on optimal chemical composition. It is essential to provide the higher content of elements that inhibit the cementite and/or carbide precipitation in order to ensure a sufficient fraction of retained austenite in a steel structure at ambient temperature [2]. The optimal content of retained austenite varies from 10 to 15 %. [1,2]. Conventional TRIP steel alloying elements are usually based on Mn (approx. 1.5 wt. %), Si (approx. 1.5 wt. %) and/or Al, which can more or less substitute Si [3,4]. Variants containing
higher phosphorus content are also tested in scope of different studies [5]. The usage of different elements is related to their influence on hot-dip galvanizing. The carbon content in TRIP steels with tensile strength up to 1000 MPa is generally approx. 0.2 wt. % [1]. Optimal mechanical properties are achieved by a proper heat treatment that usually includes two-step annealing – intercritical annealing and annealing in the region of bainitic transformation. During both annealing processes the retained austenite is enriched by carbon up to 1.0 % or even more. It provides the austenite stability at ambient temperature [2]. One of the basic technological demands is easy hot-dip galvanizing of the TRIP steels in order to ensure their corrosion resistance [6]. Pre-treatment processes, e. g. acid pickling in different kinds of acids (preferentially in HCl), precede the hot-dip galvanizing. This operation represents a risk of hydrogen embrittlement as hydrogen can enter the steel during acid pickling [7]. Hydrogen embrittlement could cause even a total destruction of the construction elements and that is why it is necessary to know the resistance of the TRIP steels to hydrogen embrittlement. Generally, high resistance of the TRIP steels to hydrogen embrittlement is assumed thanks to the higher content of retained austenite. The retained austenite in steels forms favourable traps which can strongly bind hydrogen [8]. The TRIP steel resistance to hydrogen embrittlement can be reduced by the same way as in case of other steels due to the presence of non-metallic inclusions especially if they are big and/or elongated. Another reason for hydrogen embrittlement of the TRIP steels is the presence of marked segregations [7].

The presented paper is devoted to the evaluation of the resistance to hydrogen embrittlement in three variants of the TRIP 800 steel with tensile strength min. 800 MPa by means of tensile test on electrolytically hydrogen charged specimens.

2. EXPERIMENTAL MATERIALS AND TECHNIQUES

Three different variants of TRIP 800 steels with guaranteed yield strength min. 420 MPa and tensile strength min. 800 MPa were used for the experimental study. The first of the studied variants (designated as A in following text) is industrially made sheet from the C–Mn-Si TRIP steel with thickness of 1.5 mm. No detailed information about production process was supplied. The second variant (designated as B in following text) is the sheet produced from the C–Mn–Si TRIP steel with thickness of 1.5 mm in laboratory conditions – using the laboratory rolling mill at FMME VŠB - Technical University of Ostrava. The third variant (designated as C in following text) is the sheet from the C–Si–Mn–Al TRIP steel with the same thickness. Variant C was also prepared in laboratories at FMME VŠB - TUO. Chemical composition of all three studied TRIP steels is given in Table 1.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.22</td>
<td>1.65</td>
<td>1.71</td>
<td>0.020</td>
<td>0.004</td>
<td>0.03</td>
<td>0.01</td>
<td>0.02</td>
<td>0.043</td>
</tr>
<tr>
<td>B</td>
<td>0.20</td>
<td>1.48</td>
<td>1.48</td>
<td>0.014</td>
<td>0.004</td>
<td>0.17</td>
<td>0.01</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>C</td>
<td>0.21</td>
<td>1.57</td>
<td>1.05</td>
<td>0.013</td>
<td>0.005</td>
<td>0.16</td>
<td>0.01</td>
<td>0.07</td>
<td>0.54</td>
</tr>
</tbody>
</table>

It is clear that variants A and B represent the „classical“ TRIP steels based on Mn and Si. In the variant C, Si was partially replaced by Al. The Al content of approx. 0.5 wt. % was chosen in order to prevent the presence of high amount of non-metallic inclusions based on Al₂O₃. The high amount of non-metallic inclusions might deteriorate both mechanical properties of the steel and its resistance to hydrogen embrittlement.

The steel variants B and C were submitted to the two-step annealing:
• Variant B - 810°C/6 minutes/accelerated cooling faster than 10°C·s⁻¹/410°C/5 minutes/air;
• Variant C - 810°C/6 minutes/accelerated cooling faster than 10°C·s⁻¹/425°C/5 minutes/air.

The resistance of the TRIP steels to hydrogen embrittlement was studied by means of the tensile tests when a part of specimens was electrolytically charged in hydrogen. The hydrogen charging was performed in 1N water solution of H₂SO₄ at a current density of 30 mA·cm⁻². In some cases KSCN in a concentration of 1 g·l⁻¹ was added to the solution. KSCN acts as “hydrogen poison”, it prevents the hydrogen atom recombination and increases the amount of hydrogen that can enter the steel structure [8]. For the classification of the steel resistance to hydrogen embrittlement the so called index of hydrogen embrittlement \( I_{emb} \) was chosen. It is defined by the following equation:

\[
I_{emb} = \frac{EL_0 - EL_\mu}{EL_0} \times 100 \quad (\%)
\]

where \( EL_0 \) is elongation of the specimen in the initial state without hydrogen charging (%);

\( EL_\mu \) is elongation of the specimen after hydrogen charging (%).

After hydrogen charging and tensile tests the fractographic and metallographic analysis was performed by means of the scanning electron microscopy (SEM) and the light microscopy. For the variant A, the hydrogen content in steel after electrolytic hydrogen charging was determined using vacuum extraction method at the temperature of 600°C at the heating rate 100°C per hour.

3. RESULTS AND DISCUSSION

3.1. Mechanical properties and structure of the TRIP steels

Mechanical properties of the studied variants of the TRIP steels are shown in Table 2.

Table 2 Mechanical properties of the studied TRIP steels

<table>
<thead>
<tr>
<th>Steel</th>
<th>Yield strength (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>496</td>
<td>948</td>
<td>27.5</td>
</tr>
<tr>
<td>B</td>
<td>440</td>
<td>890</td>
<td>29.5</td>
</tr>
<tr>
<td>C</td>
<td>425</td>
<td>880</td>
<td>29.5</td>
</tr>
</tbody>
</table>

It is evident that all the studied variants meet the requirements of mechanical properties for the TRIP 800 steel, i.e. yield strength higher than 420 MPa and tensile strength higher than 800 MPa. The variant A showed higher yield strength and tensile strength in comparison with the variants B and C, this fact can be attributed to the higher Mn and Si content but also to the lower content of residual austenite as it will be discussed later. The content of retained austenite in the studied steels was estimated using X-ray diffraction analysis. For the steel variant A the content of retained austenite was 7 ± 2%, which is less than the recommended value [1,2]. In the variant B the retained austenite content was higher 11 ± 2% and the variant C contained 13 ± 2% of residual austenite. The highest value of the retained austenite in the variant C can explain the lowest values of its mechanical properties.
Microstructure of all studied variants was the same from the point of view of the light microscopy. The fine grain microstructure consisted predominantly of proeutectoid ferrite and bainite. In some locations it was possible to see small regions of martensite. It is not possible to identify the retained austenite using the light microscopy. The only trustworthy method to reveal residual austenite in TRIP steels is transmission electron microscopy (TEM). At present the substructure analysis of variants B and C is performed using TEM, but the results are not yet available. An example of the microstructure of the variant B obtained using the light microscopy is shown in Fig. 1. In this micrograph only regions of ferrite and bainite can be clearly distinguished.

**Fig. 1.** Microstructure of the TRIP steel, variant B

### 3.2. Resistance to hydrogen embrittlement

Results of the resistance of all three studied variants of the TRIP 800 steel to hydrogen embrittlement are shown in Fig. 2 using the index of hydrogen embrittlement $I_{emb}$ for the current density of electrolytic hydrogen charging of 30 mA·cm$^{-2}$ and the time of 4 hours. The hydrogen charging was performed with and without „hydrogen poison“. Four hours of electrolytic charging represent the shortest possible time of hydrogen charging for the thickness of 1.5 mm taking into account the value of the hydrogen diffusion coefficient in TRIP steels at ambient temperature, which is approximately $10^{-7}$ cm$^2$·s$^{-1}$. This value is at least by one order lower in comparison with common steels with the bbc lattice [7]. The low value of the hydrogen diffusion coefficient in TRIP steels can be related to the higher amount of residual austenite.

It is evident from the results presented in Fig. 2 that both two variants of the TRIP steels prepared in laboratory conditions (B and C) had higher resistance to hydrogen embrittlement. It can be attributed to the higher fraction of retained austenite in these two variants. While in case of the A variant application of KSCN resulted in a significant increase of the hydrogen embrittlement index, in case of the variants B and C an increase of this index was rather negligible. This difference can be also explained by the positive influence of residual austenite, which represents favourable and very deep traps in the steel structure. More detailed conclusions will be available when the substructure analysis of the studied TRIP steels is finished. For the given testing conditions the variant B seems to be more resistant to hydrogen embrittlement than the variant C. This difference can be related to the higher fraction of non-metallic inclusions in the variant C, which contains higher amount of Al. In this variant of the TRIP steel aluminium oxides, presented mainly in the centre of the sheet thickness, and also aluminium nitrides were found. Especially aluminium nitride particles could provoke cleavage fracture in this steel.

**Fig. 2.** Index of hydrogen embrittlement for the studied TRIP steels
The hydrogen content after electrolytic hydrogen charging was until now determined only in the variant A. For 4 hours of hydrogen charging and the current density of 30 mA·cm\(^{-2}\) the hydrogen content was approximately 9 ppm if “hydrogen poison” was not used. In cases when “hydrogen poison” was added to the testing solution the hydrogen content rose to 35-40 ppm, very probably due to the high content of retained austenite. This value exceeds significantly the hydrogen content in common steels with the bcc lattice and low content of residual austenite [7,8].

3.3. Fractography

The fractographic analysis was performed in some specimens after the tensile tests. Both initial state without hydrogen charging and the state after hydrogen charging were studied. In the initial state the failure characteristics of all variants corresponded to the ductile failure with dimple morphology. Fracture surfaces of specimens tested after hydrogen charging revealed that hydrogen embrittlement manifested itself by changing the failure mode. Transgranular cleavage fracture was dominant on fracture surfaces of the specimens tested after hydrogen charging. Very often small secondary cracks were also observed (Fig. 3a). Special defects provoked by hydrogen and initiated on non-metallic inclusions, so-called “fish eyes” were only rarely found in the variants B and C (Fig. 3b). In case of sufficiently long time of electrolytic hydrogen charging (24 hours) even irreversible hydrogen embrittlement was observed. In this case the high amount of hydrogen provoked the crack formation already during electrolytic hydrogen charging, i.e. prior to the tensile test itself (Fig. 3c).

4. CONCLUSIONS

The presented paper was devoted to the evaluation of the resistance of three variants of TRIP steels to hydrogen embrittlement, two of which were based on C–Mn–Si composition and one was based on C–Mn–Si-Al composition. The studied steels differed in the nature of their fabrication (industrial/laboratory) and slightly in mechanical properties and in the content of retained austenite. The hydrogen embrittlement was evaluated using tensile tests on previously electrolytically hydrogen charged specimens. The hydrogen embrittlement index based on a relative drop of elongation and fractographic analysis were used to describe the resistance of the studied steels to hydrogen embrittlement. Laboratory variants of the TRIP steels showed higher resistance to hydrogen embrittlement, very probably due to the higher fraction of retained austenite. What concerns the failure mechanism, hydrogen embrittlement manifested itself mainly by transgranular cleavage fracture. Special defects initiated on non-metallic inclusions – “fish eyes” – were observed only rarely. In case of the long period of hydrogen charging the irreversible hydrogen embrittlement was observed, when hydrogen provoked crack formation already during the hydrogen charging without any necessity of external loading.
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LITERATURE


