Design of hot stamped high strength steels through process optimization to enhance their hydrogen embrittlement resistance

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Outline

• Background
• Materials and methods
• Results
• Conclusions
Background – Hydrogen embrittlement and trapping

Traps in microstructure: grain boundaries, martensite boundaries, dislocations, etc.
- Hot stamped steel
- Lightweight - Impact resistance - Formability
- High UTS → High risk for HE
- Deep trapping sites
- Vanadium → Vanadium carbides
Background - Role of vanadium carbide

I. Better strength and ductility

II. Better resistance to hydrogen embrittlement (hydrogen trapping)

Cho et al., Materials Science & Engineering A 735 (2018) 448–455


- Size and distribution of carbides
- Coherency of the precipitate/matrix interface
- Chemical composition of the carbide $VC, V_xC_y$
- Best hydrogen trapping ability
Materials and methods - Material and process simulation

Immediately after hot rolling, the sheets were placed in a lab furnace to simulate coiling and coil annealing at 500 °C and 700 °C.

Hot rolling/heat treatment to form VC for hydrogen trapping.

Ladle metallurgy/continuous casting

Press hardening process

Press hardening simulations

Austenitization

Heat treatment simulating galvanization

Metal coated PH steel processing

Recrystallization annealing

Cold Rolling

Gleeble simulations

<table>
<thead>
<tr>
<th>Element, wt%</th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Ti</th>
<th>N</th>
<th>V</th>
<th>Al</th>
<th>B</th>
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</thead>
<tbody>
<tr>
<td>Alloy 1</td>
<td>96.94</td>
<td>0.348</td>
<td>0.49</td>
<td>1.47</td>
<td>0.006</td>
<td>0.004</td>
<td>0.6</td>
<td>0.02</td>
<td>0.024</td>
<td>0.003</td>
<td>&lt;0.005</td>
<td>0.026</td>
<td>0.0031</td>
</tr>
<tr>
<td>Alloy 2</td>
<td>96.72</td>
<td>0.352</td>
<td>0.52</td>
<td>1.5</td>
<td>0.005</td>
<td>0.002</td>
<td>0.59</td>
<td>0.02</td>
<td>0.026</td>
<td>0.003</td>
<td>0.15</td>
<td>0.037</td>
<td>0.003</td>
</tr>
</tbody>
</table>
**Methods**

**Characterization of carbides**
- Size
- Chemical composition
- Structure

**STEM and SPED**
- Carbon replica
- EDX mapping
- Image processing
- Diffraction

**Impact of particles** - Hydrogen trapping ability

**Cathodic charging of samples**
- 48 h at RT
- 3 wt. % NaCl + 1 g/l thiourea
- 1 mA/cm²

**Storage at air at RT** (effusion of hydrogen)
- 0 h
- 1 h
- 3 h

**TDMS analysis**
- Diffusible and deeply trapped hydrogen content

**Settings**
- RT to 800 °C, 1°C/s
TEM dark field image - carbon replica

Coiling temperature: 500°C
0 wt.% V

Coiling temperature: 500°C
0.15 wt.% V

Coiling temperature: 700°C
0.15 wt.% V
STEM-EDX

- Provides information about carbide composition
- 0 wt.% V material contained less carbides than 0,15 wt.% material

0 wt.% V
Coiling temp: 500 °C

0,15 wt.% V
Coiling temp: 500 °C

0,15 wt.% V
Coiling temp: 700 °C
Scanning precession electron diffraction (SPED)

- Orientation
- Information about phases

Example:

- VC, cubic
- Fe$_2$C, hexagonal
- TiC, cubic
### Average carbide composition and size

**STEM-EDX**

![STEM imaging and image processing](image)

**Parameters**:

<table>
<thead>
<tr>
<th>Parameters</th>
<th>0wt% V 500°C</th>
<th>0.15wt% V 500°C</th>
<th>0.15wt% V 700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>μ</td>
<td>3.49</td>
<td>2.38</td>
<td>2.40</td>
</tr>
<tr>
<td>σ</td>
<td>0.45</td>
<td>0.58</td>
<td>0.62</td>
</tr>
<tr>
<td>Offset</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Median, nm</td>
<td>32.7</td>
<td>10.8</td>
<td>11.0</td>
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<tr>
<td>Average, nm</td>
<td>36.3</td>
<td>12.8</td>
<td>13.4</td>
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<tr>
<td>Std</td>
<td>17.3</td>
<td>8.0</td>
<td>9.1</td>
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<tr>
<td>Number of particles</td>
<td>141</td>
<td>543</td>
<td>654</td>
</tr>
</tbody>
</table>
Results – TDMS

- All samples showed hydrogen uptake
Results – TDMS

• All samples showed hydrogen uptake
• 0 wt.% V, coiling temp: 500 °C:
  Two peaks
Results – TDMS

- All samples showed hydrogen uptake
- 0 wt.% V, coiling temp: 500 °C:
  Two peaks
- 0.15 wt.% V, coiling temp: 500 °C:
  Multiple peaks
Results – TDMS

- All samples showed hydrogen uptake
- 0 wt.% V, coiling temp: 500 °C:
  Two peaks
- 0.15 wt.% V, coiling temp: 500 °C:
  Multiple peaks
- 0.15 wt.% V, coiling temp: 700 °C:
  Less peaks than 0.15 wt.% V, coiling temp: 500 °C

![Graph showing hydrogen desorption rate vs. temperature for different conditions](image-url)
Results – Hydrogen trapping capacity

0 wt.% V, 500 °C coiling temp.

0,15 wt.% V, 500 °C coiling temp.

0,15 wt.% V, 700 °C coiling temp.
Results – Hydrogen trapping capacity

0 wt.% V, 500 °C coiling temp.

Temp. ↑ = Activation energy ↑

0 h

1 h

3 h

0 wt.% V, 500 °C, 0h
0 wt.% V, 500 °C, 1h
0 wt.% V, 500 °C, 3h

0,15 wt.% V, 500 °C coiling temp.

0,15 wt.% V, 500 °C, 0h
0,15 wt.% V, 500 °C, 1h
0,15 wt.% V, 500 °C, 3h

0,15 wt.% V, 700 °C coiling temp.

0,15 wt.% V, 700 °C, 0h
0,15 wt.% V, 700 °C, 1h
0,15 wt.% V, 700 °C, 3h
Results – Hydrogen trapping capacity

0.15 wt.% V, 500 °C coiling temp.

- Grain boundaries, dislocations
- Vanadium carbides
- Titanium carbides

Hydrogen desorption rate ($H_2$ wppm/s) vs. Temperature (°C)

• Hydrogen content decreases with time at air
- Hydrogen content decreases with time at air.
- Indication: 0.15 wt.% V material with a coiling temp of 500 °C can retain most hydrogen.
Discussion

• Stochiometry of vanadium carbides
  • $V_4C_3$ can trap more H atoms than VC and is the dominant phase for H trapping

• Carbide-matrix coherency
  • VC
    • (100)Fe/(100)VC coherent interface is only a weak trap\(^1\)
    • But C-vacancies at Fe-VC interface and VC bulk are stronger traps\(^1\)
  • $V_4C_3$
    • Misfit dislocation cores on semi-coherent $V_4C_3$ platelets are strong hydrogen traps\(^2\)

\(^1\) S. Echeverri Restrepo, International journal of hydrogen energy, 45, 2020, 2383-2389
\(^2\) Takahashi et al., Acta Materialia, Volume 153, July 2018, Pages 193-204
Conclusions

- High strength steels with 0 wt.% V & 500 °C coiling temp. and 0.15 wt.% V & 500 °C / 700 °C coiling temp. were investigated.
- The vanadium carbides were characterized using STEM-EDX (carbide composition) and SPED (orientation, phase information)
- To study their hydrogen trapping efficiency, the materials were cathodically charged and hydrogen contents were measured using TDMS at 0, 1 and 3 hours after charging.
- Vanadium carbides formed at both coiling temperatures in the vanadium containing material.
- The vanadium carbides show a similar size distribution but differ in chemical composition.
- The TDMS results indicate that 0,15 wt.% V material coiled at 500 °C showed better trapping capacity of diffusible hydrogen compared to 0,15 wt.%, 700 °C.
- Observed differences might be caused by number, stochiometry (VC, V₄C₃) and coherency state of particles.
- Further testing to improve statistics is needed.
Thank you very much for your kind attention!

Acknowledgements