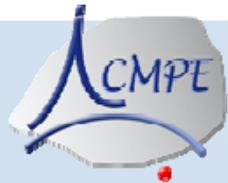


Twinning in very high temperatures Ru-based shape memory alloys



- P. Vermaut, C. Declairieux, F. Prima and R. Portier
- A. Manzoni, A. Denquin,
- P. Ochin

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
- ...

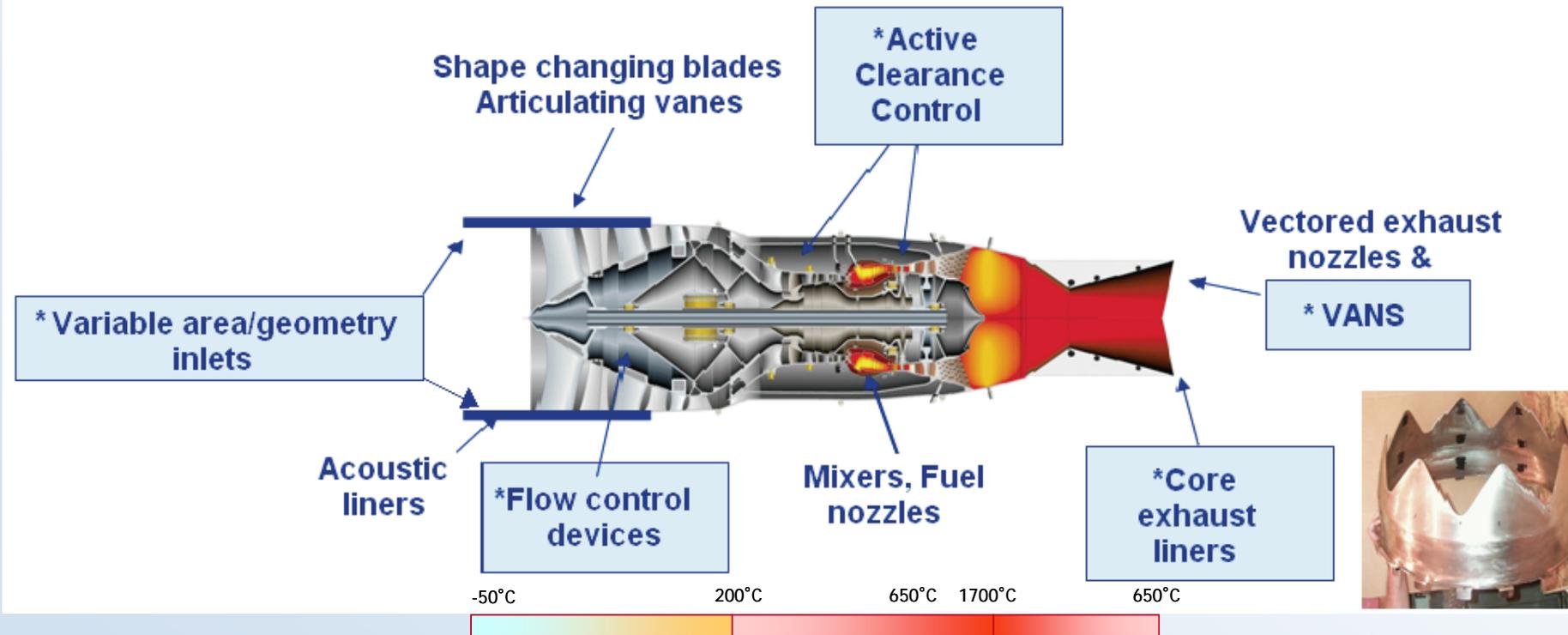
3 systems investigated :

HfPd

RuTa and RuNb

TiAu

Potential aeronautic applications



actuators to control hot gaz flux into the turbomachines

Goals:

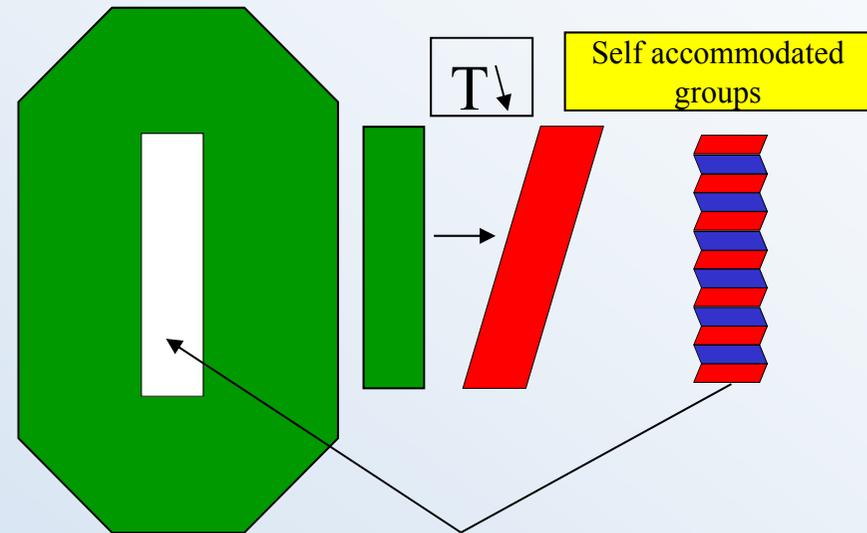
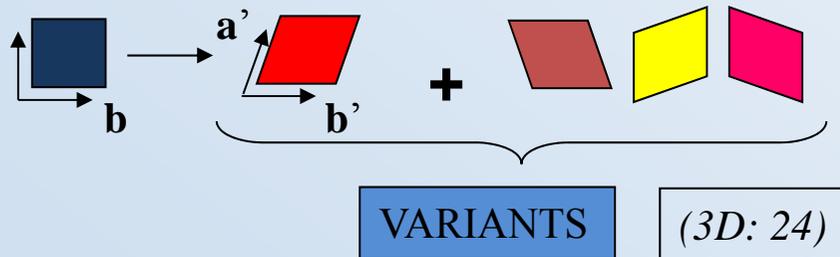
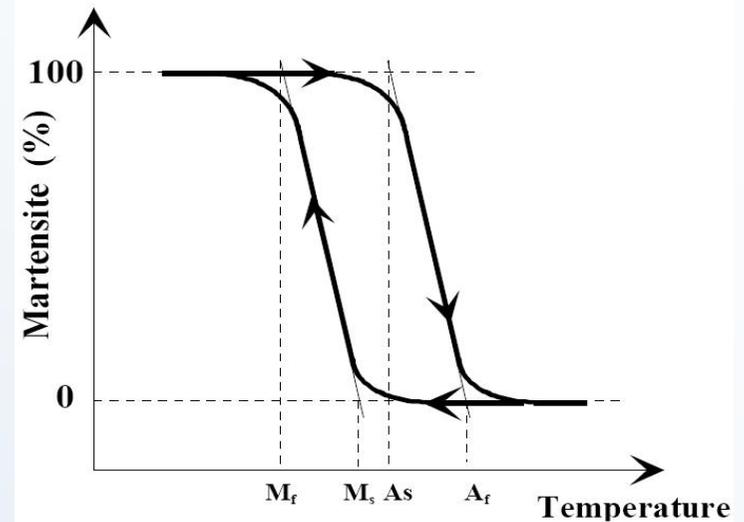
- reduction of fuel consumption and pollution emission
- noise reduction



ParisTech

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).

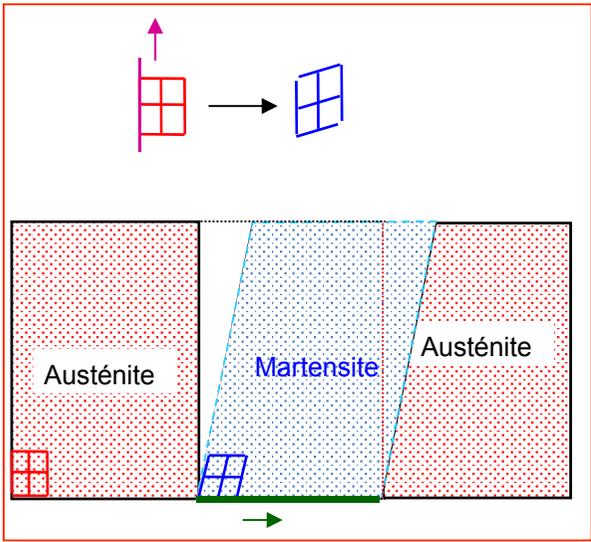
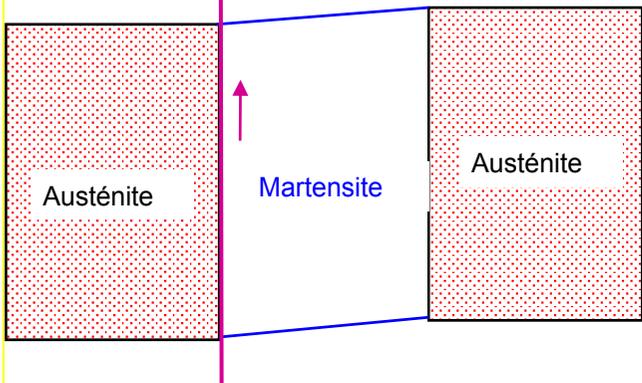


macroscopic

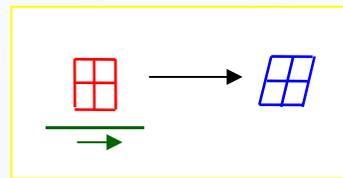
microscopic

contradiction !

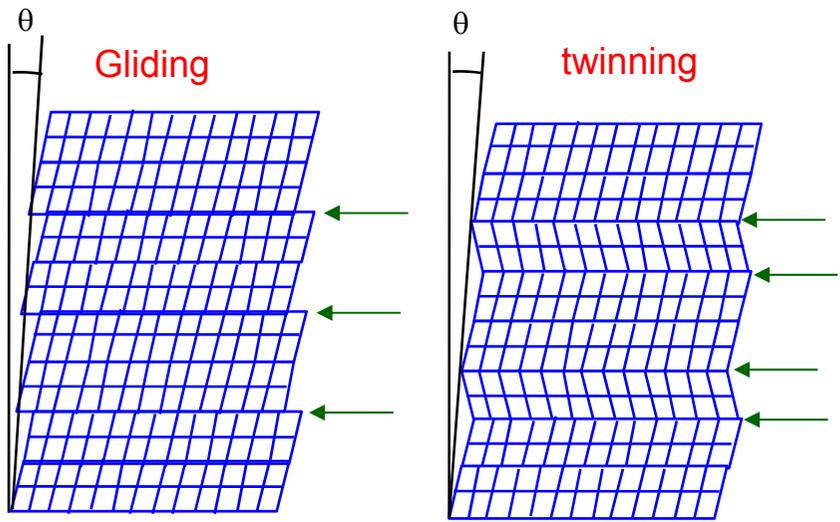
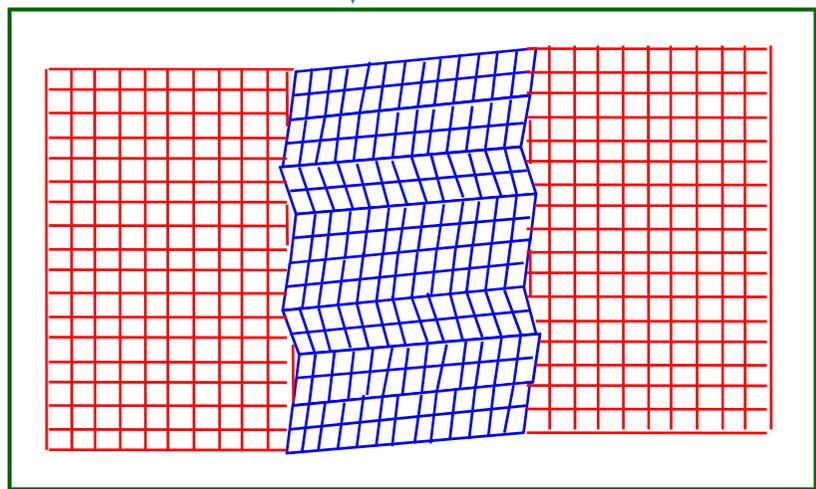
habit plane = plane of macroscopic shear



1- Homogeneous deformation
Bain deformation



2- Lattice Invariant Shear

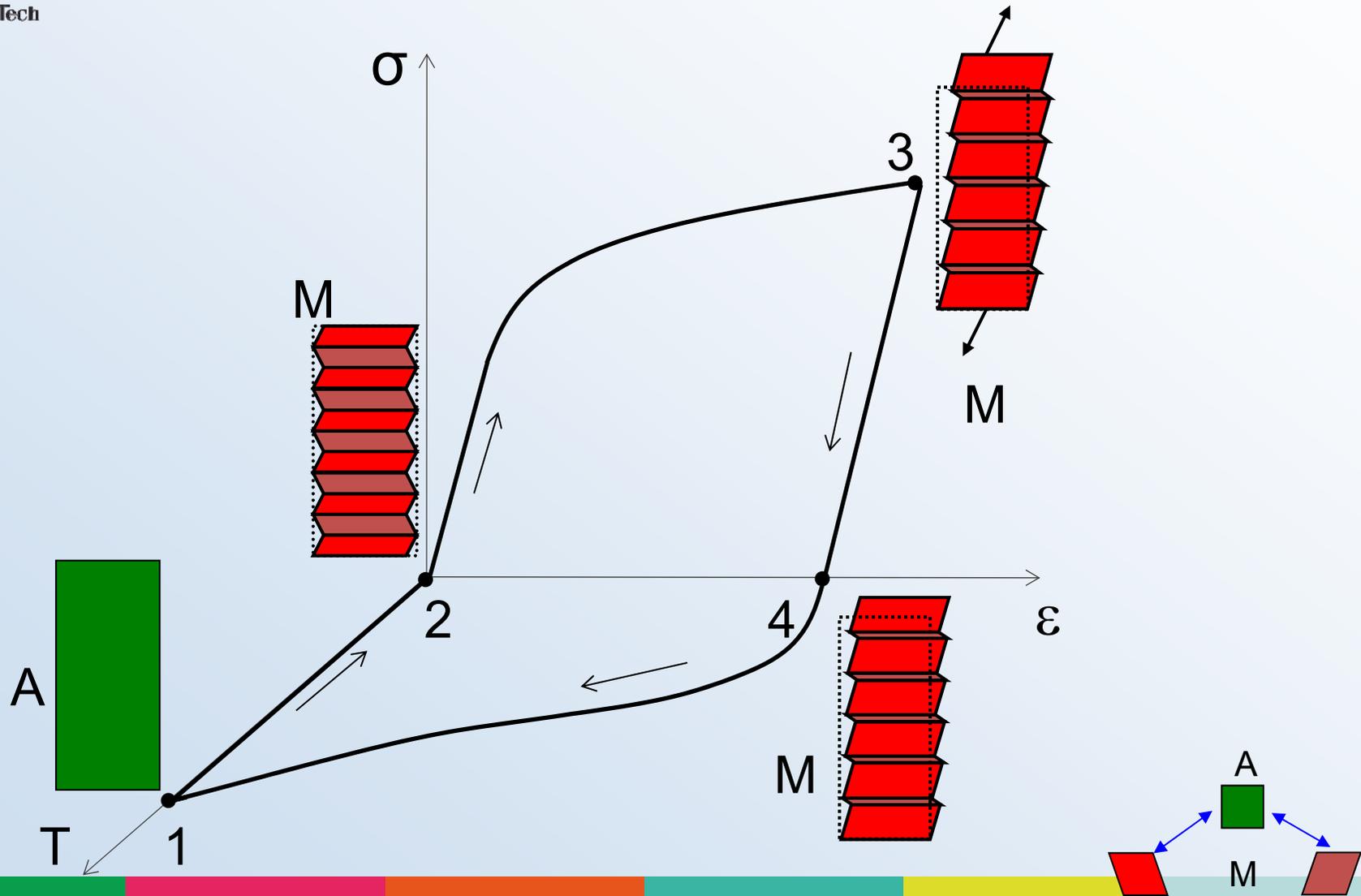


3- Rigid body Rotation θ



ParisTech

One-way Shape Memory Effect



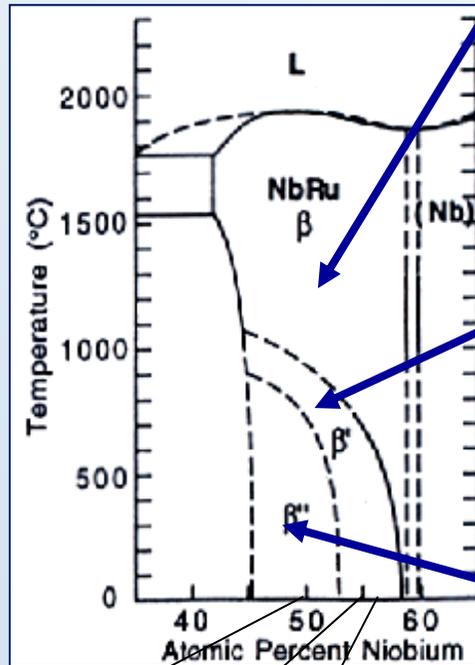
Ru-based alloys

Very promising candidates for very High Temperature SMA :

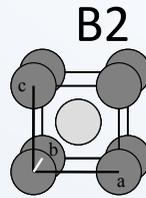
- Very high Martensitic Transformation temperature
- Very good resistance to ageing
- Good shape memory effect

Complex microstructures and mechanical behavior
→ **two successive Martensitic Transformations**

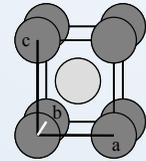
Control of the Martensitic Transformation temperatures
→ **chemical composition, out of stoichiometry**



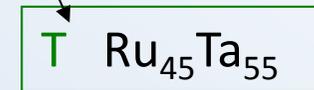
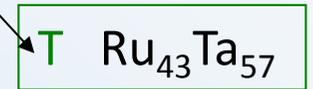
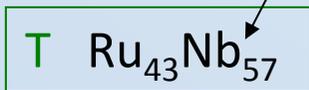
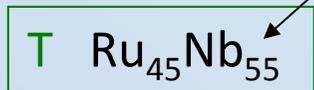
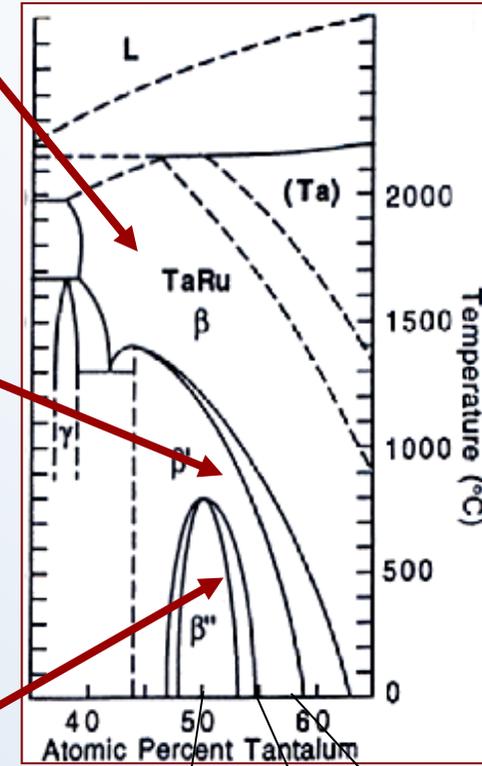
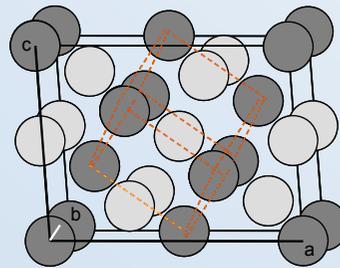
β austenite



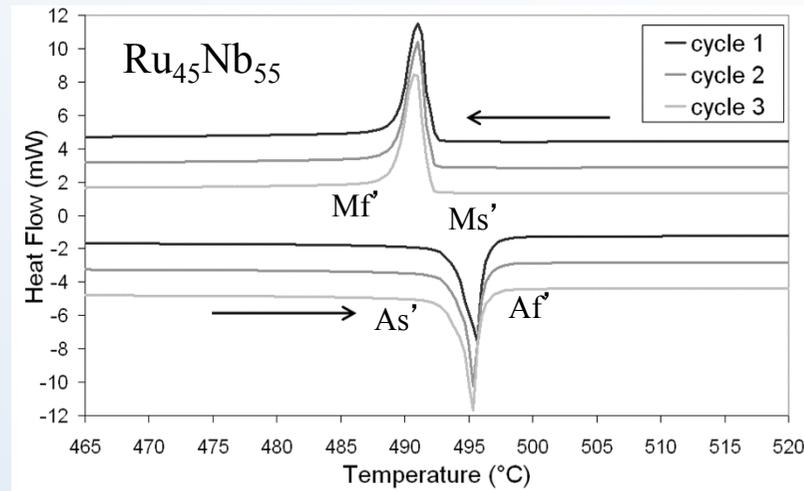
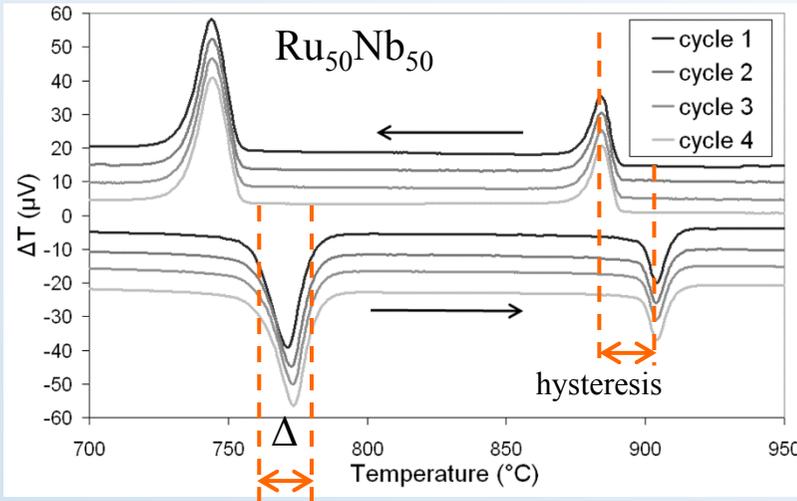
β' martensite
Tetragonal



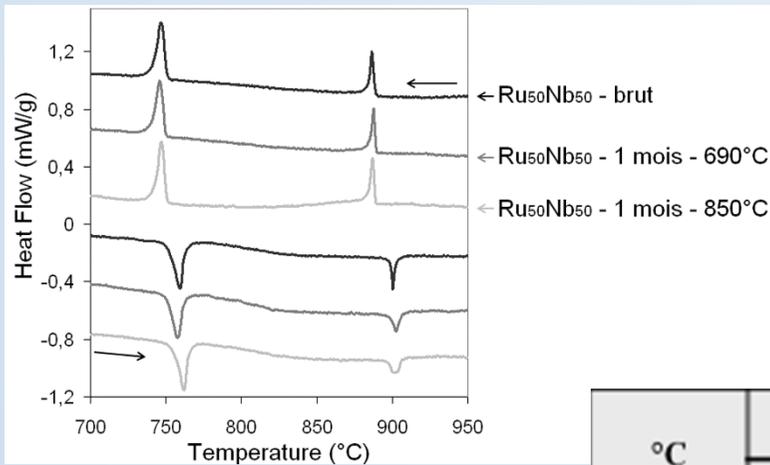
β'' martensite
Monoclinic



Transformation temperatures and stability



cycling



aging

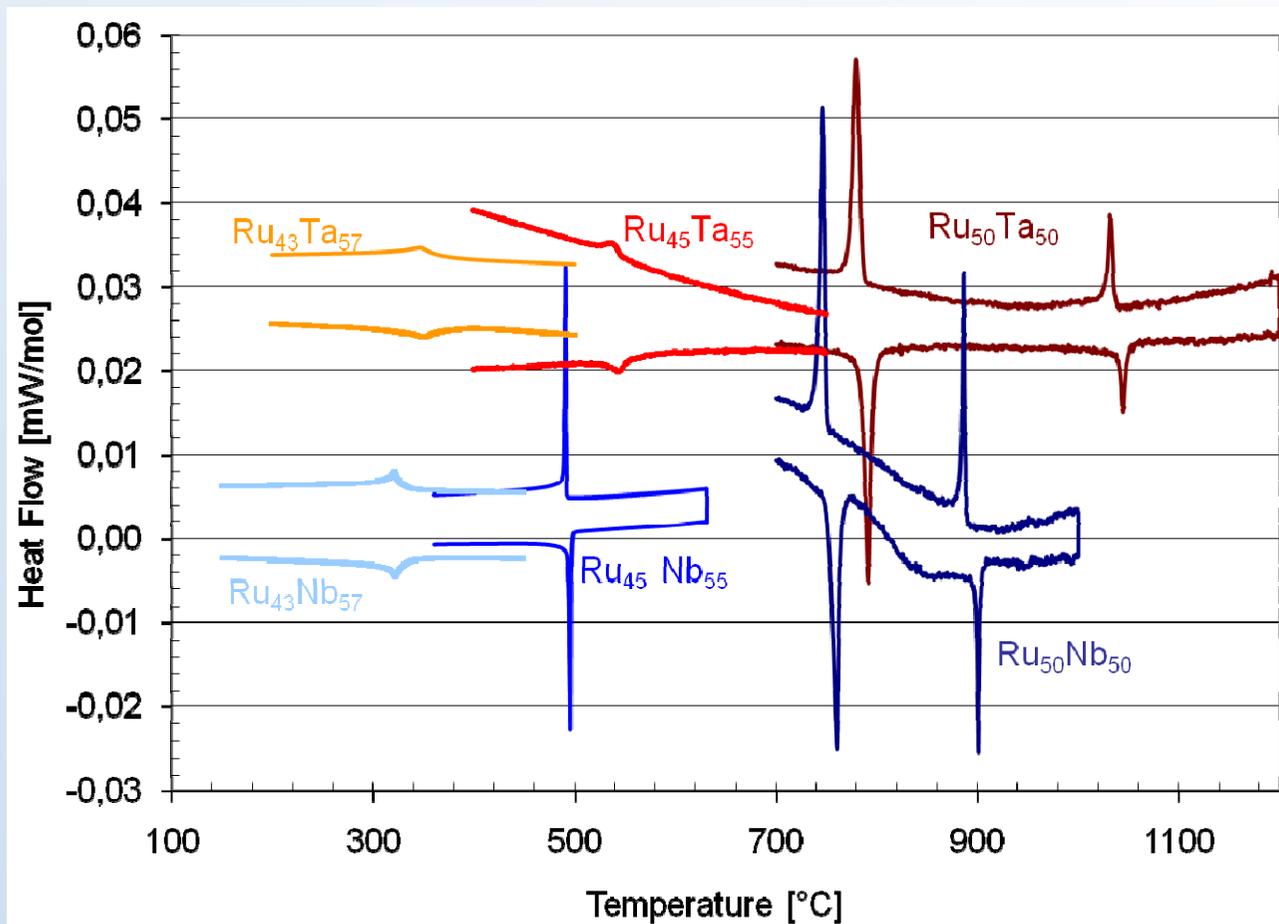
1 month at 690 $^{\circ}C$: [β'' phase]
 1 month at 850 $^{\circ}C$: [β' phase]

temperatures and transformation energy stables

↓
 stabilisation of β' and β'' phases

$^{\circ}C$	high temperature transformation β/β'			low temperature transformation β'/β''		
	Ms'	Δ	Hyst	Ms''	Δ	Hyst
Ru₅₀Nb₅₀	887.0	2.2	13.0	751.5	12.0	14.0
Ru₄₈Nb₅₂	732.8	16.6	16.6	567.6	22.9	11.2
Ru₄₆Nb₅₄	574.0	6.0	2.3	x	x	x
Ru₄₅Nb₅₅	492.0	3.2	5.3	x	x	x

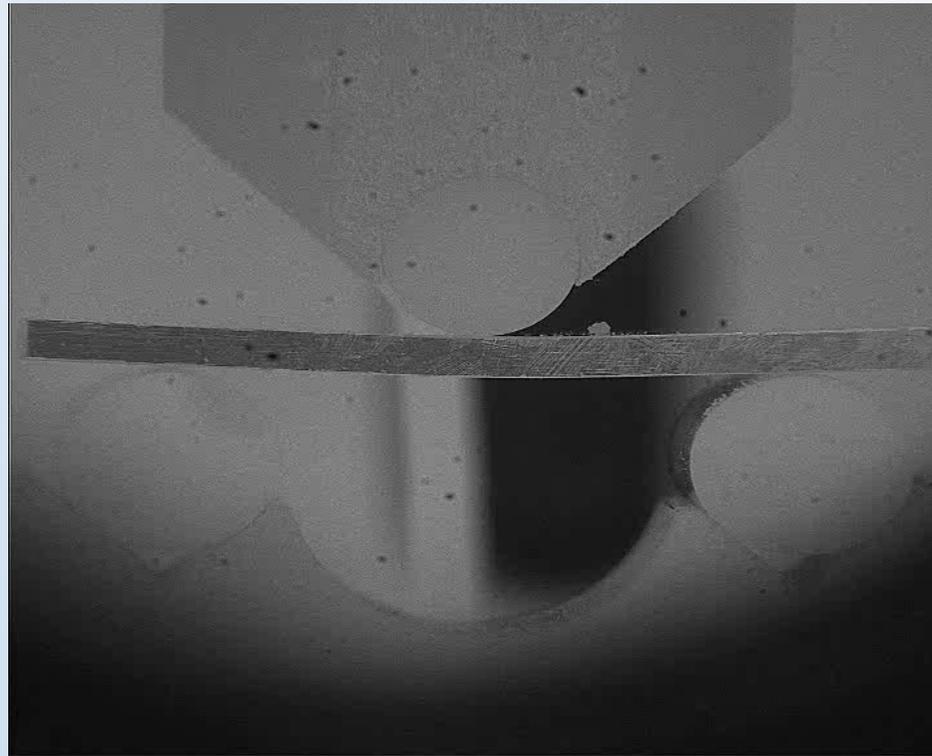
Control of the transformation temperatures by the chemical composition



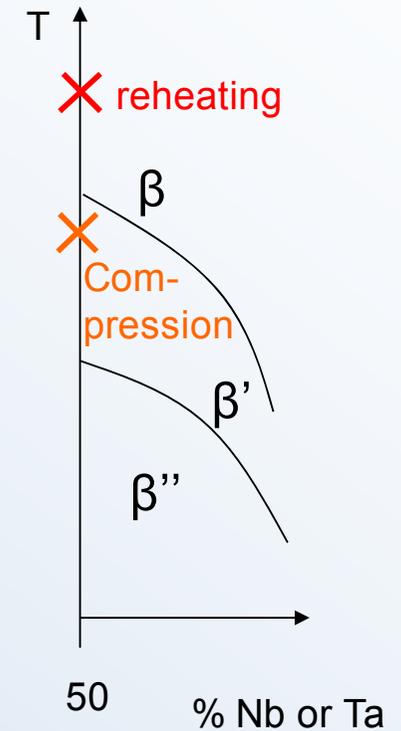
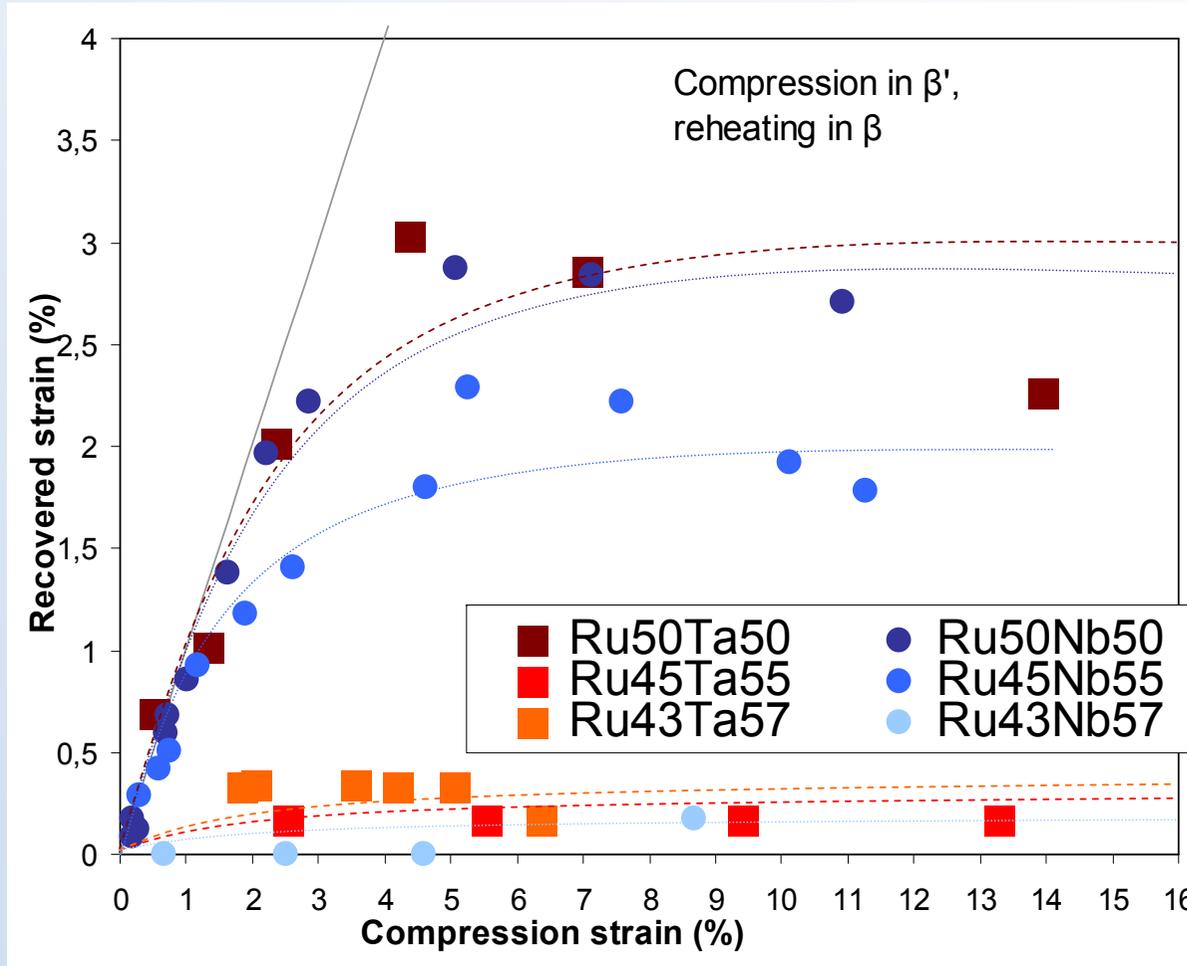
Direct observation of the Shape Memory Effect

3 points bending test

- deformation of β' at 830° C
- reverse transformation when heating up to 950° C

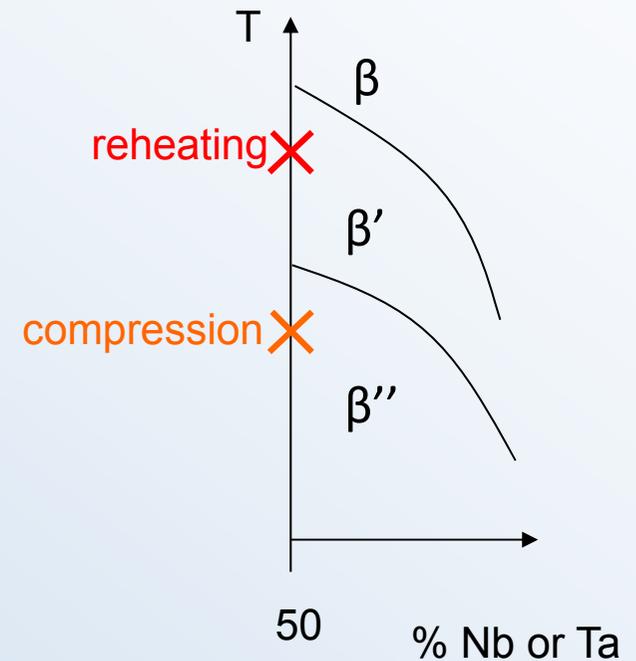
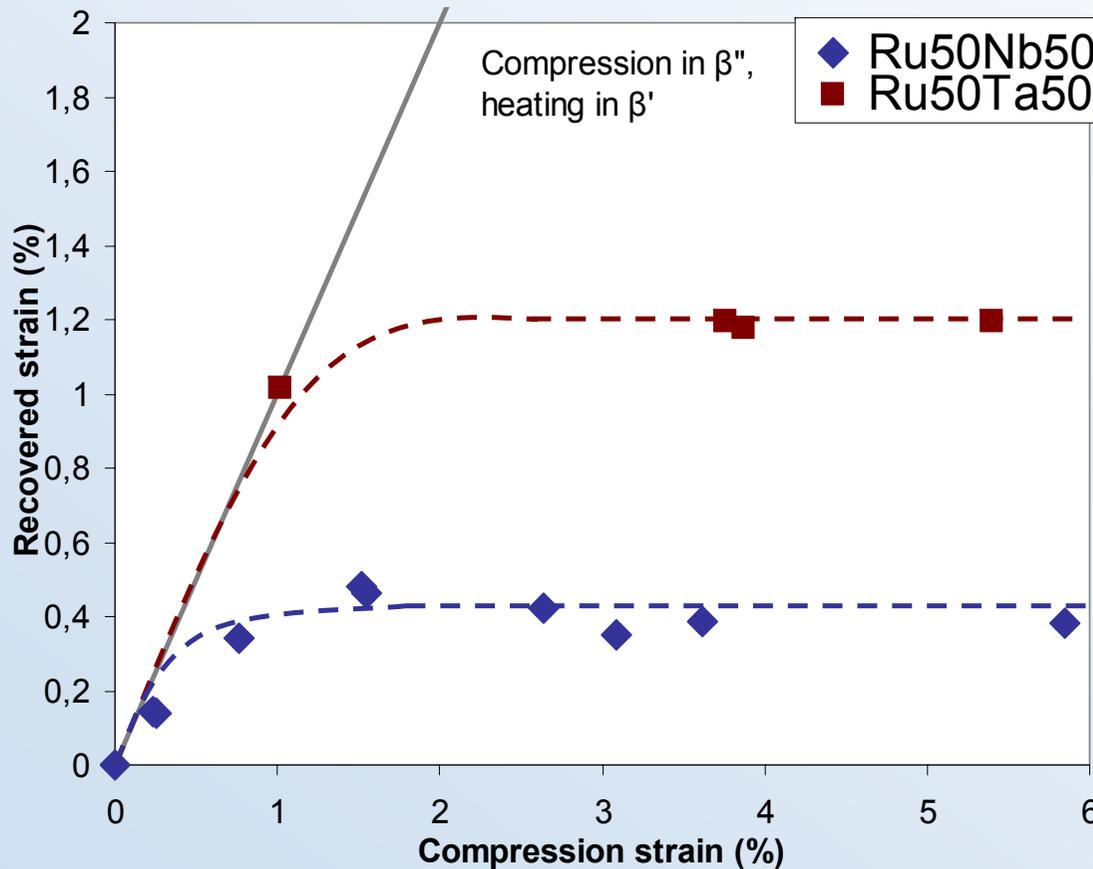


Shape memory effect decreases with Ru content



- 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 β' variants instead of β'' ?

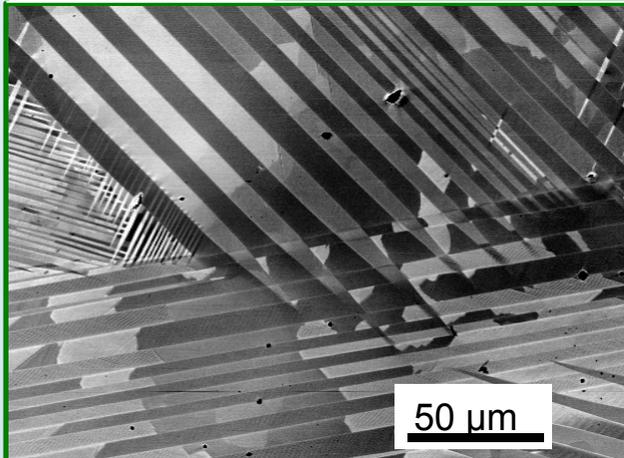
Microstructures Analysis

- SEM at room temperature
- crystallographic approach
- TEM
- in-situ neutron diffraction
- EBSD

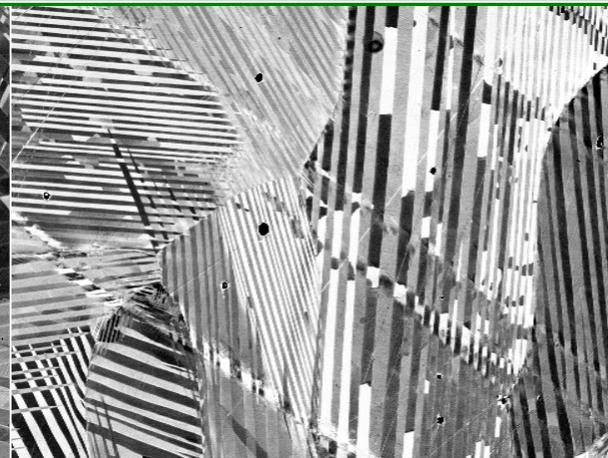
SEM

Tetragonal

Monoclinic



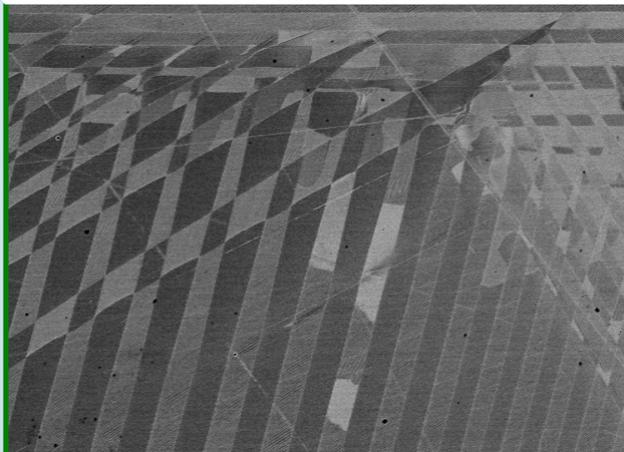
$Ru_{43}Ta_{57}$



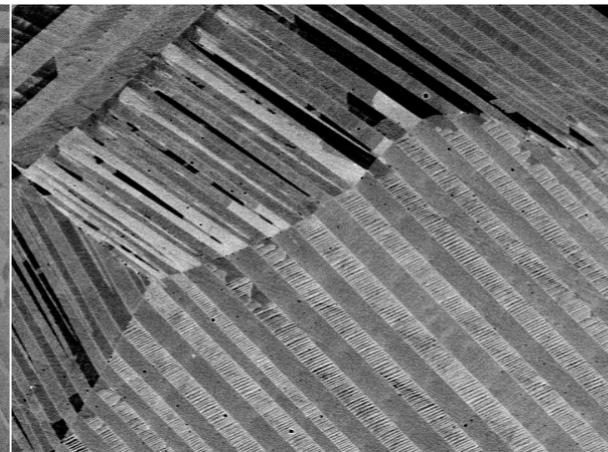
$Ru_{45}Ta_{55}$



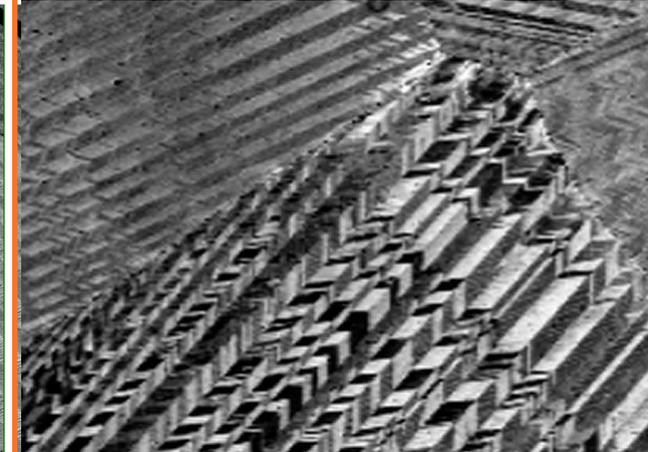
$Ru_{50}Ta_{50}$



$Ru_{43}Nb_{57}$



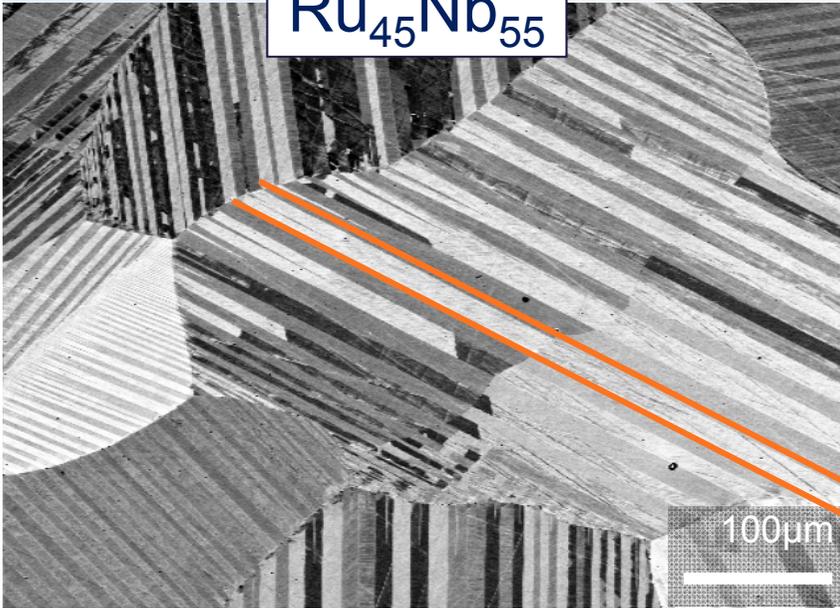
$Ru_{45}Nb_{55}$



$Ru_{50}Nb_{50}$

1, 2 or 3 laminates (polytwins) noted

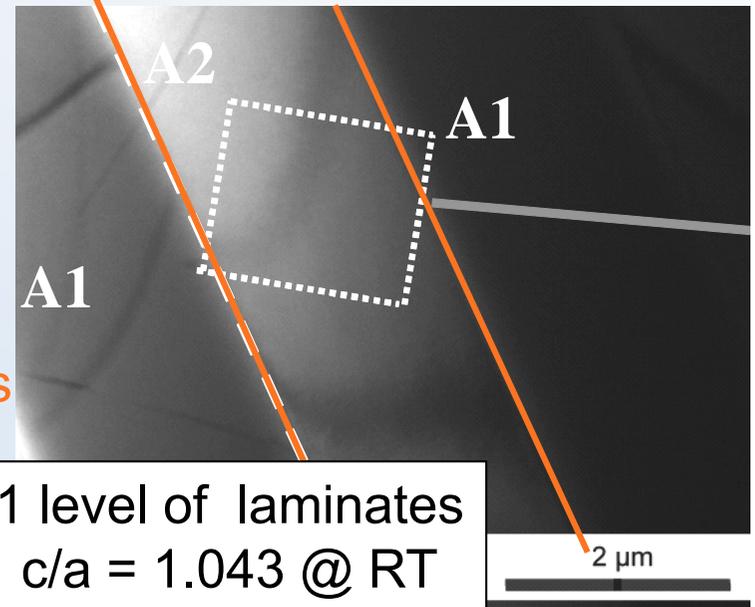
A (Large)
B (Medium)
C (Small)



Microstructure of β' martensite in Tetragonal alloys

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

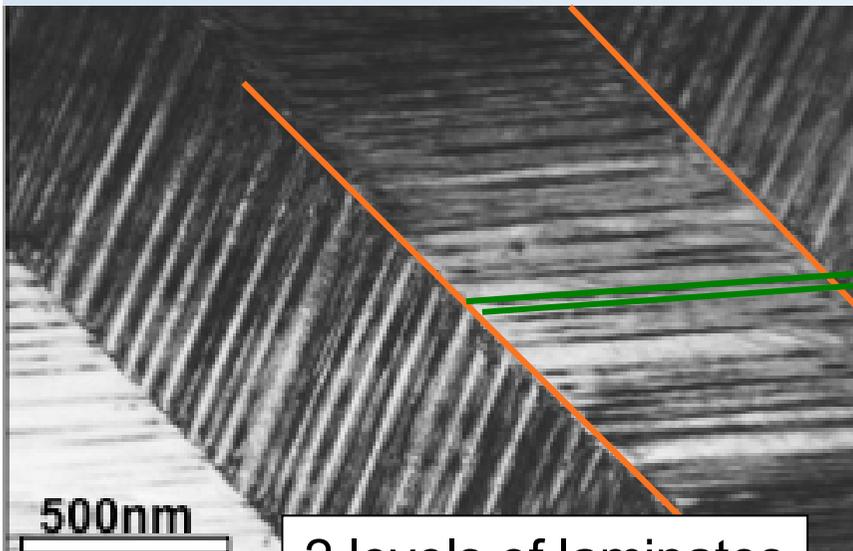
Large A twins



Small C twins

+

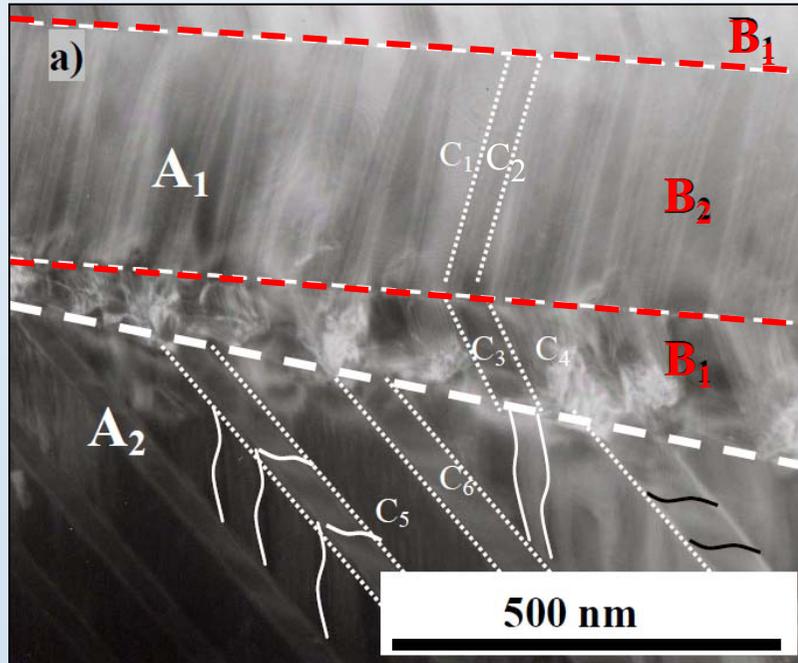
Large A twins



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

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

Microstructure of β'' martensite in Monoclinic alloys



3 levels of laminates (twins)

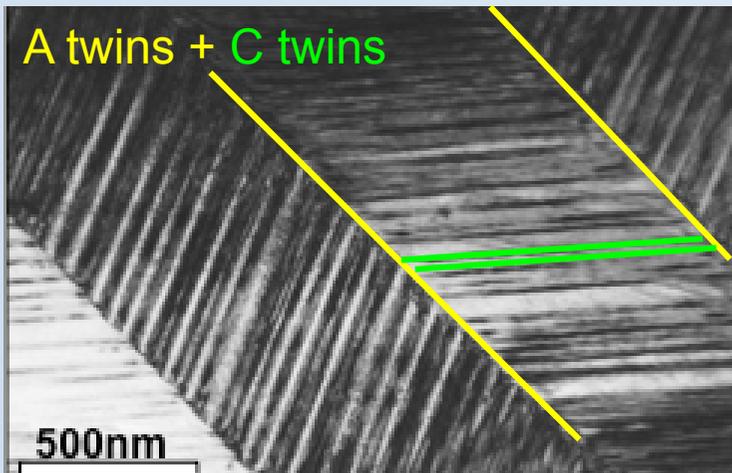
A (L)

NEW B intermediate size (M)

C (S)

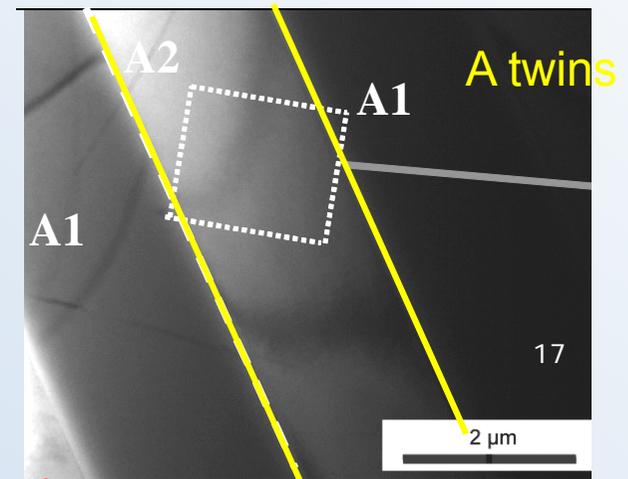
wavy translation boundaries

(no background difference)

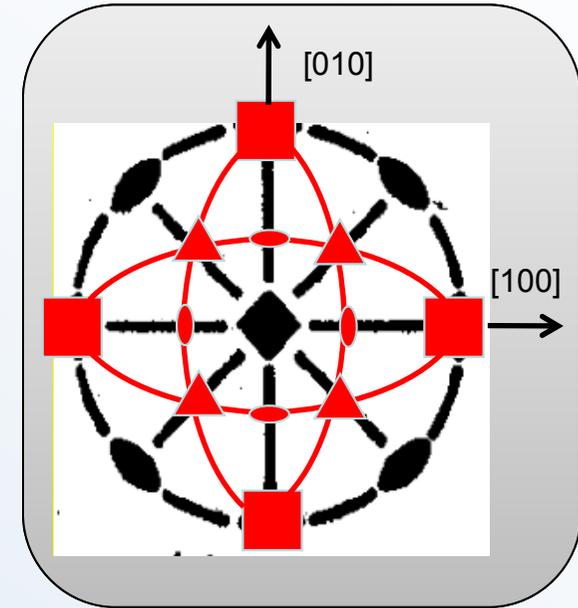
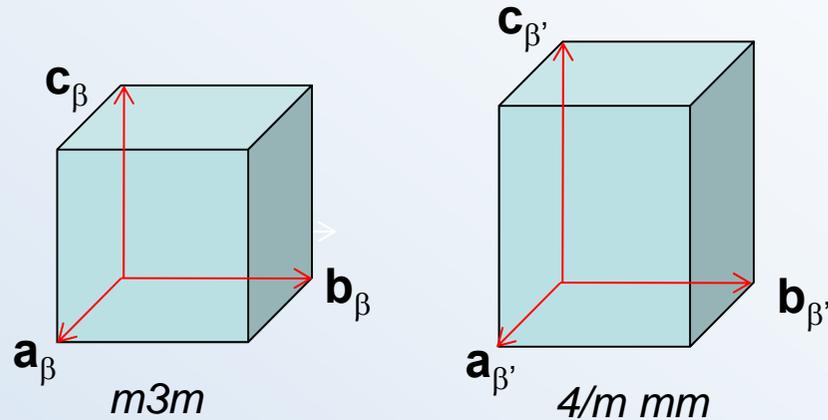


from the β' phase

all the structural features of β' are **inherited** by β'' = all the interfaces

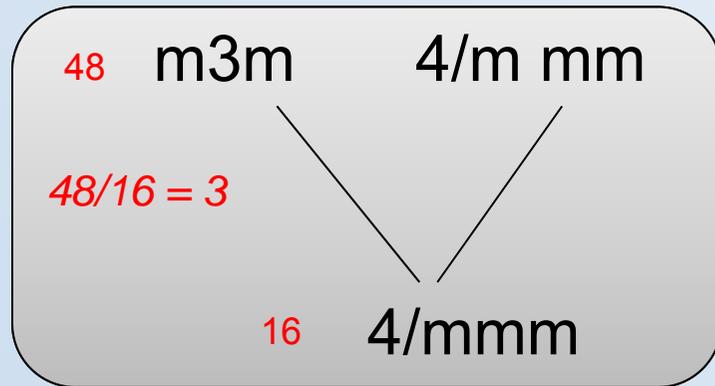


Crystallographic analysis : $\beta \rightarrow \beta'$ transformation



Group-subgroup relationship :

$$(a_{\beta}, b_{\beta}, c_{\beta}) \approx (a_{\beta'}, b_{\beta'}, c_{\beta'})$$



High atom density of the plane
Mirror plane = twin plane

lost cubic mirrors

- $m(101)_{\beta}$
- $m(10-1)_{\beta}$
- $m(011)_{\beta}$
- $m(01-1)_{\beta}$

Twinning planes

3 orientation variants

$\beta' \rightarrow \beta''$ transformation

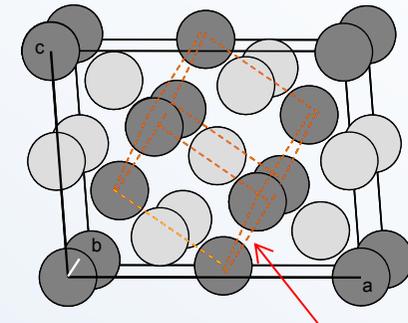
β' martensite
Tetragonal

β'' martensite
Monoclinic

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

Group-subgroup relationship :

$$\begin{aligned} a_{\beta''} &= a_{\beta'} - b_{\beta'} + 2c_{\beta'} \\ b_{\beta''} &= -a_{\beta'} - b_{\beta'} \\ c_{\beta''} &= a_{\beta'} - b_{\beta'} - c_{\beta'} \end{aligned}$$

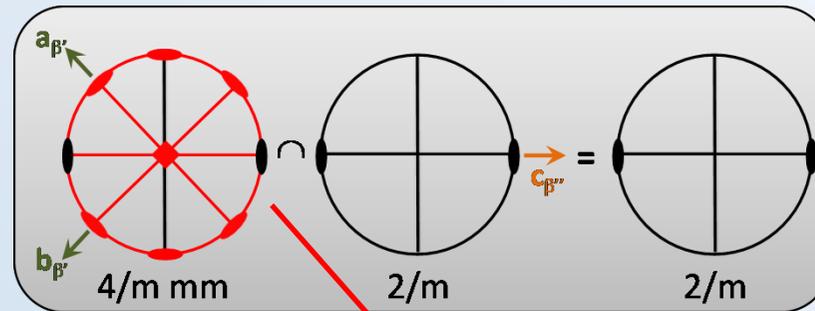


Previous tetragonal unit cell

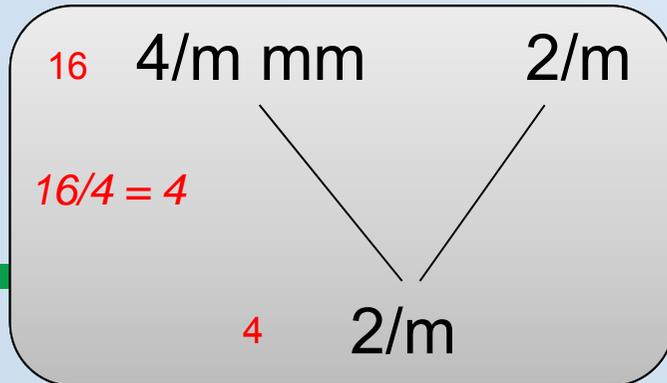
$$\text{Vol}_{\beta''} = 6 \text{Vol}_{\beta'}$$

$$[2]_{\beta''} // [110]_{\beta'}$$

$$(m)_{\beta''} // m(110)_{\beta'}$$



4 orientation variants



lost tetragonal mirrors

$$\begin{aligned} m(010)_{\beta'} &\rightarrow (-1-1-1)_{\beta''} \\ m(100)_{\beta'} &\rightarrow (1-11)_{\beta''} \\ m(1-10)_{\beta'} &\rightarrow (101)_{\beta''} \\ m(001)_{\beta'} &\rightarrow (20-1)_{\beta''} \end{aligned}$$

→ Twins

6 translation variants related by 5 lost translations

$$\begin{aligned} [1-11]_{\beta'} & [1-10]_{\beta'} & [010]_{\beta'} \\ [1-21]_{\beta'} & [01-1]_{\beta'} & \end{aligned}$$

→ translation boundaries

Shape Memory Effect \longleftrightarrow unit cell deformation

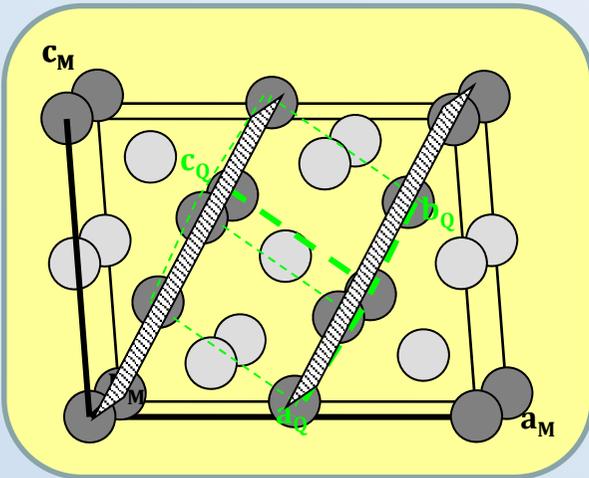
\longrightarrow lattice parameters versus temperature is needed

cubic \longrightarrow tetragonal

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

tetragonal \longrightarrow monoclinic

transformation : $c/a \text{ equivalent}$



$$c_{\beta'} \longrightarrow d(20-1)_{\beta''}$$

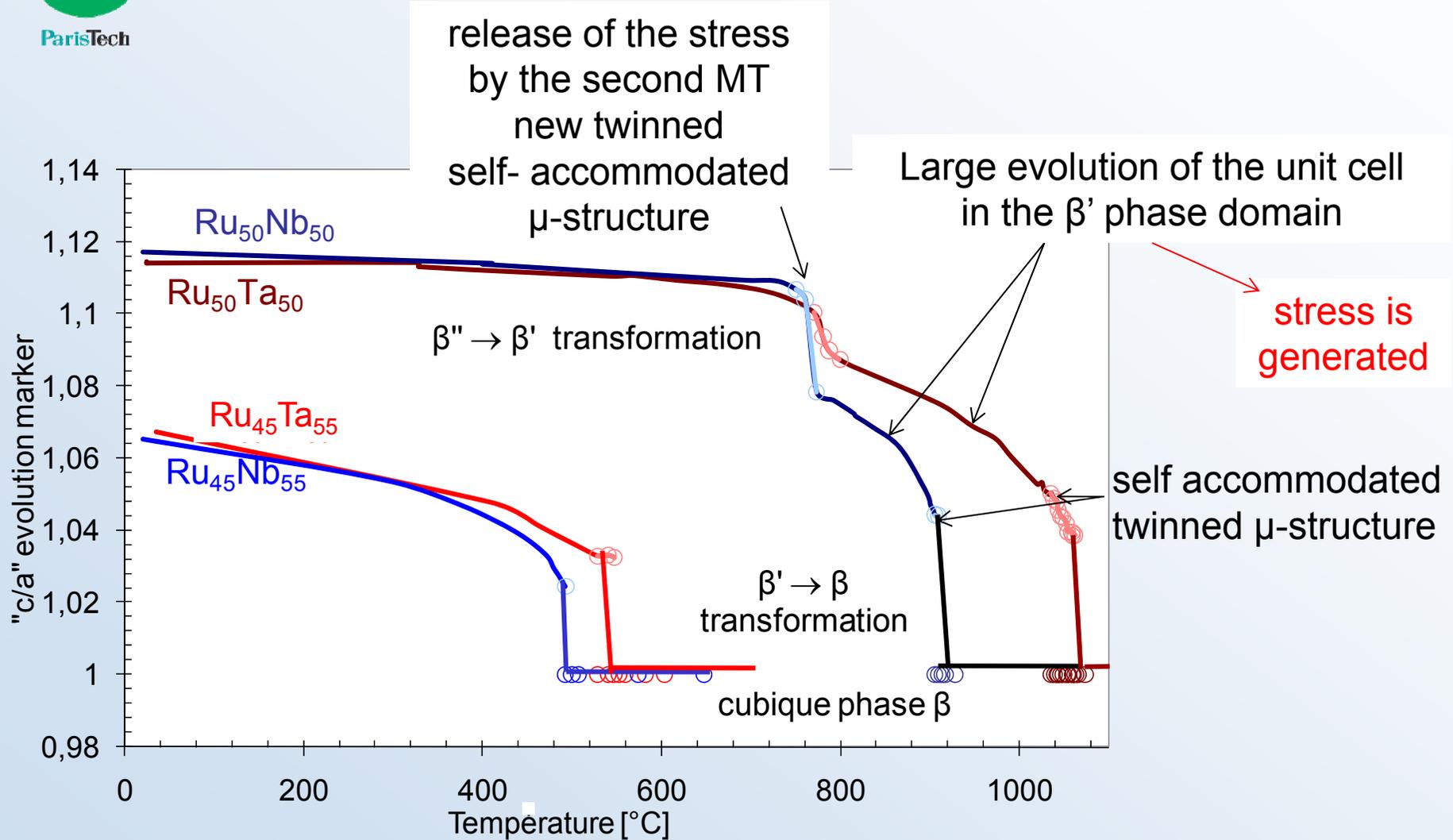
$$b_{\beta'} \longrightarrow d(111)_{\beta''}$$

$$a_{\beta'} \longrightarrow d(1-11)_{\beta''}$$

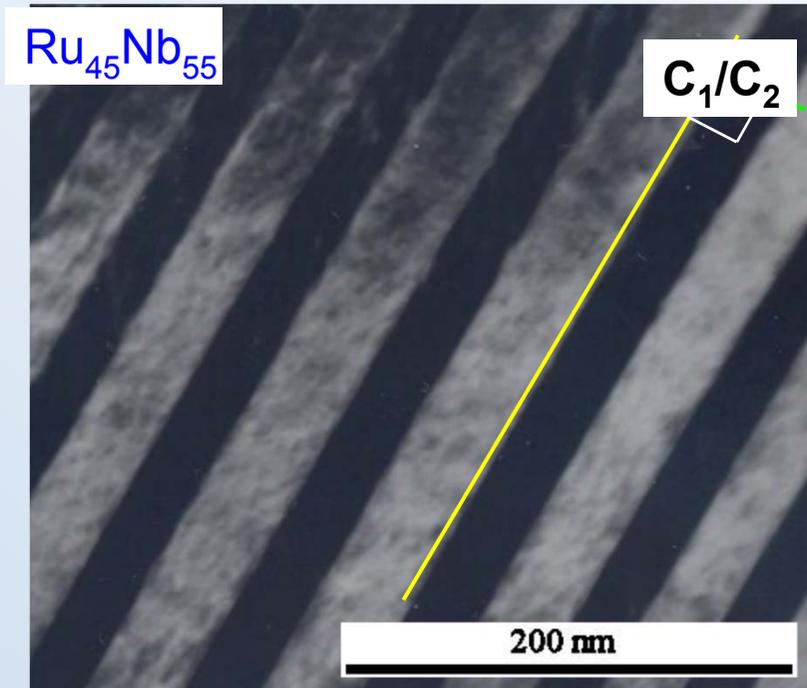
In-situ neutron diffraction / $T^\circ \longrightarrow \mathbf{a}_{\beta''}, \mathbf{b}_{\beta''}, \mathbf{c}_{\beta''}, \beta \longrightarrow \ll \text{evolution marker} \gg$

\hookrightarrow Laue-Langevin Institute Grenoble (France)

Unit cell deformation evolution with temperature

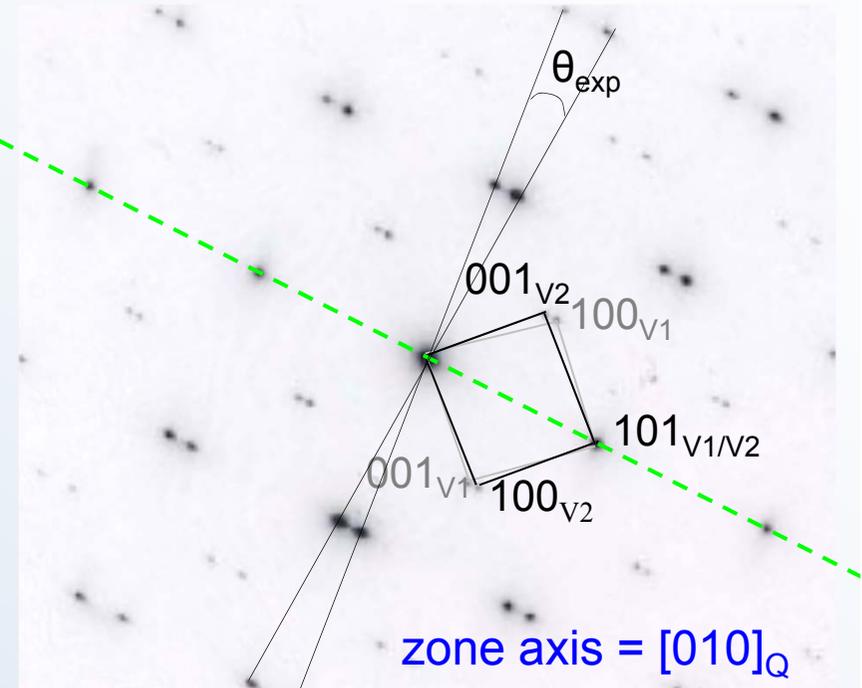


TEM characterization of twins in tetragonal alloys



A + C twins (variants)

all twins are $\{101\}_T$ type
 → cubic mirrors lost



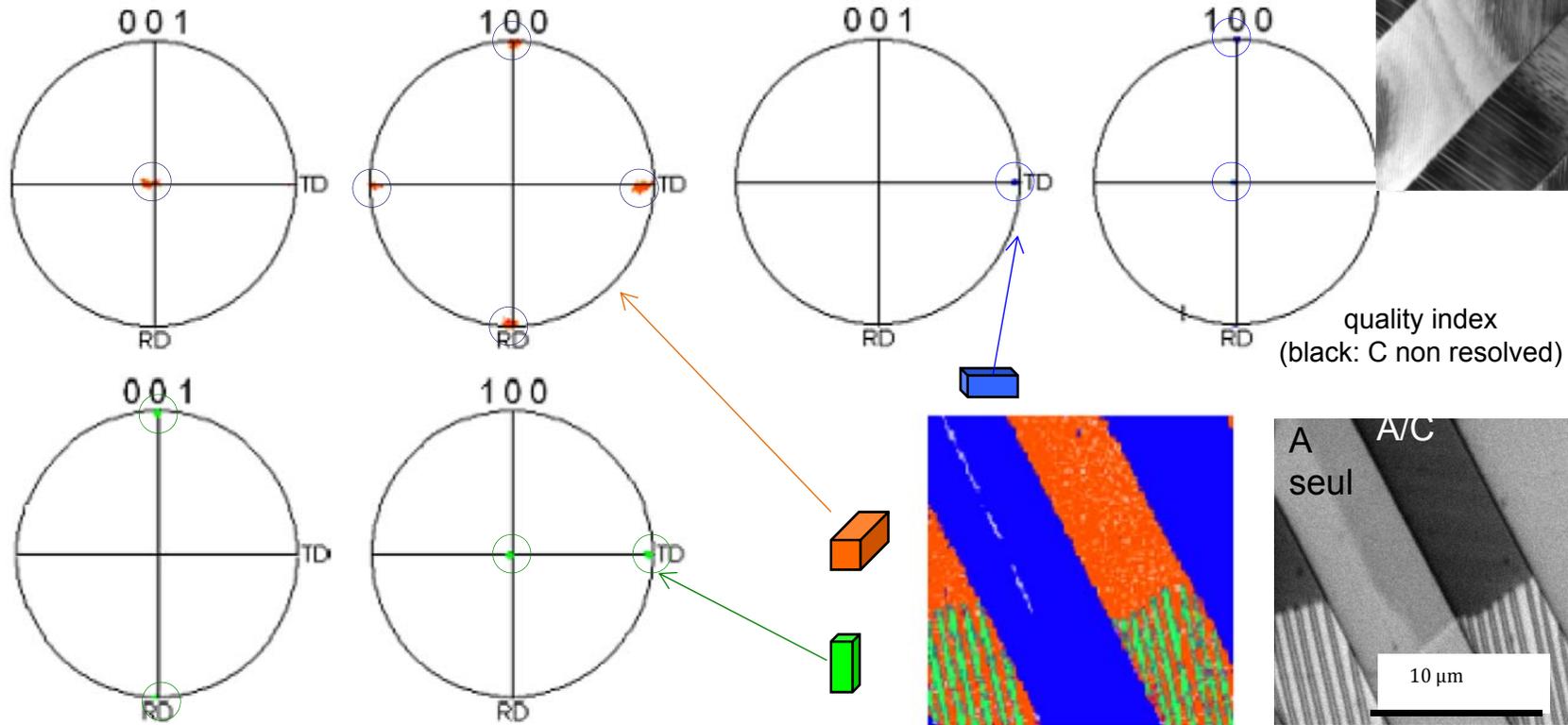
(101) Compound twin

K_1, K_2, η_1, η_2 rational

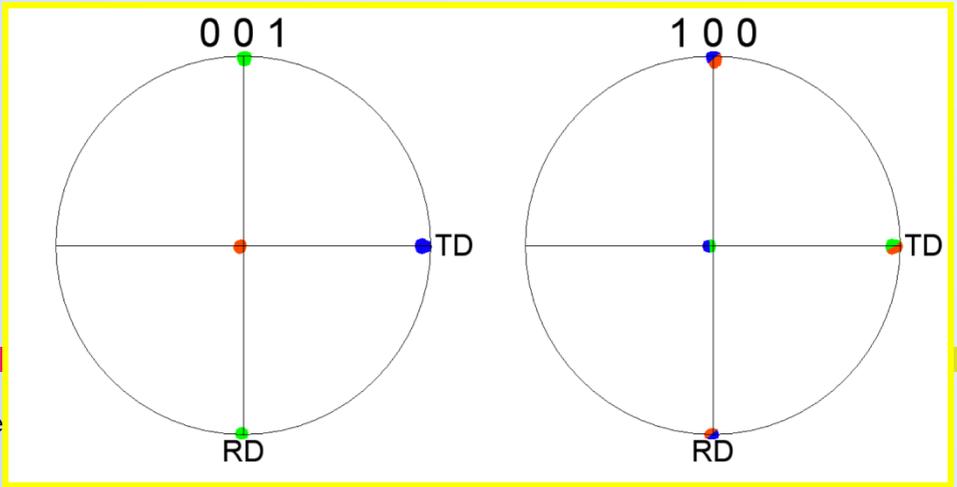
alloy	shear amplitude
$Ru_{45}Ta_{55}$	0.13
$Ru_{43}Ta_{57}$	0.09
$Ru_{45}Nb_{55}$	0.11
$Ru_{43}Nb_{57}$	0.08

single laminates of A type twins is possible

EBSD observations in tetragonal alloy

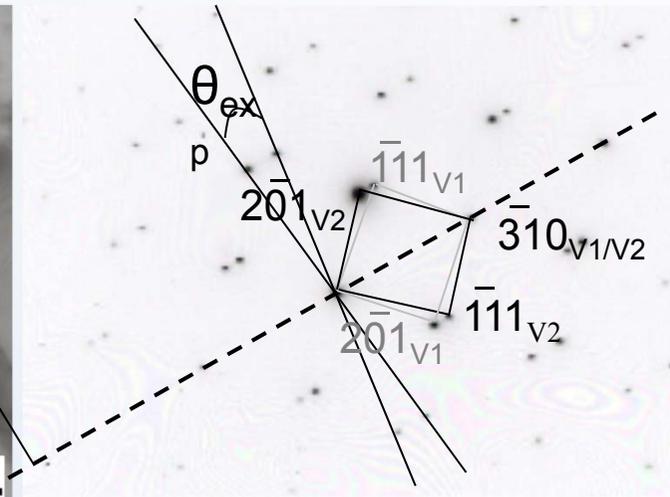
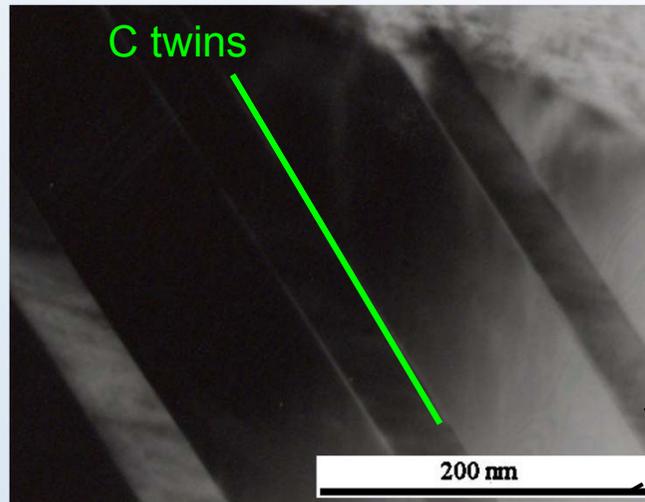


3 variants of martensite



Zeiss DSM960
Saarbrücken

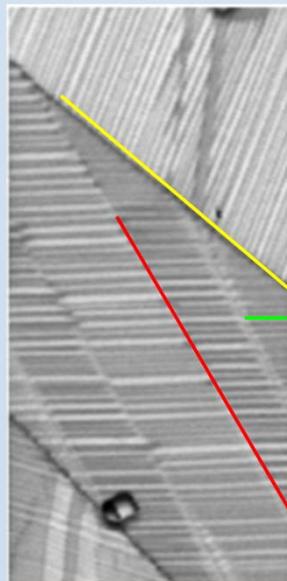
TEM characterization of twins in monoclinic alloys



twin plane = $(3 - 1 0)_{\beta''}$

Indices of $(3-10)_{\beta''}$ plane in the β' tetragonal structure $\rightarrow (101)_{\beta'}$

\rightarrow C twin of $\beta \rightarrow \beta'$

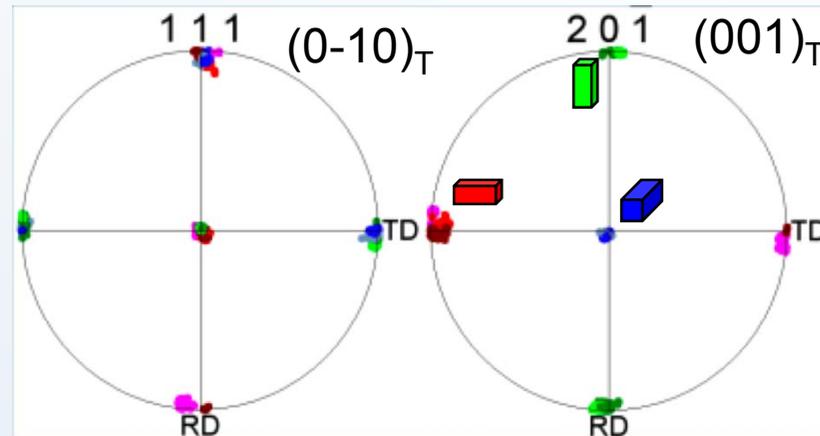
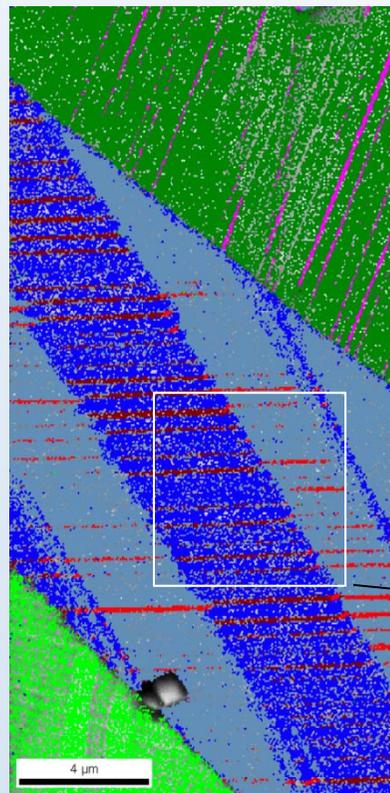
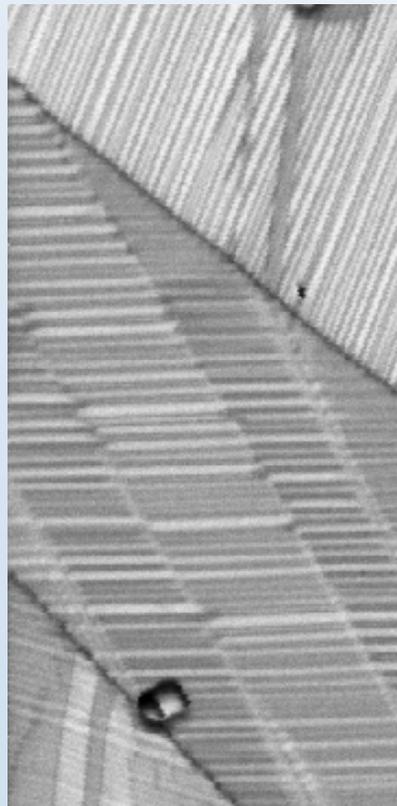


A twins
C twins

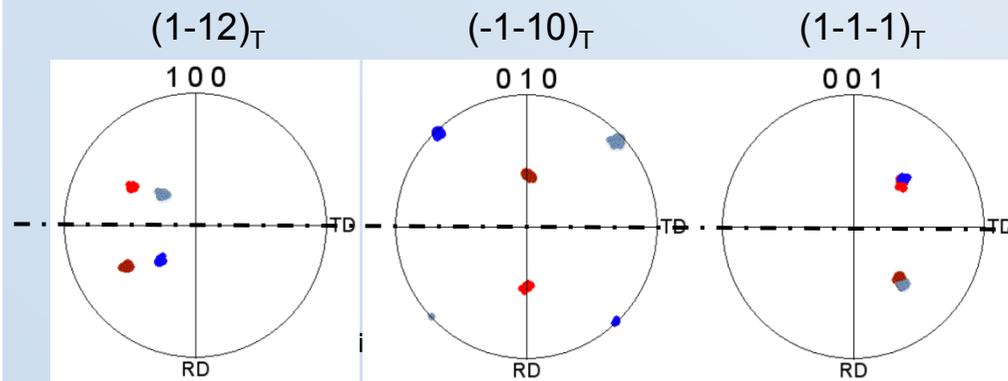
+ new B twins generated during $\beta' \rightarrow \beta''$

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

EBSD characterization of twins in monoclinic alloys



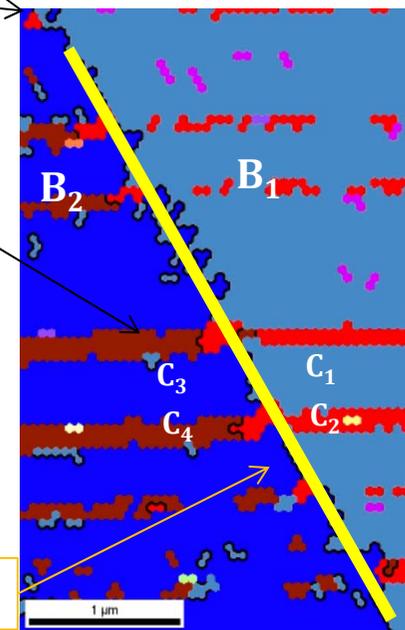
3 principal orientations coming from $\beta \rightarrow \beta'$ inherited tetragonal microstructure



(100) mirrors of   tetragonal variants lost during $\beta' \rightarrow \beta''$

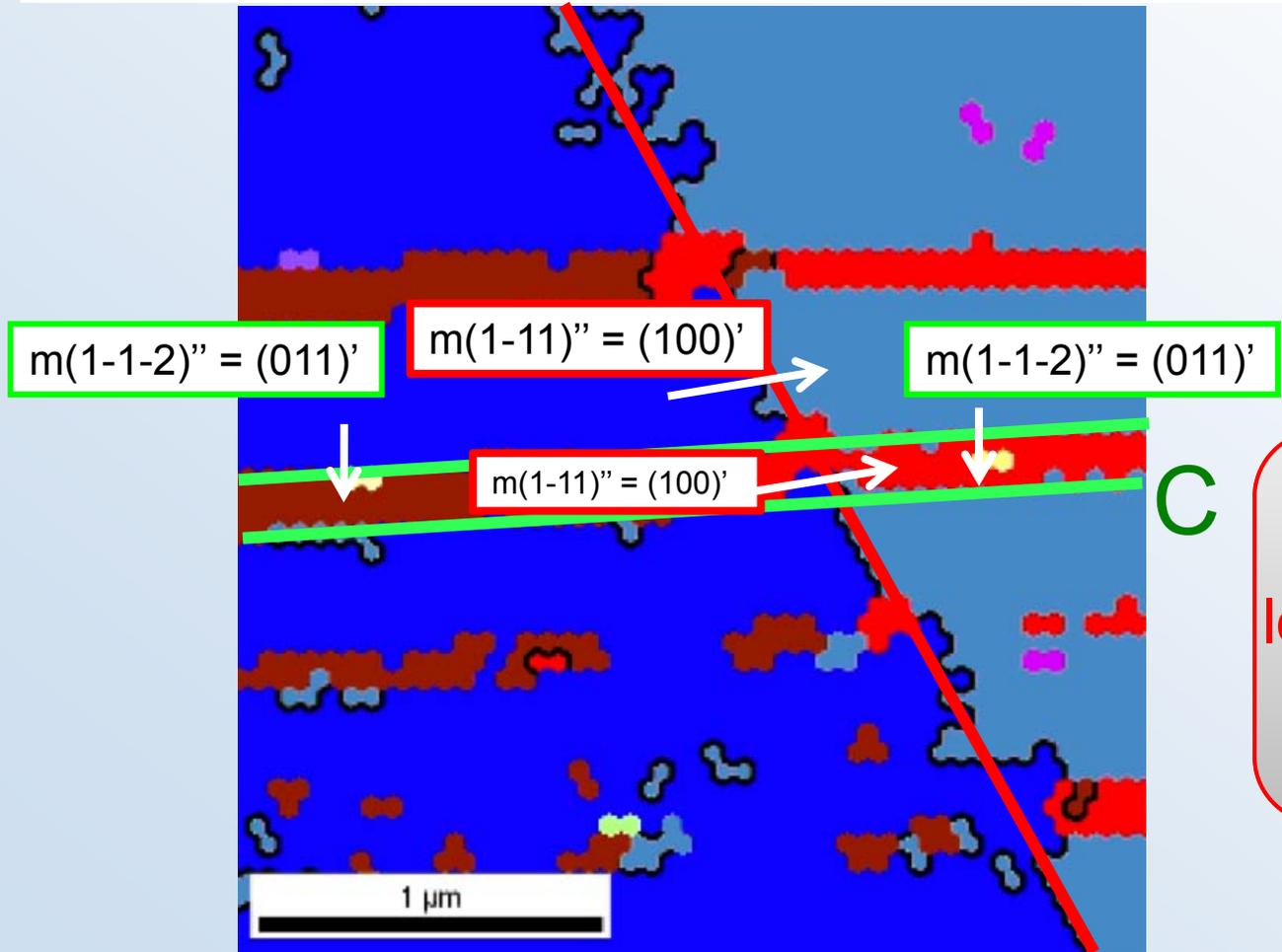
$\beta' \rightarrow \beta''$: B twin

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



EBSD analysis of the operation between variants : the chosen operation being a mirror and the interface being parallel to this mirror

B → TWIN



C-TWIN:
lost cubic mirror
=
 $\beta \rightarrow \beta'$

new
B-TWIN :
lost tetragonal mirrors
=
 $\beta' \rightarrow \beta''$

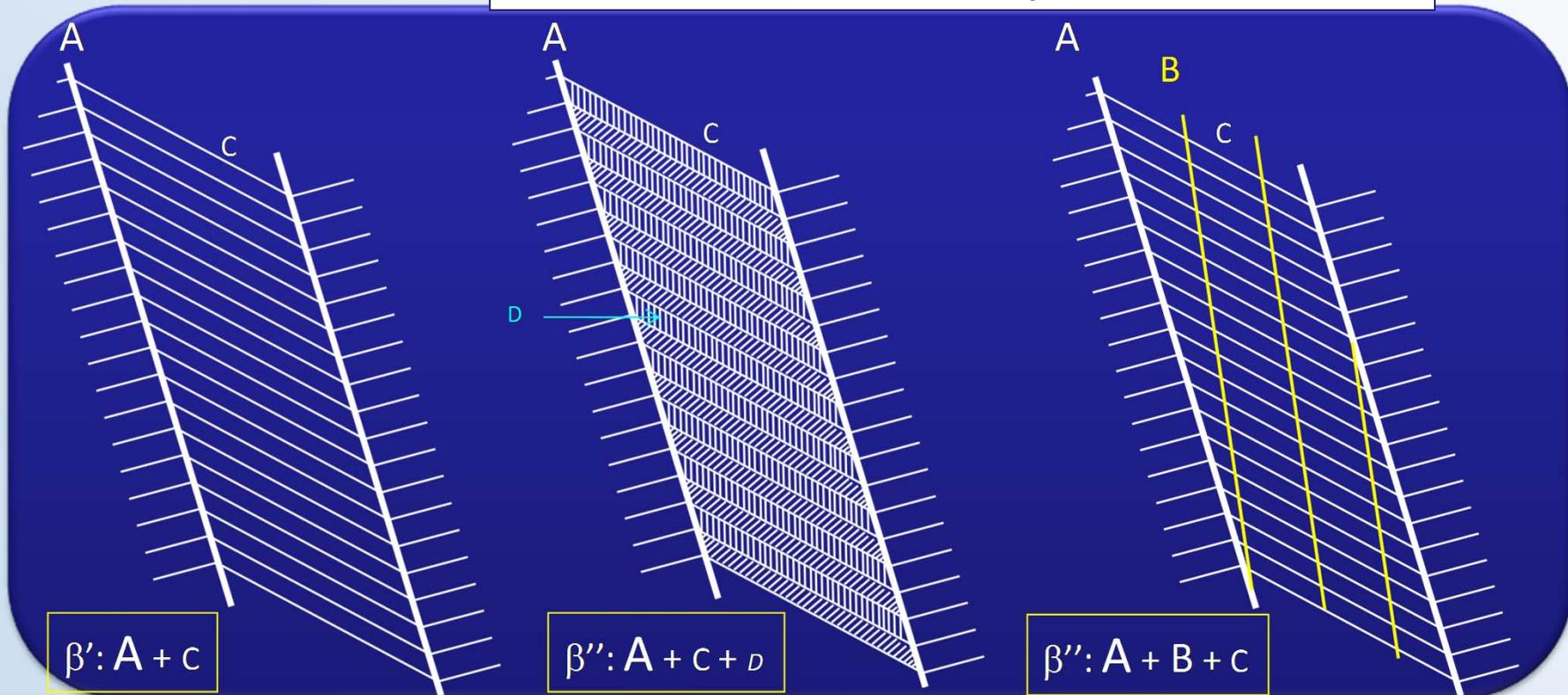
→ unexpected microstructure

Microstructural transformation mechanism

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

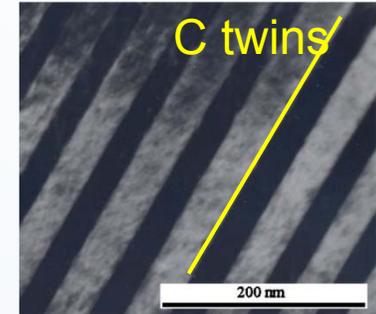
- special conditions for $\beta' \rightarrow \beta''$

normal conditions versus experimental evidence



$\beta' \rightarrow \beta''$ constrained transformation

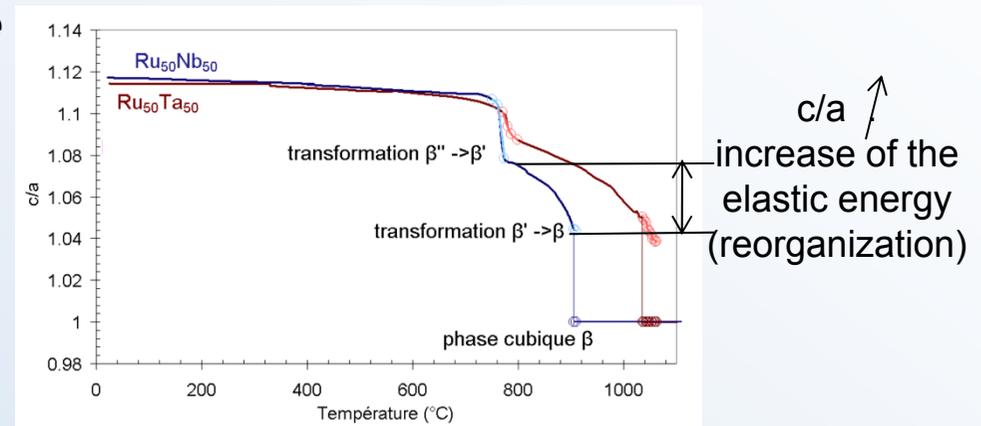
- **geometrically constrained**: very small thickness ($n \approx 10$ nm) of the C-twin domains
only one β'' variant in thickness



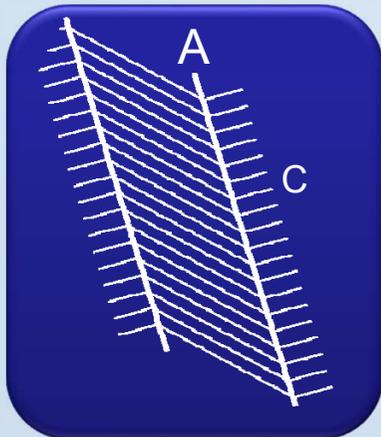
- **elastically constrained** : increase of the elastic energy

→ oriented nucleation of β''

same β'' variants in alternative corresponding β' twin domains of the laminate

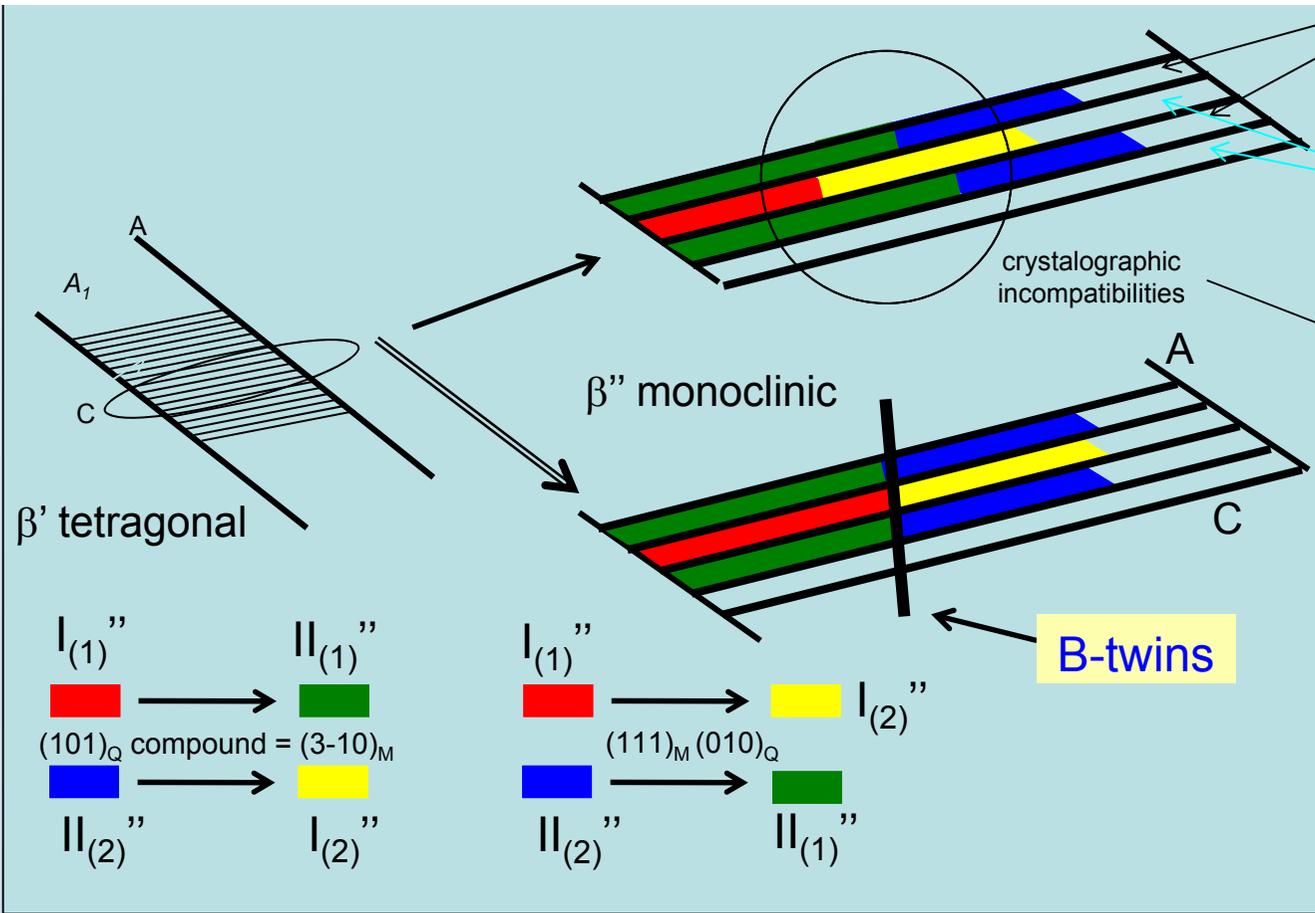


- **crystallographically constrained**: A or (A + C) β' twins are inherited and must still be twin operations for β'' structure

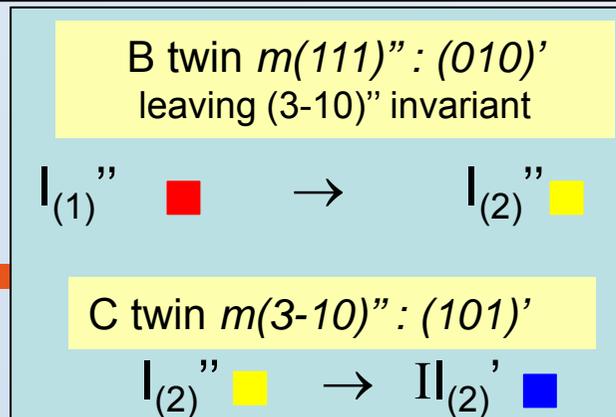
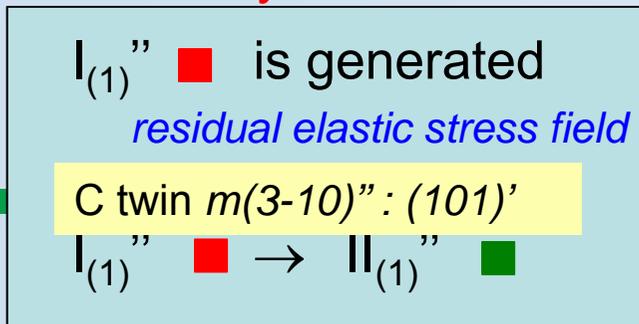


β'' variants in two successive β' twin domains are related by the $C_{\beta'}$ twin element, written in β'' referential

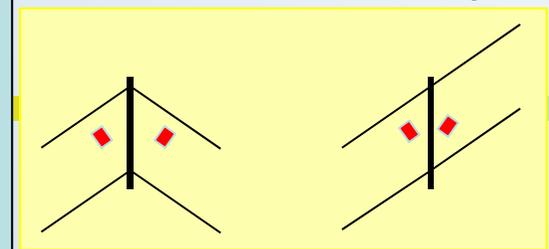
crystallographically constrained : the C-twin are inherited



Elastically constrained :



the B-twinning acts on the cells but not on the shape



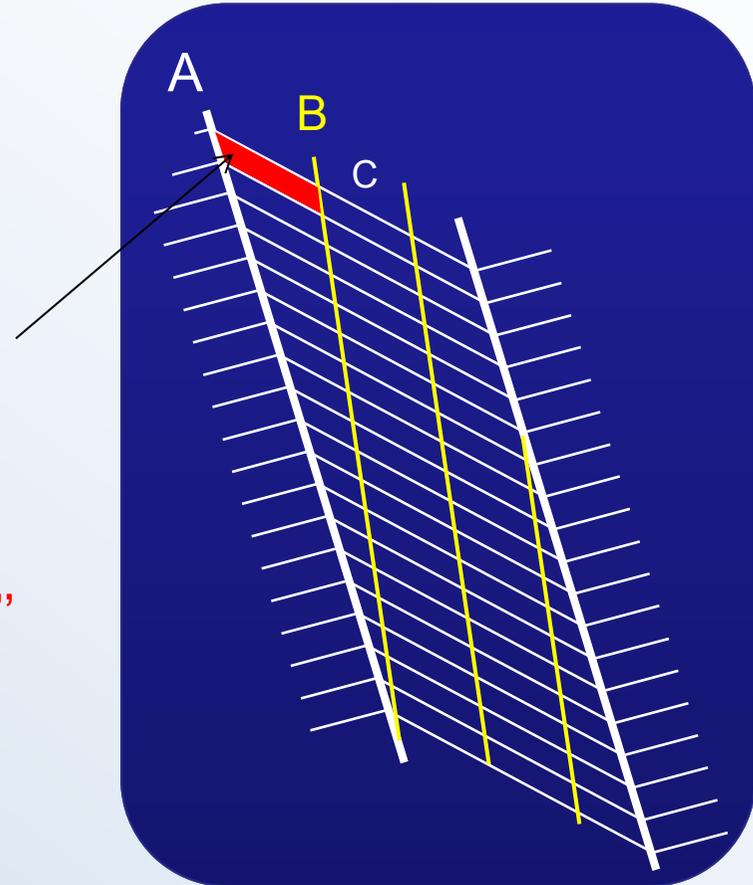
$\beta' \rightarrow \beta''$ constrained transformation

The 2nd martensitic transformation is geometrically and crystallographically constrained

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



special match between β' and β'' 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**