Introduction to Shape Memory Alloys (SMAs)

- (Micro)structural aspects of martensitic transformations (MT)
- Thermodynamic issues of MT
- Self-accommodation modes
- Detwinning
- One-way shape memory effect
- Superelasticity
- Two-way shape memory effect
- Superelasticity – Pseudoelasticity
- Nitinol alloys
- Applications
(Micro)structural aspects

Thermally induced martensitic transformation

BAIN STRAIN
(Micro)structural aspects
(Micro)structural aspects

**Graph and Diagram**

- **Austenite**
- **Martensite**

**Chemical Phase Diagram**

- **Temperature vs. Weight Percent Nickel**
- **Temperature vs. Atomic Percent Nickel**

**Phase Transitions**

- **L**
- **(αTi)**
- **TiNi**
- **(Ni)**

**Crystal Structures**

- **Austenite**
- **Martensite**

**SMAs**
(Micro)structural aspects

**AUSTENITE:**
Cubic (B2)
*high symmetry*

**MARTENSITE:**
Monoclinic (B19)
*low symmetry*
(Micro)structural aspects

Ni ●
Ti ○

[011]_{B2} CUBIC

[001] ORTHORHOMBIC

[001] MONOCLINIC

(010)\textsubscript{M} Twin Plane

SMAs
Thermodynamic issues
Main features of the MT:
- First order
- Athermic
- Non diffusive
- Reversible
Thermodynamic issues
Thermodynamic issues
Thermodynamic issues
Thermodynamic issues

### Material data sheet

<table>
<thead>
<tr>
<th>Alloy</th>
<th>NiTI-Alloy M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date of delivery</td>
<td>31 July 2003</td>
</tr>
<tr>
<td>Date of production</td>
<td>n/a</td>
</tr>
<tr>
<td>Customer</td>
<td>Università di Trento</td>
</tr>
</tbody>
</table>

#### Chemical composition

<table>
<thead>
<tr>
<th></th>
<th>Ni [wt-%]</th>
<th>Ti [wt-%]</th>
<th>all others</th>
<th>C [ppm]</th>
<th>O [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>nominal (a.r.from manufacturer)</td>
<td>55.32</td>
<td>44.67</td>
<td>n/a</td>
<td>&lt;500</td>
<td>&lt;500</td>
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<tr>
<td>own chemical analysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Trans. temp. [°C] (as cast condition, a.r. from manufacturer)

<table>
<thead>
<tr>
<th>Trans. temp. [°C]</th>
<th>A&lt;sub&gt;peak&lt;/sub&gt;:</th>
<th>A&lt;sub&gt;s&lt;/sub&gt;:</th>
<th>M&lt;sub&gt;peak&lt;/sub&gt;:</th>
<th>M&lt;sub&gt;s&lt;/sub&gt;:</th>
<th>R:</th>
</tr>
</thead>
<tbody>
<tr>
<td>88°C</td>
<td>n/a</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

#### Hot deformation

- Extrusion
- Rolling sheet
- Rolling Bar

---

### Material data sheet

<table>
<thead>
<tr>
<th>Alloy</th>
<th>NiTI-Alloy S (superelastic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date of delivery</td>
<td>31 July 2003</td>
</tr>
<tr>
<td>Date of production</td>
<td>24.01.2002</td>
</tr>
<tr>
<td>Customer</td>
<td>Università di Trento</td>
</tr>
</tbody>
</table>

#### Chemical composition

<table>
<thead>
<tr>
<th></th>
<th>Ni [wt-%]</th>
<th>Ti [wt-%]</th>
<th>all others</th>
<th>C [wt-%]</th>
<th>O [wt-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>nominal (a.r.from manufacturer)</td>
<td>55.9</td>
<td>44.08</td>
<td>&lt;0.20</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>own chemical analysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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#### Trans. temp. [°C] (as cast condition, a.r. from manufacturer)

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<th>Trans. temp. [°C]</th>
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<th>A&lt;sub&gt;s&lt;/sub&gt;:</th>
<th>M&lt;sub&gt;peak&lt;/sub&gt;:</th>
<th>M&lt;sub&gt;s&lt;/sub&gt;:</th>
<th>R:</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3°C</td>
<td>n/a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Hot deformation

- Extrusion
- Rolling sheet
- Rolling Bar
Thermodynamic issues
Thermodynamic issues
### Non-ferrous alloys exhibiting perfect shape memory effect and superelasticity

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition (at%)</th>
<th>Structure change</th>
<th>Temperature hysteresis (K)</th>
<th>Ordering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag–Cd</td>
<td>44–49 Cd</td>
<td>B2–2H</td>
<td>~ 15</td>
<td>ordered</td>
</tr>
<tr>
<td>Au–Cd</td>
<td>46.5–48.0 Cd</td>
<td>B2–2H</td>
<td>~ 15</td>
<td>ordered</td>
</tr>
<tr>
<td></td>
<td>49–50 Cd</td>
<td>B2–trigonal</td>
<td>~ 2</td>
<td>ordered</td>
</tr>
<tr>
<td>Cu–Zn</td>
<td>38.5–41.5 Zn</td>
<td>B2–M (modified) 9R</td>
<td>~ 10</td>
<td>ordered</td>
</tr>
<tr>
<td>Cu–Zn–X</td>
<td>A few at%</td>
<td>B2–M9R</td>
<td>~ 10</td>
<td>ordered</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu–Al–Ni</td>
<td>28–29 Al, 3.0–</td>
<td><strong>DO$_3$–2H</strong></td>
<td>~ 35</td>
<td>ordered</td>
</tr>
<tr>
<td></td>
<td>4.5 Ni</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu–Sn</td>
<td>~ 15 Sn</td>
<td><strong>DO$_3$–2H, 18R</strong></td>
<td>—</td>
<td>ordered</td>
</tr>
<tr>
<td>Cu–Au–Zn</td>
<td>23–28 Au</td>
<td>Heusler–18R</td>
<td>~ 6</td>
<td>ordered</td>
</tr>
<tr>
<td></td>
<td>45–47 Zn</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni–Al</td>
<td>36–38 Al</td>
<td>B2–3R, 7R</td>
<td>~ 10</td>
<td>ordered</td>
</tr>
<tr>
<td>Ti–Ni</td>
<td>49–51 Ni</td>
<td><strong>B2–monoclinic</strong></td>
<td>~ 30</td>
<td>ordered</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>B2–R-phase-(monoclinic)</strong></td>
<td>~ 2</td>
<td>ordered</td>
</tr>
<tr>
<td>Ti–Ni–Cu</td>
<td>8–20 Cu</td>
<td>B2–orthorhombic-(monoclinic)</td>
<td>4–12</td>
<td>ordered</td>
</tr>
<tr>
<td>Ti–Pd–Ni*</td>
<td>0–40 Ni</td>
<td>B2–orthorhombic</td>
<td>30–50</td>
<td>ordered</td>
</tr>
<tr>
<td>In–Tl</td>
<td>18–23 Tl</td>
<td>FCC–FCT</td>
<td>~ 4</td>
<td>disordered</td>
</tr>
<tr>
<td>In–Cd</td>
<td>4–5 Cd</td>
<td>FCC–FCT</td>
<td>~ 3</td>
<td>disordered</td>
</tr>
<tr>
<td>Mn–Cd</td>
<td>5–35 Cu</td>
<td>FCC–FCT</td>
<td>—</td>
<td>disordered</td>
</tr>
</tbody>
</table>
Thermodynamic issues
Thermodynamic issues

NiTiCu5 – d=0.9 mm

% di fase austenitica

Temperatura

riscaldamento
raffreddamento
Thermodynamic issues

![Graph showing thermodynamic issues](image)

- Temperatura (°C)
- % di fase trasformata
- % di fase martensitica
- % di fase austenitica

**Integral**: -4.23 mg\(^{-1}\) g
**Onset**: 5.40 min
**Peak**: 7.08 min
**Endset**: 7.05 min
Thermodynamic issues

- Electrical Resistance
- Length Change
- Volume Change
  etc.

![Diagram of thermodynamic issues](image)

- $M_s$: martensite start temperature
- $M_f$: martensite finish temperature
- $A_s$: start of reverse transformation of martensite
- $A_f$: finish of reverse transformation of martensite

Typically $20^\circ C$
Self accommodation modes

(a) 

(b) 

(c) martensite interface 

(d) martensite interface
INVARIANT SHEAR STRAIN:
Mechanisms for accommodating shape and/or volume changes
SLIP

Self accommodation modes
Self accommodation modes

IN Variant SHEAR STRAIN: 
Mechanisms for accommodating shape and/or volume changes 
TWINNING
Self accommodation modes
Self accommodation modes

TWINNING: Thermally reversible strain!

Some features of twins:
• Low energy
• High mobility
• No break of chemical bonds

Diagram of twin structure with blue and red dots, and a scale bar indicating 1 µm.
Self accommodation modes

SEVERAL VARIANTS... i.e., ORIENTATIONS
Self accommodation modes
Self accommodation modes
Self accommodation modes

About thermal hysteresis: a comparison between transformation nature...

THERMOELASTIC (Au-Cd)

Fully MARTENSITIC, i.e., no THERMOELASTIC (Fe-Ni)

Au-Cd:
A→M - nucleation/growth
M→A - inversion

Fe-Ni:
A→M & M→A
nucleation/growth
Self accommodation modes

Result of self accommodation: the shape is preserved.
Detwinning
Detwinning
Detwinning

\[ T < M_f \]
Detwinning

\[ T \leq M_f \]
Detwinning

Tension

Compression

Tension

Compression
Detwinning
Detwinning

Compression 4%

Tension 4%
One-way shape memory effect

1) austenite->martensite (thermally induced)
2) deformation of martensite
3) martensite->austenite (thermally induced)…SHAPE RECOVERY!
One-way shape memory effect
Requirements for shape recovery:

• Twinning as accommodation mode of Martensite;

• Very small or nil volume changes involved in the A<>M transformation (<<1%).
One-way shape memory effect

FIRST CIRCLE

A  M  M  A

T↓  σ  T↑

SECOND CIRCLE

A  M

T↓  M

Shape change occurs just once:

One Way Shape Memory Effect (OWSME)

Leghe a memoria di forma
One-way shape memory effect

Temperature vs. Ae Diagram

Max. oneway SME (%)
Superelasticity

Mechanically induced martensitic transformation

AUSTENITE

MARTENSITE

OWSME

T > Af

\(\sigma\)
Superelasticity
Superelasticity

\[ T > A_f \]
Superelasticity
Superelasticity

**SUPERELASTICITY**: elevated strains (8%)... *Fully recoverable* (reversible)
Superelasticity

\[
\frac{d\sigma}{dT} = \frac{\Delta H_{M>A}}{\Delta V_{def} T_t}
\]
Superelasticity

![Graph showing the relationship between temperature and stress](image-url)
Superelasticity

![Graph showing stress vs. temperature for superelastic materials](image)

- **Detwinned Martensite**
- **Twinned Martensite**
- **Austenite**

Key points:
- $\sigma_f$: Upper yield stress
- $\sigma_s$: Lower yield stress
- $M_f$, $M_s$, $A_s$, $A_f$: Transition temperatures
- $C^M$, $C^A$: Critical stresses
- $M^t$ to $M^d$, $M^d$ to $A$: Temperature ranges
Superelasticity

<table>
<thead>
<tr>
<th>Sistema</th>
<th>Isteresi</th>
<th>Ms Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiTi</td>
<td>20-30 °C</td>
<td>-60/60 °C</td>
</tr>
<tr>
<td>NiTiCu</td>
<td>5-10°C</td>
<td>30°C/50 °C</td>
</tr>
<tr>
<td>AgCd</td>
<td>15°C</td>
<td>-80°C</td>
</tr>
<tr>
<td>CuZnAl</td>
<td>10°C</td>
<td>-20/50°C</td>
</tr>
<tr>
<td>CuAlNi</td>
<td>35°C</td>
<td>80/130 °C</td>
</tr>
<tr>
<td>NiTiNb</td>
<td>40-120°C</td>
<td>-20/-50°C</td>
</tr>
</tbody>
</table>
### Table 2.1. Non-ferrous alloys exhibiting perfect shape memory effect and superelasticity

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<thead>
<tr>
<th>Alloy</th>
<th>Composition (at%)</th>
<th>Structure change</th>
<th>Temperature hysteresis (K)</th>
<th>Ordering</th>
<th>Ref. on structure</th>
<th>Ref. on crystallography, SME and SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag–Cd</td>
<td>44–49 Cd</td>
<td>B2–2H</td>
<td>~ 15</td>
<td>ordered</td>
<td>26</td>
<td>27, 28</td>
</tr>
<tr>
<td>Au–Cd</td>
<td>46.5–48.0 Cd</td>
<td>B2–2H</td>
<td>~ 15</td>
<td>ordered</td>
<td>29, 30</td>
<td>31–34</td>
</tr>
<tr>
<td></td>
<td>49–50 Cd</td>
<td>B2–trigonal</td>
<td>~ 2</td>
<td>ordered</td>
<td>35, 36</td>
<td>33, 37</td>
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<tr>
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<td>38.5–41.5 Zn</td>
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<td>ordered</td>
<td>38</td>
<td>10, 39</td>
</tr>
<tr>
<td>Cu–Zn–X</td>
<td>A few at %</td>
<td>B2–M9R</td>
<td>~ 10</td>
<td>ordered</td>
<td>38</td>
<td>9, 10, 11, 28, 40</td>
</tr>
<tr>
<td>(X = Si,Sn,Al,Ga)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu–Al–Ni</td>
<td>28–29 Al, 3.0–4.5 Ni</td>
<td>DO$_3$–2H</td>
<td>~ 35</td>
<td>ordered</td>
<td>41, 42</td>
<td>3, 8, 43–45</td>
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<tr>
<td>Cu–Sn</td>
<td>~ 15 Sn</td>
<td>DO$_3$–2H, 18R</td>
<td>---</td>
<td>ordered</td>
<td>46, 47</td>
<td>48</td>
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<td>23–28 Au</td>
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<td>49</td>
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<td>53–56</td>
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<td>Ti–Ni</td>
<td>49–51 Ni</td>
<td>B2–monoclinic</td>
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<td>57</td>
<td>59–61</td>
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<td></td>
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<td>B2–R-phase (monoclinic)</td>
<td>~ 2</td>
<td>ordered</td>
<td>58</td>
<td>62, 63, 64</td>
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<tr>
<td>Ti–Ni–Cu</td>
<td>8–20 Cu</td>
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<td>66</td>
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<td>Ti–Pd–Ni*</td>
<td>0–40 Ni</td>
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<td>30–50</td>
<td>ordered</td>
<td>67, 68</td>
<td>69–71</td>
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<tr>
<td>In–Ti</td>
<td>18–23 Ti</td>
<td>FCC–FCT</td>
<td>~ 4</td>
<td>disordered</td>
<td>72</td>
<td>73–75</td>
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<tr>
<td>In–Cd</td>
<td>4–5 Cd</td>
<td>FCC–FCT</td>
<td>~ 3</td>
<td>disordered</td>
<td>76</td>
<td>76</td>
</tr>
<tr>
<td>Mn–Cd</td>
<td>5–35 Cu</td>
<td>FCC–FCT</td>
<td>---</td>
<td>disordered</td>
<td>77</td>
<td>78</td>
</tr>
</tbody>
</table>

*Ti–Pd–Ni alloys with high Pd content do not exhibit good SME unless specially thermomechanically treated.
Superelasticity – One-way shape memory effect
Superelasticity – One-way shape memory effect
Superelasticity - Pseudoelasticity

\( T < M_f \)

\( T > A_f \)

\( T \approx M_d \)

\( T > M_d \)
Superelasticity - Pseudoelasticity

\[ T < M_f \]

\[ T > M_d \]
Superelasticity - Pseudoelasticity
Superelasticity - Pseudoelasticity

\[ \text{Stress} \quad \text{loading} \quad \text{unloading} \]

\[ \text{Strain} \]

\[ \text{Stress} \quad \text{loading} \quad \text{unloading} \]

\[ \text{Strain} \]
Superelasticity - Pseudoelasticity

$T < M_f$

0% 1.2% 4% 6%

Allungamento %

Stress $\sigma$, MPa
Two-way shape memory effect: phenomenology

**One-Way SME**

A \[ \Downarrow T \] M \[ \sigma \] M \[ \uparrow T \] A

**Two-Way SME**

A \[ \Downarrow T \] M \[ \uparrow T \] A
Two-way shape memory effect: training

1- Raffreddamento
T < M_f

2 - Deformazione intensa

High strain of martensite

Riscaldamento
T > A_f

Carico e deformazione

Scarico

One-way shape memory cycles

Raffreddamento
T < M_f

Deformazione

Riscaldamento
T > A_f

Superelastic (mechanical) cycles
Two-way shape memory effect: training
Two-way shape memory effect: training
Two-way shape memory effect: decay of the effect