VDM® Alloy 699 XA a new alloy for Syngas Applications under metal dusting conditions

29.10.2019

Dr. Tatiana Hentrich (VDM), John Groth (VDM USA),

Application Engineer Sales  Applications Engineering Manager
tatiana.hentrich@vdm-metals.com John.groth@vdm-metals.com

Dr. Heike Hattendorf (VDM), Alejandra Lopez (Tubacex)
Agenda

I. Introduction
II. Composition
III. Corrosion
IV. Creep
V. Tensile Tests / V Notch Impact Tests
VI. Welding
VII. Conclusion
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Metal Dusting

- In iron, nickel or cobalt base alloys
- In hydrogen, ammonia, methanol and gas-to-liquids plants
- Typically between 400 and 800°C
- Carbon precipitating atmospheres - i.e. mixtures of CO, H₂, H₂O and CO₂
- Carbon - formation at the metallic surface, diffusion into the substrate
- Supersaturating of the metallic substrate in carbon
- Decomposition into a mixture of graphite, oxidic, carbidic, and metallic particles (“metal dust”)
- Formation of pits or general attack and Failure
Background
• Increasing demand for an alloy more metal dusting resistant than VDM® Alloy 602 CA

Target of the alloy development
• High metal dusting resistance than VDM® Alloy 602 CA
• Creep resistance at least like alloy 601
• Outstanding workability (seamless tube production)
• Good weldability
Operational Capabilities

Integrated manufacturing chain with capabilities in melting, hot forming and finishing

Germany Meltshop (Unna)
- Melting
  - Electronic Arc
  - Induction
  - Vacuum Induction
- Secondary Metallurgy
  - Vacuum Ladle
  - Vacuum Oxygen Decarburisation
- Remelting
  - Vacuum Arc
  - Electro Slag Remelting
- Powder Atomisation
  - VIGA

US Meltshop (Florham Park)
- Melting
  - Vacuum Induction
  - Electro Slag Remelting
- Remelting
  - Vacuum Induction

Finishing
- Flat
  - Duisburg (Hot Rolling)
  - Siagen (Plate Rolling)
- Long
  - Unna (Forging)
  - Hot Rolling
  - Weddohl (Bar & Plate Finishing)
- Powder
  - Bars
  - Small Plates
  - Shapes
  - Rounds

Melting
- Long
  - Unna (Forging)
  - Weddohl (Wire Drawing Mill)
- Powder
  - Bars
  - Small Plates
  - Shapes
  - Rounds
VDM® Alloy 699 XA – Tube production, Route (I)

BAR PREPARATION  INDUCTION HEATING  EXPANSION  EXTRUSION  HEAT TREATMENT

STRAIGHTENING  CUTTING  DEGLASSING+PICKLING  PASSIVATION  QUALITY CONTROL

HOT-FINISHED TUBES
VDM® Alloy 699 XA – Tube Production

Manufacturing Route (II)

- HOT-FINISHED HOLLOWs
- COLD-PILGERING
- DEGREASING
- HEAT TREATMENT

- STRAIGHTENING
- CUTTING
- PICKLING
- PASSIVATION
- QUALITY CONTROL

- COLD-FINISHED TUBES
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VDM® Alloy 699 XA - Comparison to other Ni-Cr-Fe alloys

VDM® Alloy 699 XA has a high Cr and Al content, and a low Fe content

**Typical chemical composition**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>UNS</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
<th>Al</th>
<th>C</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>N08800</td>
<td>21</td>
<td>31</td>
<td>47</td>
<td>0.3</td>
<td>0.07</td>
<td>Ti</td>
</tr>
<tr>
<td>601</td>
<td>N06601</td>
<td>23</td>
<td>60</td>
<td>14</td>
<td>1.4</td>
<td>0.06</td>
<td>Ti</td>
</tr>
<tr>
<td>602 CA</td>
<td>N06025</td>
<td>25</td>
<td>60</td>
<td>9</td>
<td>2</td>
<td>0.18</td>
<td>Ti, Y, Zr</td>
</tr>
<tr>
<td>690</td>
<td>N06690</td>
<td>29</td>
<td>60</td>
<td>9</td>
<td>0.3</td>
<td>0.01</td>
<td>Ti</td>
</tr>
<tr>
<td>699 XA</td>
<td>N06699</td>
<td>30</td>
<td>bal</td>
<td>≤ 2.5</td>
<td>2</td>
<td>0.02</td>
<td>Nb, Zr</td>
</tr>
</tbody>
</table>

In mass %
### Composition

**In mass %**

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cr</th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>Ti</th>
<th>Nb</th>
<th>Cu</th>
<th>Zr</th>
<th>C</th>
<th>N</th>
<th>P</th>
<th>S</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min.</td>
<td>26.0</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.005</td>
</tr>
<tr>
<td>Max.</td>
<td>bal</td>
<td>30.0</td>
<td>3.0</td>
<td>2.5</td>
<td>0.50</td>
<td>0.50</td>
<td>0.60</td>
<td>0.50</td>
<td>0.50</td>
<td>0.10</td>
<td>0.10</td>
<td>0.05</td>
<td>0.02</td>
<td>0.01</td>
<td>0.008</td>
</tr>
</tbody>
</table>

### Standards

- **Granted Alloy Number:** 2.4842
- **Granted UNS Number:** N06699
- **Short Name:** NiCr 30 Al
- **Standards:**
  - ASTM B0163 - Seamless Tubes;
  - ASTM B0167 - Seamless Pipes and Tubes;
  - ASTM B0462 - Fittings;
  - ASTM B0516 - Welded Tubes;
  - ASTM B0166 - Rod, Bar, Wire;
  - ASTM B0168 - Sheet plate;
  - ASTM B0472 - Billets;
  - ASTM B0564 - Forgings
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Remarkable increased metal dusting resistance of alloy 699 XA.

**Time to first pit**

In hours

- **Alloy 601**
  - NiCr23Fe15Al1 - T18
  - NiCr23Fe15Al1 - T24

- **Alloy 690**
  - NiCr29Fe9 - T11
  - NiCr30Fe10 - T21

- **Alloy 602 CA**
  - NiCr25Fe9Al2 - T01
  - NiCr25Fe9Al2 - T04

**Lab Melts: Low Fe Alloys - Alloy 699 XA**

- NiCr30Fe0.1 - T16
- NiCr30Fe0.5 - T15
- NiCr28Al2.6Fe0.5 - T08
- NiCr30Al2.8Fe0.5 - T09

- No pits and no attack on edges up to 5693 h (Close down in Apeldoorn).
- Resistance against metal dusting is increased by protective oxide scales (Chromia, alumina, silica)
  => High Cr, Al, Si content of the alloy (Cr+Al ≥ 30 %)
- Increasing amount of less protecting (Fe, Cr) spinels in the oxides scales shortens incubation time for pit formation (K. Natesan, Z. Zeng, Corrosion 2005):
  => Low Fe content of the alloy

H. Hattendorf, R. IJzerman*, C. G. M. Hermse*) **, *) TNO, **) now Shell

Partly also in Corrosion 2018, paper no. C2018 11200, also EFC Workshop, Frankfurt Sept. 2018
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Creep resistance of VDM® alloy 699 XA is at least like VDM® Alloy 601.

Larson - Miller - Plot

\[ P = (T + 273^\circ C)(18 + \log t_b) \]

VDM® Alloy 699 XA
Data on bar: H. Hattendorf (VDM) S. Siegfanz, P. Neddermann (SZMF Duisburg); A. Cueva (MPA/IFW Uni Darmstadt)
Data on tube: A. Lopez (Tubacex)

VDM® Alloy 601 and 600
Data on plate: K. Drefahl, H.-J. Henrich and I. Müller, Metal Laboratory Frankfurt; W. Bendickt, W. Pfeifer (SZMF Duisburg)
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VDM® Alloy 699 XA - Mechanical Properties

Elongation in the range of VDM® Alloy 601.

Tensile test at room temperature - Typical values, (solution annealed)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$R_{P0.2}$ in MPa</th>
<th>$R_m$ in MPa</th>
<th>$A_5$ in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>VDM® Alloy 699 XA - 2.4842</td>
<td>255 - 395</td>
<td>650 - 750</td>
<td>47 - 68</td>
</tr>
<tr>
<td>(2 mother melts- plate, bar, tube)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VDM® Alloy 601 - 2.4851</td>
<td>220 - 300</td>
<td>550 - 710</td>
<td>44 - 68</td>
</tr>
<tr>
<td>VDM® Alloy 602 CA - 2.4633</td>
<td>270 - 390</td>
<td>675 - 780</td>
<td>30 - 54</td>
</tr>
<tr>
<td>VDM® Alloy 690 - 2.4642</td>
<td>240 - 400</td>
<td>610 - 740</td>
<td>40 - 63</td>
</tr>
<tr>
<td>VDM® Alloy 800 H - 1.4876</td>
<td>180 - 280</td>
<td>510 - 580</td>
<td>35 - 61</td>
</tr>
</tbody>
</table>
Hot Tensile Tests - Typical values of the yield strength and elongation, (solution annealed)

Yield Strength of VDM® Alloy 699 XA larger equal then the one of VDM® Alloy 601

Data on bar: H. Hattendorf, S. Siegfanz*
Data on tube: A. Lopez
*) SZMF
VDM® Alloy 699 XA - Mechanical Properties

The values are well above the preliminary minimum value of 70 J

Histogram of V-notch bar impact energy $KV_2$ at $20^\circ C$, after DIN EN ISO 148-1, average values of 3 samples

The values are well above the preliminary minimum value of 70 J.

In Joule

VDM® Alloy 699 XA
Solution annealed

Min. requirement

LEGEND
bar
plate
tube
weld
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VDM® Alloy 699 XA - Welding

VDM® Alloy 699 XA is weldable under argon

Welding with VDM® FM 699 XA - VDM Welding Competence Center (699-11-1, welding report 3591)

<table>
<thead>
<tr>
<th>Thickness in mm</th>
<th>Welding Process</th>
<th>FM Ø in mm</th>
<th>Root pass</th>
<th>Intermediate and Final Passes</th>
<th>Welding velocity in cm/min</th>
<th>Shield Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>GTAW</td>
<td>2.0</td>
<td>2.0 – 2.4</td>
<td>125 12</td>
<td>190 13</td>
<td>4 10</td>
</tr>
</tbody>
</table>

Welding procedure test according to DIN EN ISO 15614-1 successfully done
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Conclusions

• VDM® Alloy 699 XA contains 30% chromium and 2% aluminum and is highly resistant against metal dusting. It shows a remarkable larger time to first pit in comparison to VDM® Alloy 602 CA. Oxidation resistance similar to 602 CA.

• Hot strength properties/creep properties of VDM® Alloy 699 XA are similar or better than 601.

• Ductility at room temperature of Alloy 699 XA is comparable to 601.

• VDM® Alloy 699 XA is weldable under argon.

• Approvals (VdTÜV, ASME) and field tests are ongoing.

• Hot and cold rolled plate, welding wire and rods, forged bars and billets, rolled bars, power (by VDM) and seamless tubes (by Tubacex) were successfully produced.

• **Samples on stock: VDM:** Plate: 150 x 500 mm, thicknesses 5 mm and 16 mm
  Welding rods: 1.6, 2.0, 2.4 and 3.2 mm; welding wire 1.2 mm

  **Tubacex** Remains of Seamless Tubes tailor made to customer needs (⌀ 20-160 mm)