VDM Ti-X
Titanium Alloy for Exhaust Applications

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Objectives

- Oxidation resistant
- Microstructure-stabilized
- Cold-workable
- Low alloyed – cost-efficient
- Industrially produced
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Alloy development

Properties
- formability at room temperature
  CP-Ti Grade 1S soft grade
- oxidation resistance
  Nb diffusion barrier, reduced mismatch
  Si : Fe ≈ 4 : 1 increased Si diffusion (simulation)
- microstructure stabilisation
  Hf formation of grain boundary particles

Melting and processing
- Si content as low as possible embrittlement / avoidance of Titanium-Silicide formation
- addition of Fe suitable Nb : Fe-ratio, use of master alloy
- low amount of Nb and Hf cost reduction

Compositions investigated in laboratory scale
- Ti 0.4Si 0.1Fe (0.05 - 2)Nb (0.1 - 2)Hf
- fixed Si- and Fe-contents
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Oxidation behavior of titanium and the role of niobium

Titanium without Niobium addition  
- linear oxide layer growth
  - spontaneous formation of TiO$_2$ (few atomic layers) on Titanium surface
  - above 600°C: partial transformation of TiO$_2$ to TiO / TiO$_2$ / Ti$_2$O$_3$ (Ti$^{4+}$, Ti$^{3+}$, Ti$^{2+}$, O$^{2-}$)
  - vacancy formation in Oxygen sub-lattice of the oxide layer
  - enhanced Oxygen diffusion through oxide layer to oxide-metal interface

Titanium with Niobium addition  
- parabolic oxide layer growth
  - Niobium compensates lattice mismatch in oxide layer: Nb$_2$O$_5$ (Nb$^{5+}$, O$^{2-}$)
  - Ti$^{3+}$ and Nb$^{5+}$ lead to Me$^{8+}$-configuration in metal sub-lattice, in addition: formation of Nb$_2$O$_5$
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The role of hafnium

- 15 compositions investigated (flow curves, oxidation at 800°C, microstructure and hardness)
- results:
  - increasing Hf contents lead to accelerated oxidation
  - 0.05% Nb ensures sufficient oxidation behaviour in Si-containing alloys
  - microstructure stabilisation by $\text{Hf}_5\text{Si}_3$ particles (detected by synchrotron radiation)
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Formation of Hf-Silicides (synchrotron analysis)

Ti 0.4Si 0.1Fe 0.05Nb 0.1Hf (P07 @ PETRA III, $\lambda = 0.012587$ nm)

- Ti 0.4Si 0.1Fe 0.05Nb 0.1Hf (cold rolled to 1.2 mm and recrystallisation annealed)
  - $\alpha$-phase, lattice parameter slightly increased, very low amounts of Hf$_5$Si$_3$
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Oxidation behavior

oxidation experiments at 800°C

- all Ti 0.4Si 0.1Fe x*Nb y*Hf alloys show excellent oxidation resistance
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Industrial scale

- production of Ti 0.4Si 0.1Fe 0.05Nb 0.1Hf in industrial scale
  - 2 x vacuum arc remelting (VAR), ingot of approx. 3.5 tons
  - forging, hot and cold rolling (final thicknesses: 1.2 mm and 0.9 mm)
  - recrystallisation annealing
- microstructure and phase analyses, oxidation experiments
- Erichsen cupping, mechanical properties
### VDM Exhaust Grade Ti-X
#### Mechanical properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Ti 0.4Si 0.1Fe 0.05Nb 0.1Hf cold rolled, annealed thickness: 1.2 mm</th>
<th>Ti 0.4Si 0.1Fe 0.05Nb 0.1Hf cold rolled, annealed thickness: 0.9 mm</th>
<th>CP-Ti Grade 1S cold rolled, annealed thickness: 0.5 - 0.7 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>alloy composition</td>
<td>Ti 0.4Si 0.1Fe 0.05Nb 0.1Hf</td>
<td>Ti 0.4Si 0.1Fe 0.05Nb 0.1Hf</td>
<td>CP-Ti Grade 1S</td>
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<tr>
<td>property</td>
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<td>RD</td>
<td>RD</td>
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<tr>
<td>yield strength YTS [MPa]</td>
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<td>340</td>
<td>200</td>
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<tr>
<td>ultimate tensile strength UTS [MPa]</td>
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<td>320</td>
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<td>elongation at rupture A50 [%]</td>
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<td>30¹)</td>
<td>49</td>
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<td>yield strength YTS [MPa]</td>
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<td>ultimate tensile strength UTS [MPa]</td>
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<td>330</td>
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<tr>
<td>elongation at rupture A50 [%]</td>
<td>33</td>
<td>31¹)</td>
<td>38</td>
</tr>
<tr>
<td>Erichsen cupping depth [mm]</td>
<td>11.6</td>
<td>11.3</td>
<td>11.3</td>
</tr>
</tbody>
</table>

- **Ti 0.4Si 0.1Fe 0.05Nb 0.1Hf (cold rolled to 1.2 mm / 0.9 mm and annealed)**
  - good workability at room temperature
  - Hf₅Si₃ precipitations do not influence the deformation characteristics
  ¹) A80
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Microstructure, strip

- Ti 0.4Si 0.1Fe 0.05Nb 0.1Hf (cold rolled to 1.2 mm and recrystallisation annealed)
  - homogeneous, fine-grained microstructure
  - equiaxed α-grains in rolling and transverse direction
  - average grain size: 23 µm (ASTM E112, grain size number 8)
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Oxidation behavior of the strip

Virgin material

ASTM grain size No: 8 – ca. 23 µm

200 h / 800°C

ASTM grain size No: 5 – 6, 45 – 65 µm

cross section
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Summary

- Based on CP-Titanium Ti grade 1S (soft grade)
- Improved oxidation resistance due to a concerted addition of silicon, iron and niobium
- Microstructure stability by the precipitation of hafnium-silicides mainly on the grain boundaries
- Good cold-deformation properties
- Production route is the same as CP titanium
- Alloy composition: Ti – 0.4Si – 0.1Fe – 0.05Nb – 0.1Hf
- Ready for application in exhaust systems of planes or cars at 800°C and above
- Strip material (thickness 0.9 mm and 1.2 mm, width 750 mm) available for application/sampling
- Smaller thicknesses ready for rolling
Thank you for your attention!