Twinning in very high temperatures
Ru-based shape memory alloys

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AMFORTAS project:
Investigation on potential HTSMA for aeronautics applications

Requirements for High Temperature actuators:
- High Temperature Martensitic Transformation
- Good Shape Memory Effect
- Stability to thermal cycling and ageing
- Ability to produce work at high temperatures
- Good oxidation resistance
- ...

3 systems investigated:
- HfPd
- TiAu
- RuTa and RuNb
Goals:
- reduction of fuel consumption and pollution emission
- noise reduction
Martensitic transformation

- Solid –Solid phase transformation between Austenite (A) and Martensite (M)
  - Displacive dominated by shear (+shuffle, $\Delta V \approx 0$)
  - Nucleation and growth
  - One invariant plane strain
  - morphology controlled by deformation energy
- Can be thermoelastic ($\Delta V \approx 0$, SMA) or not ($\Delta V \neq 0$, steels).
1- Homogeneous deformation 
*Bain deformation*

2- Lattice Invariant Shear

3- Rigid body Rotation $\theta$

**contradiction!**

habit plane = plane of macroscopic shear
One-way Shape Memory Effect
Ru-based alloys

Very promising candidates for very High Temperature SMA:
- Very high Martensitic Transformation temperature
- Very good resistance to ageing
- Good shape memory effect

Complex microstructures and mechanical behavior
→ two successive Martensitic Transformations

Control of the Martensitic Transformation temperatures
→ chemical composition, out of stoichiometry
β austenite

B2

β′ martensite
Tetragonal

β″ martensite
Monoclinic

M Ru₅₀Nb₅₀
T Ru₄₅Nb₅₅
T Ru₄₃Nb₅₇

T Ru₄₃Ta₅₇
T Ru₄₅Ta₅₅
M Ru₅₀Ta₅₀
**Transformation temperatures and stability**

![Graphs showing transformation temperatures and stability](image)

**Ru$_{50}$Nb$_{50}$**
- 1 month at 690° C: [β” phase]
- 1 month at 850° C: [β’ phase]

**Ru$_{45}$Nb$_{55}$**
- Temperatures and transformation energy stables
- Stabilisation of β’ and β” phases

<table>
<thead>
<tr>
<th>°C</th>
<th>high temperature transformation β/β’</th>
<th>low temperature transformation β'/β”</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ms’</td>
<td>Δ</td>
</tr>
<tr>
<td>Ru$<em>{40}$Nb$</em>{50}$</td>
<td>887.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Ru$<em>{48}$Nb$</em>{52}$</td>
<td>732.8</td>
<td>16.6</td>
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<tr>
<td>Ru$<em>{46}$Nb$</em>{54}$</td>
<td>574.0</td>
<td>6.0</td>
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<tr>
<td>Ru$<em>{48}$Nb$</em>{55}$</td>
<td>492.0</td>
<td>3.2</td>
</tr>
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</table>
Control of the transformation temperatures by the chemical composition
Direct observation of the Shape Memory Effect

3 points bending test

- deformation of β’ at 830° C
- reverse transformation when heating up to 950° C
**Shape memory effect decreases with Ru content**

- Good shape recovery for equiatomic alloys but small for low Ru content alloys
- Control of transformation temperatures → 3rd element like Fe
Smaller contribution to the SME of the second martensitic transformation

- Two way Shape Memory effect? (Measure done at RT)
- Deformation is due to reorganization of $\beta'$ variants instead of $\beta''$?
Microstructures Analysis

- SEM at room temperature
- Crystallographic approach
- TEM
- In-situ neutron diffraction
- EBSD
SEM

<table>
<thead>
<tr>
<th>Tetragonal</th>
<th>Monoclinic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru_{43}Ta_{57}</td>
<td>Ru_{50}Ta_{50}</td>
</tr>
<tr>
<td>Ru_{45}Ta_{55}</td>
<td>Ru_{50}Nb_{50}</td>
</tr>
<tr>
<td>Ru_{43}Nb_{57}</td>
<td>Ru_{45}Nb_{55}</td>
</tr>
</tbody>
</table>

1, 2 or 3 laminates (polytwins) noted

A (Large)
B (Medium)
C (Small)
Microstructure of β’ martensite in Tetragonal alloys

twinned microstructures with 2 or 1 laminates depending the c/a ratio

Large A twins

Small C twins +
Large A twins

2 levels of laminates
$c/a = 1.058 \text{ @ RT}$

1 level of laminates
$c/a = 1.043 \text{ @ RT}$

Ru$_{43}$Nb$_{57}$

Ru$_{45}$Nb$_{55}$
Microstructure of $\beta''$ martensite in Monoclinic alloys

3 levels of laminates (twins)

A (L)

NEW B intermediate size (M)

C (S)

wavy translation boundaries
(no background difference)

from the $\beta'$ phase

all the structural features of $\beta'$ are inherited by $\beta''$
= all the interfaces
Crystallographic analysis: $\beta \rightarrow \beta'$ transformation

Group-subgroup relationship:

$$(a_\beta, b_\beta, c_\beta) \approx (a'_\beta, b'_\beta, c'_\beta)$$

48 m3m

4/m mm

48/16 = 3

4/mmm

16

3 orientation variants

Lost cubic mirrors:

$m(101)_\beta$

$m(10-1)_\beta$

$m(011)_\beta$

$m(01-1)_\beta$

Twinning planes

Mirror plane = twin plane

High atom density of the plane
**β’ → β” transformation**

**β’ martensite**
Tetragonal

P4/mmm \((a_{\beta’}, b_{\beta’}, c_{\beta’})\) → P2/m \((a_{\beta''}, b_{\beta''}, c_{\beta''})\)

**β” martensite**
Monoclinic

\[
a_{\beta''} = a_{\beta’} - b_{\beta’} + 2c_{\beta’}
\]
\[
b_{\beta''} = -a_{\beta’} - b_{\beta’}
\]
\[
c_{\beta''} = a_{\beta’} - b_{\beta’} - c_{\beta’}
\]

Group-subgroup relationship:

\([2]_{\beta’} // [110]_{\beta’}\)

\((m)_{\beta’} // m(110)_{\beta’}\)

- **4 orientation variants**
  - 4/m mm
  - 2/m
  - 16
  - 16/4 = 4

- **lost tetragonal mirrors**
  - \(m (010)_{\beta’} \rightarrow (-1-1-1)_{\beta”}\)
  - \(m (100)_{\beta’} \rightarrow (1-11)_{\beta”}\)
  - \(m (1-10)_{\beta’} \rightarrow (101)_{\beta”}\)
  - \(m (001)_{\beta’} \rightarrow (20-1)_{\beta”}\)

- **6 translation variants**
  - related by 5 lost translations
    - \([1-11]_{\beta’}\)
    - \([1-10]_{\beta’}\)
    - \([010]_{\beta’}\)
    - \([1-21]_{\beta’}\)
    - \([01-1]_{\beta’}\)
  - → translation boundaries

- **Vol_{\beta”} = 6 Vol_{\beta’}**

- **→ Twins**

**Previous tetragonal unit cell**
Shape Memory Effect $\leftrightarrow$ unit cell deformation

$\rightarrow$ lattice parameters versus temperature is needed

cubic $\rightarrow$ tetragonal transformation: $c/a = \text{evolution marker}$

tetragonal $\rightarrow$ monoclinic transformation: $c/a \text{ equivalent}$

In-situ neutron diffraction / $T^\circ \rightarrow a_{\beta''}, b_{\beta''}, c_{\beta''}, \beta \rightarrow \text{« evolution marker »}$

Laue-Langevin Institute Grenoble (France)
Unit cell deformation evolution with temperature

- **Release of the stress by the second MT**
- **New twinned self-accommodated µ-structure**
- **Large evolution of the unit cell in the β’ phase domain**
- **Stress is generated**
- **Self accommodated twinned µ-structure**

**Ru₅₀Nb₅₀**
**Ru₅₀Ta₅₀**
**Ru₄₅Ta₅₅**

β'' → β' transformation

β' → β transformation

cubique phase β

"c/a" evolution marker
**TEM characterization of twins in tetragonal alloys**

<table>
<thead>
<tr>
<th>alloy</th>
<th>shear amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru$<em>{45}$Ta$</em>{55}$</td>
<td>0.13</td>
</tr>
<tr>
<td>Ru$<em>{43}$Ta$</em>{57}$</td>
<td>0.09</td>
</tr>
<tr>
<td>Ru$<em>{45}$Nb$</em>{55}$</td>
<td>0.11</td>
</tr>
<tr>
<td>Ru$<em>{43}$Nb$</em>{57}$</td>
<td>0.08</td>
</tr>
</tbody>
</table>

A + C twins (variants)

all twins are \{101\}_T type

→ cubic mirrors lost

(101) Compound twin

$K_1$, $K_2$, $\eta_1$, $\eta_2$ rational

$\theta_{\text{exp}}$

zone axis = [010]$_Q$

single laminates of A type twins is possible
**EBSD observations in tetragonal alloy**

- 3 variants of martensite
- **Ru$_{45}$Ta$_{55}$**
- A and C twins
- Zeiss DSM960 Saarbrücken
TEM characterization of twins in monoclinic alloys

Indices of \((3-10)\) plane in the \(\beta'\) tetragonal structure \(\rightarrow (101)\)

\[ \rightarrow C \text{ twin of } \beta \rightarrow \beta' \]

old A and C twins in monoclinic alloys are **inherited** from \(\beta \rightarrow \beta'\) transformation

+ new B twins generated during \(\beta' \rightarrow \beta''\)
EBSD characterization of twins in monoclinic alloys

3 principal orientations coming from $\beta \rightarrow \beta'$ inherited tetragonal microstructure

$\beta \rightarrow \beta'$: C twin

$\beta' \rightarrow \beta''$: B twin

(100) mirrors of tetragonal variants lost during $\beta' \rightarrow \beta''$
EBSD analysis of the operation between variants: the chosen operation being a mirror and the interface being parallel to this mirror.

→ TWIN

\[ \text{new} \]

C-TWIN: lost cubic mirror

\[ \beta \rightarrow \beta' \]

B-TWIN: lost tetragonal mirrors

\[ \beta' \rightarrow \beta'' \]

→ unexpected microstructure
Microstructural transformation mechanism

- normal conditions: all the variants are generated during the transformation they can be associated for the self accommodation transformation $\beta \rightarrow \beta'$

- special conditions for $\beta' \rightarrow \beta''$

normal conditions versus experimental evidence
$\beta' \rightarrow \beta''$ constrained transformation

- geometrically constrained: very small thickness (n 10 nm) of the C-twin domains
  only one $\beta''$ variant in thickness

- elastically constrained: increase of the elastic energy
  → oriented nucleation of $\beta''$
  same $\beta''$ variants in alternative corresponding $\beta'$ twin domains of the laminate

- crystallographically constrained: A or (A + C) $\beta'$ twins are inherited and must still be twin operations for $\beta''$ structure
  $\beta''$ variants in two successive $\beta'$ twin domains are related by the $C_{\beta}$ twin element, written in $\beta''$ referential
crystallographically constrained: the C-twin are inherited

the B-twin interface must be planar to prevent crystallographic incompatibilities

Elastically constrained:

- B twin $m(111)'': (010)'$ leaving (3-10)'' invariant
  
- C twin $m(3-10)'': (101)'
  
- C twin $m(3-10)'': (101)'

residual elastic stress field
The 2\textsuperscript{nd} martensitic transformation is geometrically and crystallographically constrained.

Only one variant of $\beta''$ have to grow in the C-type twin domains without twinning (LIS).

A special match between $\beta'$ and $\beta''$ lattices is needed.
Summary on Ru-based alloys

• Shape memory is effective at very high temperature
• Shape memory effect is larger for the $\beta \rightarrow \beta'$ transformation than for the $\beta' \rightarrow \beta''$ transformation
• Unit cell shape changes between both martensitic transformations
• An unexpected hierarchy of the twins is observed and suggests that the $\beta' \rightarrow \beta''$ transformation is constrained:
  ➢ crystallographically
  ➢ elastically
  ➢ geometrically