Part XIII : Théories cristallographiques des transformation martensitiques

Plan

1. Transformation par distorsion de réseau ou par shuffle
2. Martensite dans les aciers (TRIP, TWIP)
3. Martensite dans les céramiques

Pour information :

4. PTMC et théorie basée sur les dislocations/disconnections
5. Modèles à sphères dures

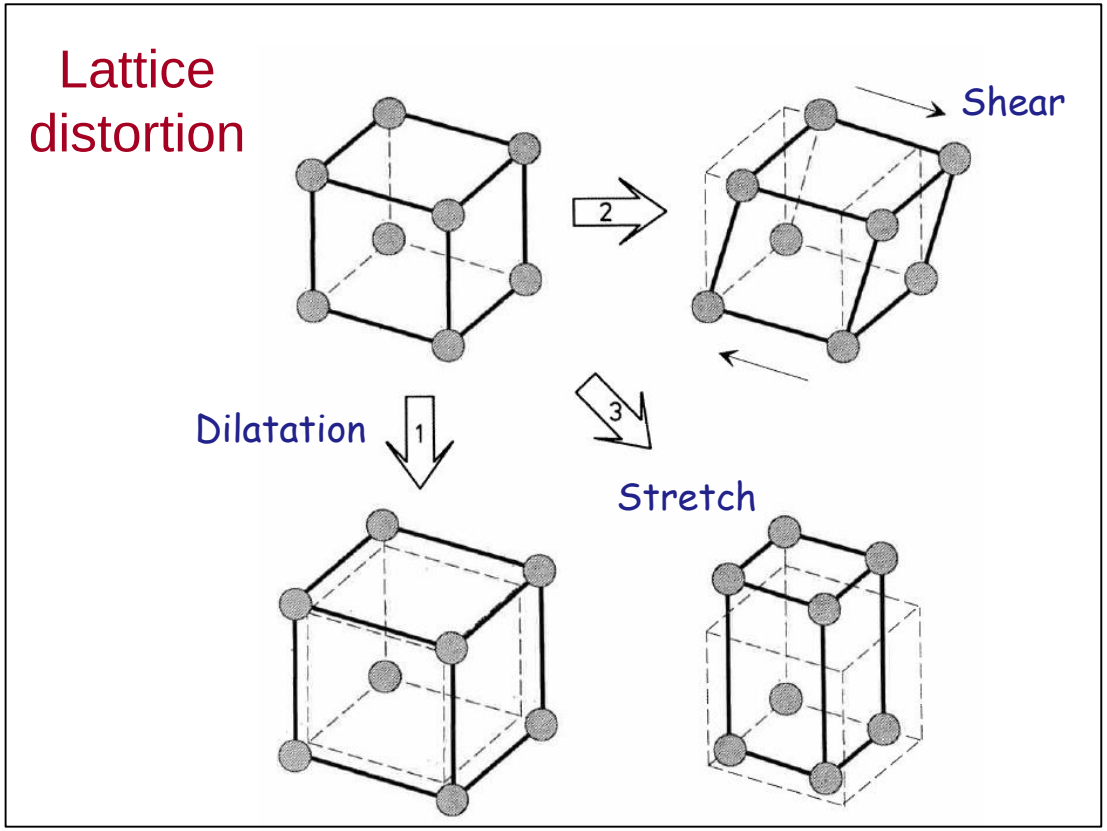
Objectifs

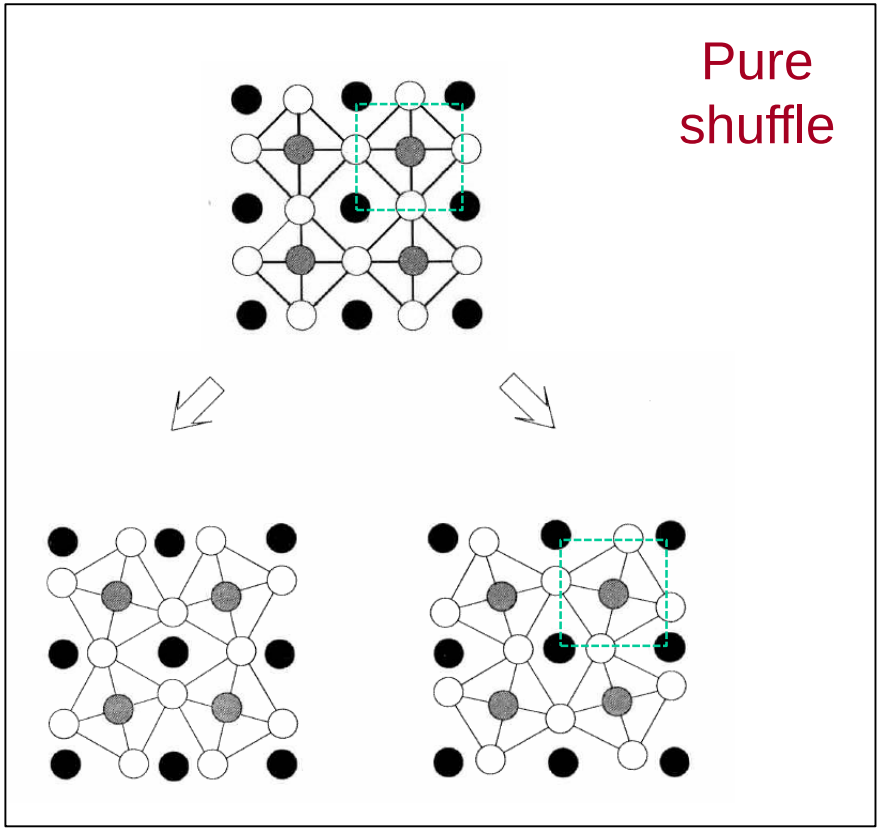
Le maclage mécanique et les transformations martensitiques sont displacives avec une composante de distorsion de réseau et éventuellement une composante « *shuffle* ». Elles impliquent un mouvement collectif des atomes, des vitesses de propagation élevées, une relation d'orientation parent-fille, des formes de martensite lenticulaires. La théorie appelée PTMC pour *phenomenological theory of martensite crystallography* a été développée dans les années 1950 pour rendre compte de ces caractéristiques. Cette théorie est toujours utilisée malgré quelques défauts et limitations. D'autres approches moins phénoménologiques sont possibles: dislocations / disconnections, sphères dures.

1. Distorsion de réseau vs *shuffle*

Distorsion de réseau: Déplacement coordonnées des atomes de tout le réseau.

« Pure shuffle »: Déplacement des atomes dans chaque maille indépendamment de la distorsion du réseau.



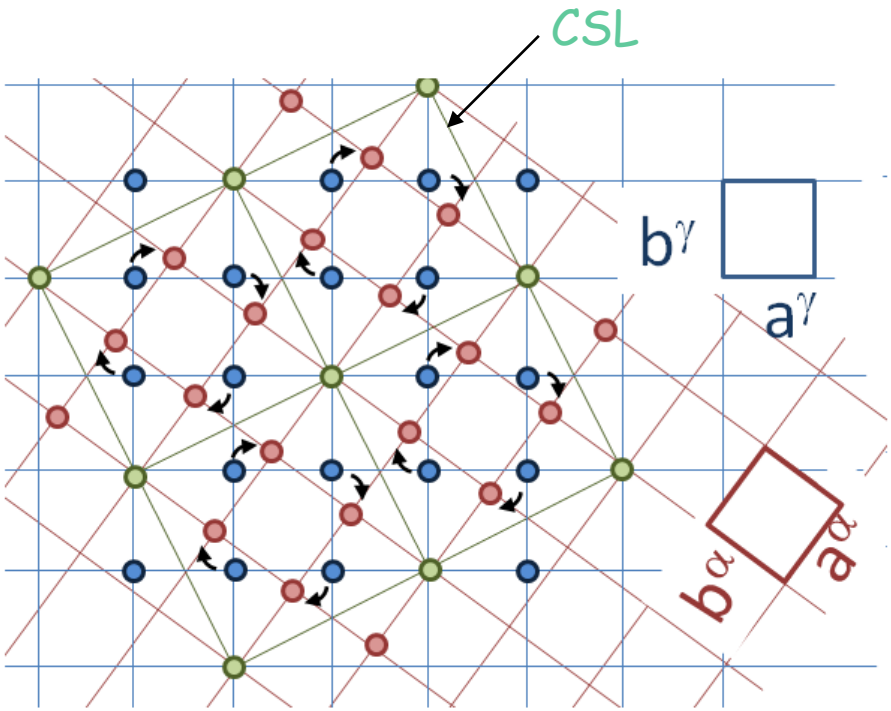


1. Distorsion de réseau vs *shuffle*

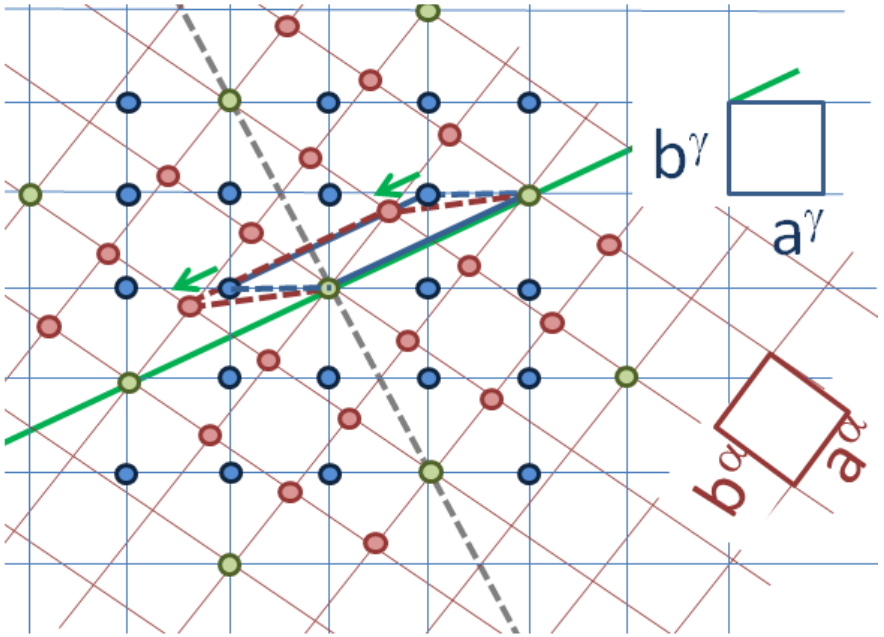
Exemple de différence entre une transformation pure shuffle (sans cisaillement) et une transformation par cisaillement simple (sans shuffle), avec même relation d'orientation finale:

γ square P4m $\rightarrow$ γ square P4m with $\Sigma 5$ OR

Pure shuffle

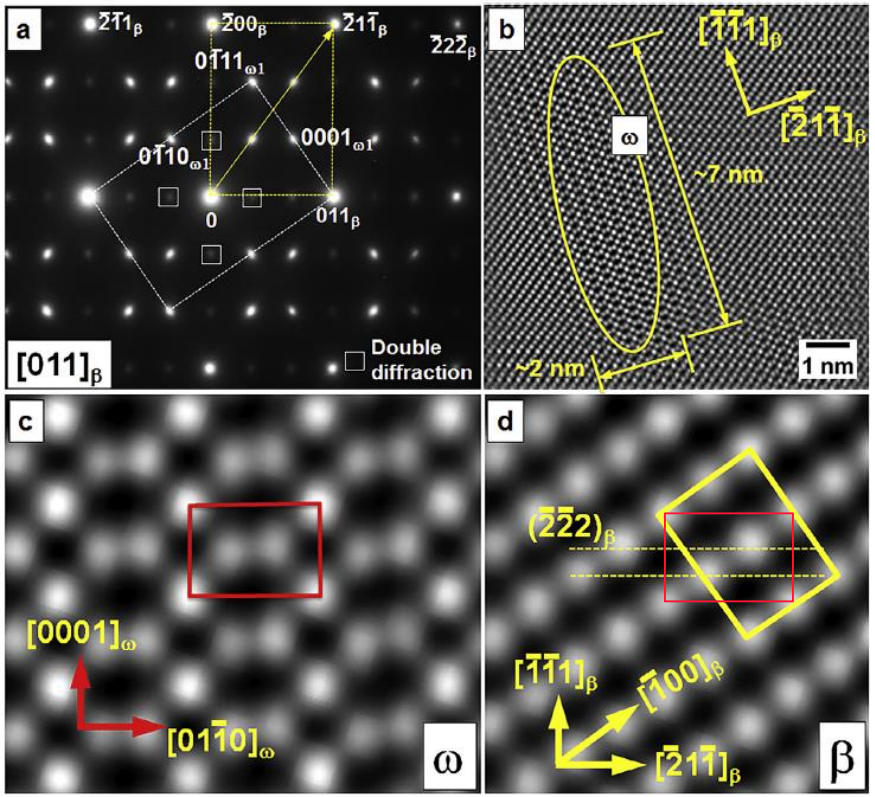


Simple shear

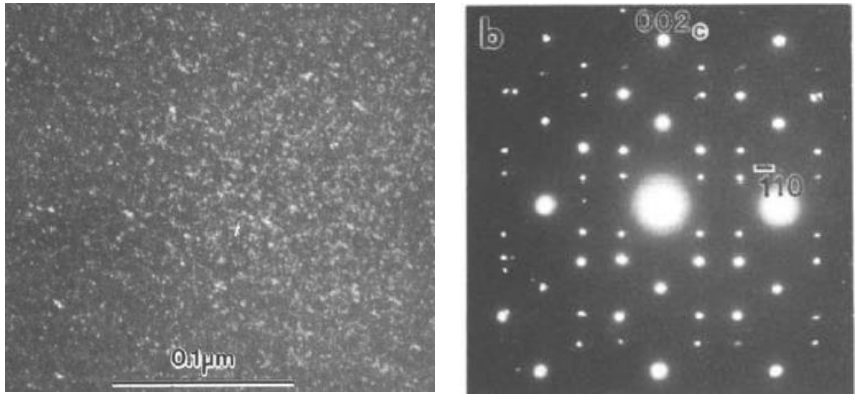


1. Distorsion de réseau vs *shuffle*

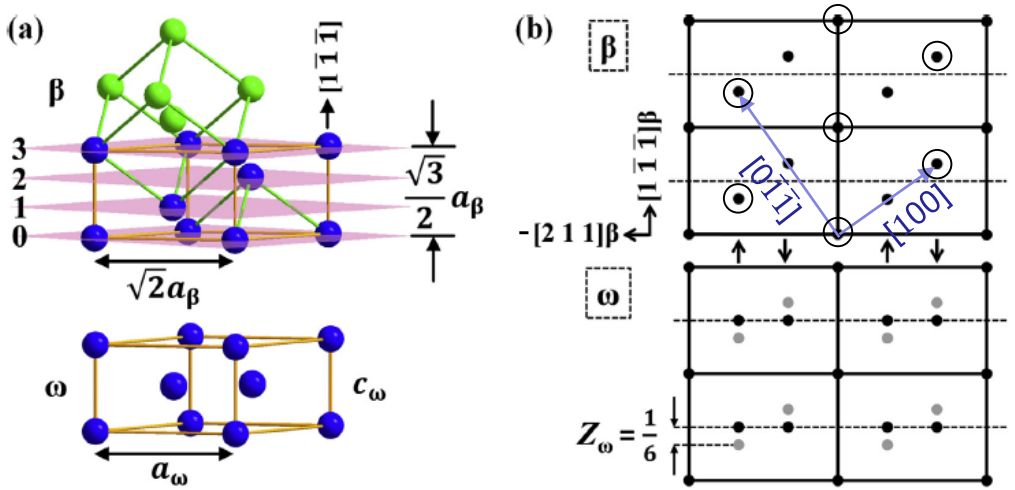
La phase ω est observée dans les alliages de titane Ti-Nb et Ti-Mo refroidis rapidement et revenus en température. La phase ω se forme par une transformation « pure shuffle » : bcc β → hexagonal ω. C'est le seul cas de transformation vraiment « pure shuffle » sans aucune distorsion de la maille.



Chouduri et al, Acta Materialia 130 (2017) 215-228



Bendersky et al, Acta metall, mater. Vol. 38, 931-943, 1990



Adapted from M.J. Lai et al. , Acta Materialia 92 (2015) 55-63
Projection along the $[011]_\beta$ direction. The Ti atoms on the same $(011)_\beta$ layer are marked by circles.

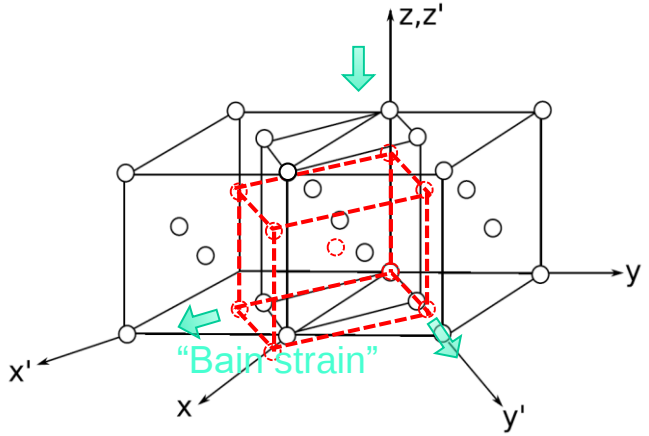
2. Martensite dans les aciers

Acier = alliage **Fe-C**-X-Y-...

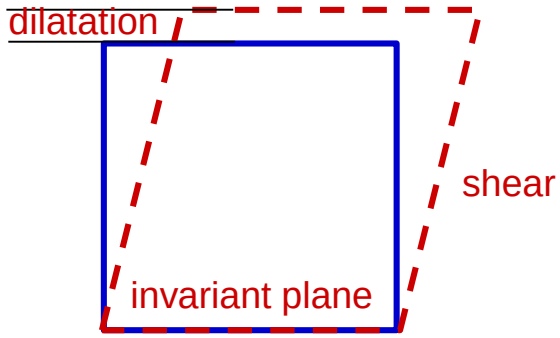
La transformation martensitique a les caractéristiques suivantes:

- Peut se propager à la **vitesse du son**
- Peut se trouver en compétition avec des transformations diffusives, comme les transformations ferritique, perlitique, bainitique
- Selon la PTMC, la martensite est générée depuis l'austénite γ fcc par des combinaisons de distorsion « stretch », rotation et cisaillement simple.
- La martensite α' est bcc dans les aciers à faible carbone (<0.2-0.5%) et bct (tétragonale centrée) pour des concentrations de carbone plus hautes. La martensite est une forme de ferrite α-Fe sursaturée en carbone.
- La relation d'orientation fcc-bcc est généralement Kurdjumov-Sachs KW, (ou NW).
- Un autre type de martensite, hcp, notée ε , existe dans les aciers à haut taux de Ni ou Mn. La plus faible énergie de faute d'empilement semble en être la raison.

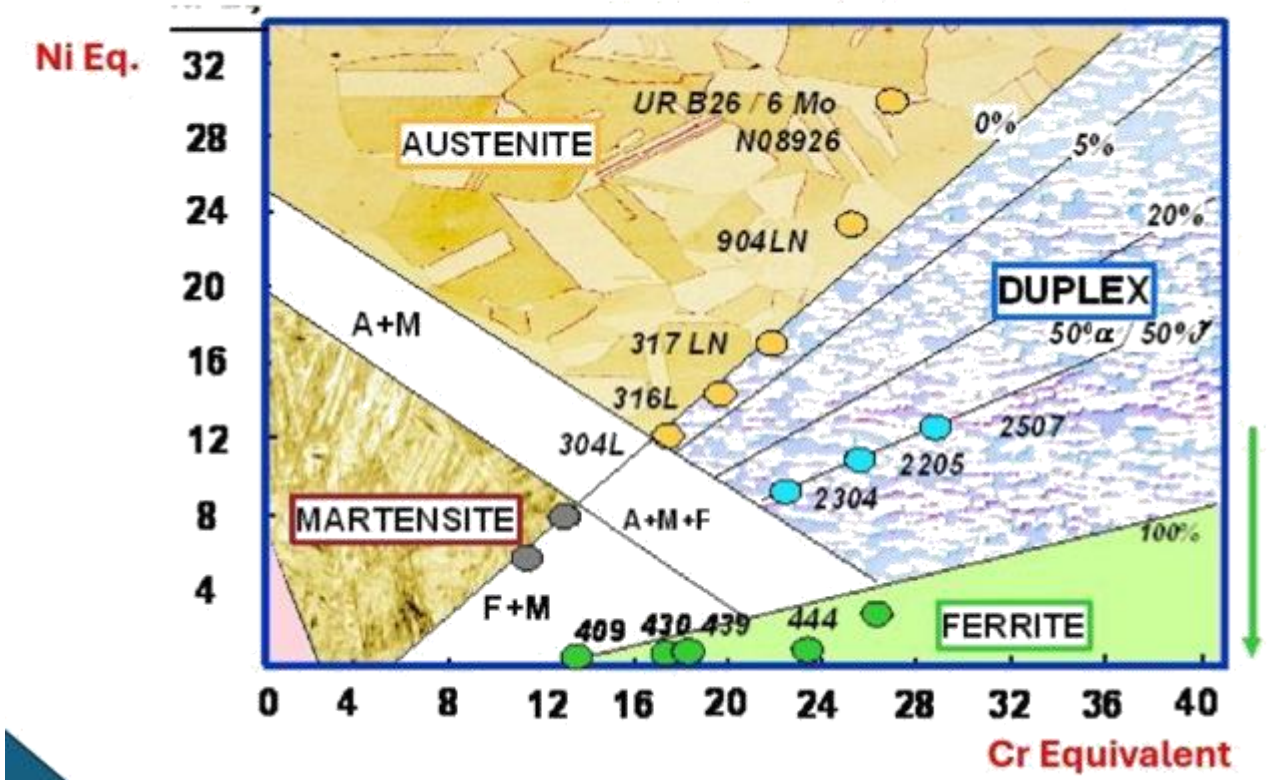
Strech distortion: Bain



Shape distortion: invariant plane strain



Schaeffler diagram

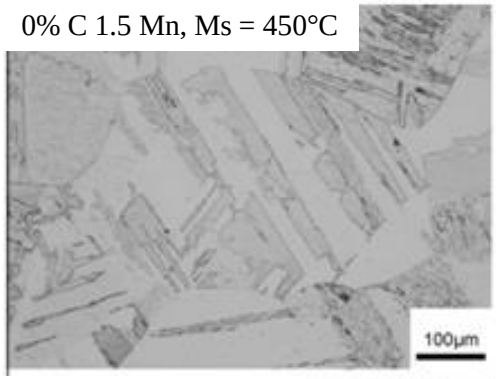


Consitution Diagram

Schaeffler Diagram (1949)	$Cr_{eq} = Cr + Mo + 1.5xSi + 0.5xNb$
	$Ni_{eq} = Ni + 30xC + 0.5xMn$
DeLong Diagram (1973)	$Cr_{eq} = Cr + Mo + 1.5xSi + 0.5xNb$
	$Ni_{eq} = Ni + 30xC + 30xN + 0.5xMn$
WRC-92 Diagram (1992)	$Cr_{eq} = Cr + Mo + 0.7xNb$
	$Ni_{eq} = Ni + 35xC + 20xN + 0.25xCu$

2. Martensite dans les aciers

100% Lath martensite



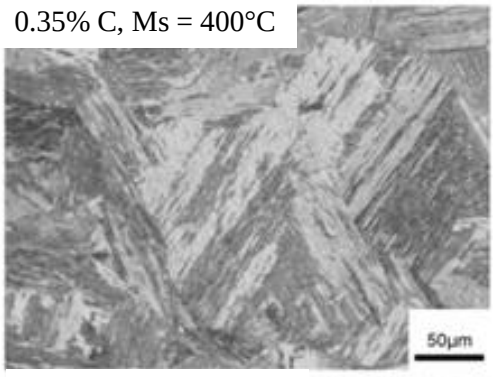
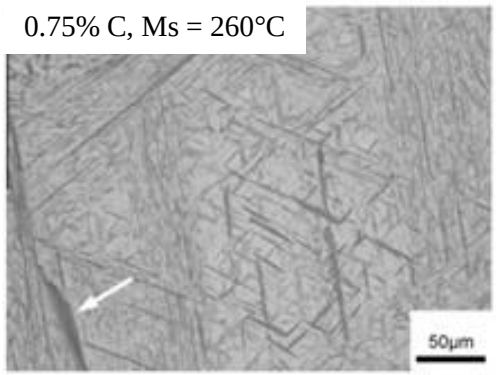
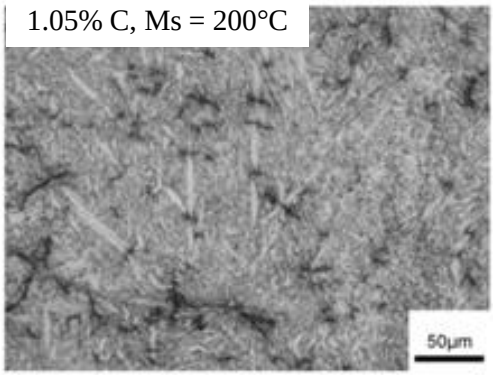
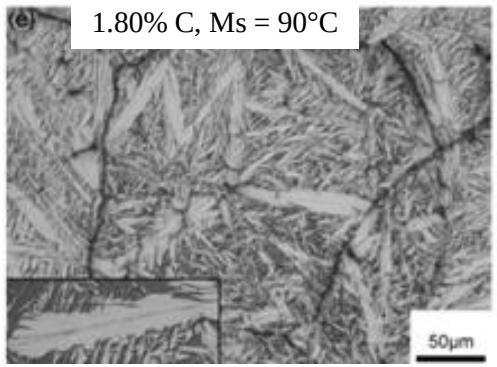


Plate martensite + Retained austenite

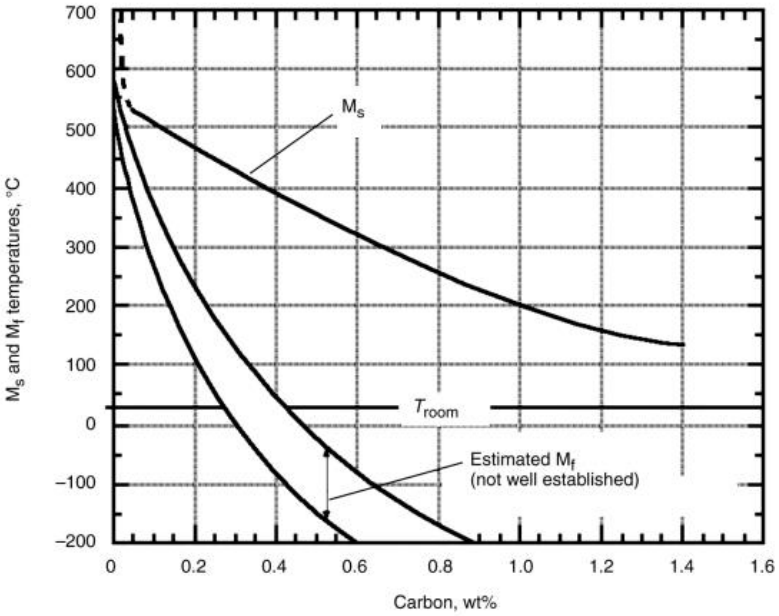




Lenticular martensite + Austenite



Effect of the carbon content



From Stormvinter, 2012

Plus l'acier est riche en carbone plus basses sont T_0 et Ms (l'austenite est stabilisée par le carbone). A faible température de transformation, la distorsion de réseau est plus difficile à accommoder par dislocations, la martensite prend des formes lenticulaires et est constituée de deux variants d'orientation (macle de transformation). Cette constitution à deux variants est trop fine pour être visible en optique ou au SEM (quelques nm); seul le TEM permet de l'observer.

2. Martensite dans les aciers

Les différentes morphologies de martensite

Fig. 5—Typical plate martensite found in an Fe-13.9 Mn alloy. (*a*) Magnification 1000 times. (*b*) Magnification 1250 times. Etched with 3 g potassium meta-bisulfite and 10 g sodium thiosulfate in 100 ml water.[56]

The Morphology of Martensite in Iron Alloys, Krauss, Marder, Metall. Trans. 1971

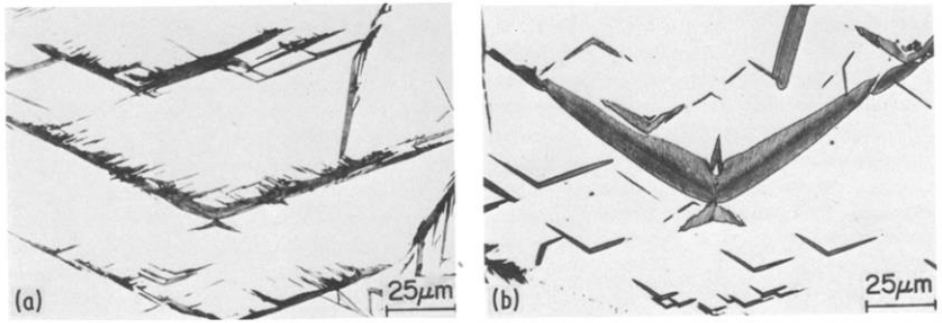


Figure 4 Optical micrograph showing type B butterfly martensites observed (a) in an Fe–1.42C alloy cooled to 373 K and (b) in an Fe–18Ni–0.7Cr–0.50C alloy cooled to 263 K.

Umemoto et al. The morphology of martensite in Fe-C, Fe-Ni-C and Fe-Cr-C alloys, J. Mater. Sci. 1983

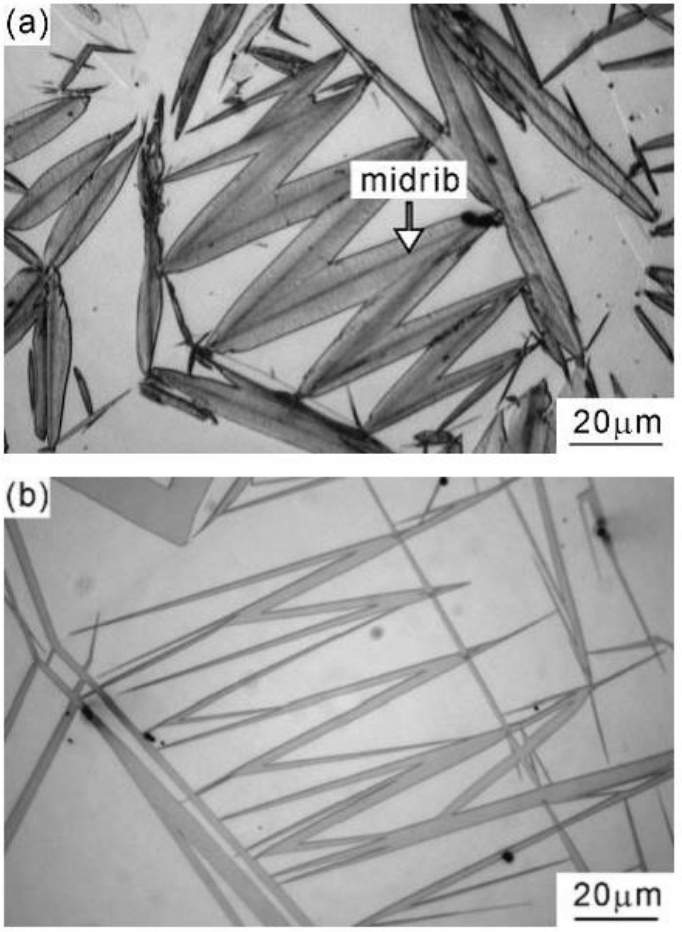
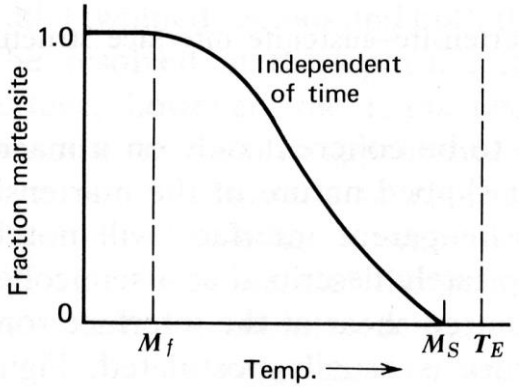


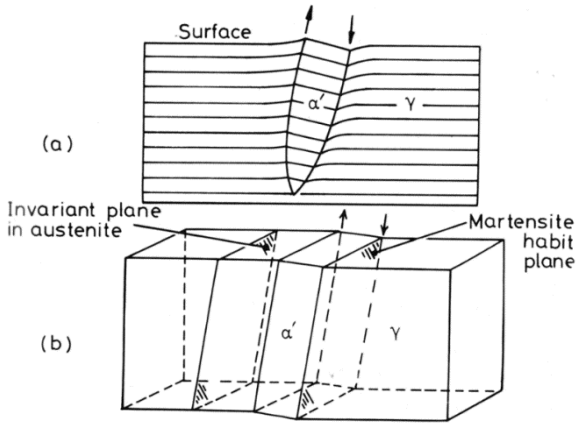
Fig. 1 Optical micrographs showing (a) lenticular martensite in Fe-29Ni-0.2C (Ms = 198 K), (b) thin plate martensite in Fe-31Ni-10Co-3Ti (Ms = 83 K), respectively.

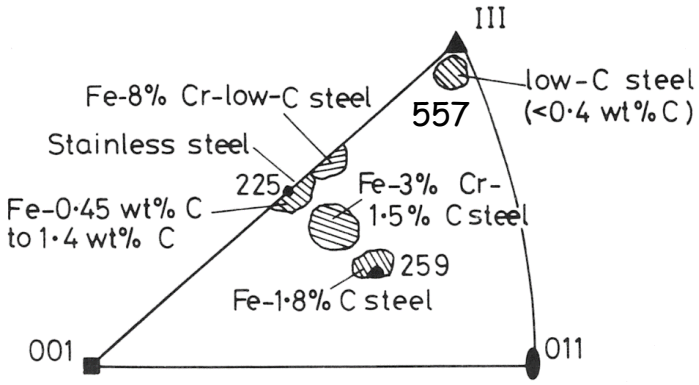
The Origin of Midrib in Lenticular Martensite, Shibata et al. Mater. Trans. 2008

2. Martensite dans les aciers

- La martensite est le plus souvent **athermale** (sa fraction depend de la temperature, sous Ms, mais pas du temps). La martensite isothermale est cependant observée dans quelques aciers.
- Le plan d'habitat (***habit plane***) entre l'austénite et la martensite est souvent irrationnel.







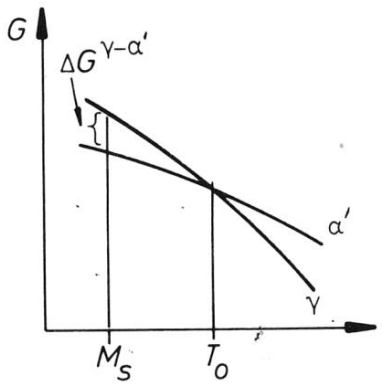
- Les éléments peuvent être classés en
  - Gamma-gène: **Ni**, C, N, Mn, Cu
  - Alpha-gène: **Cr**, Mo, Co, Al, W
- La plupart des éléments baisseT_0 et M_s sauf Co et Al:

M_s [°C] = 550 – 350C – 40Mn – 17Ni – 8W – 10(2Cr + Mo + Cu) + 15Co + 30 Al (wt-%).

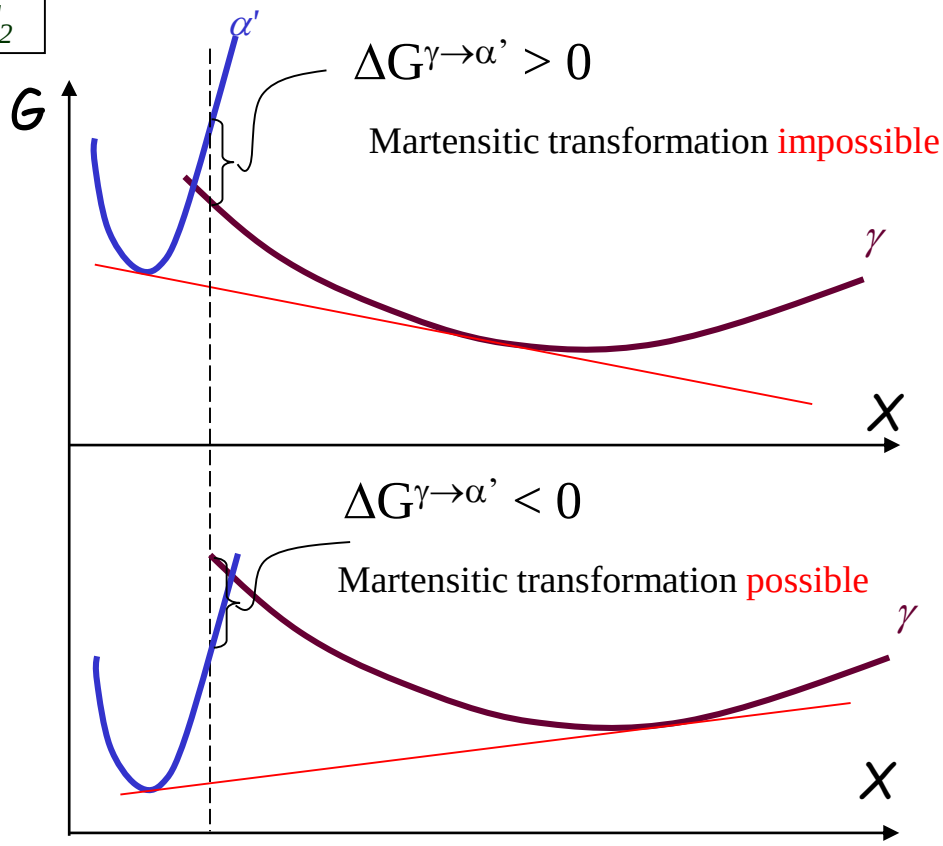
2. Martensite dans les aciers

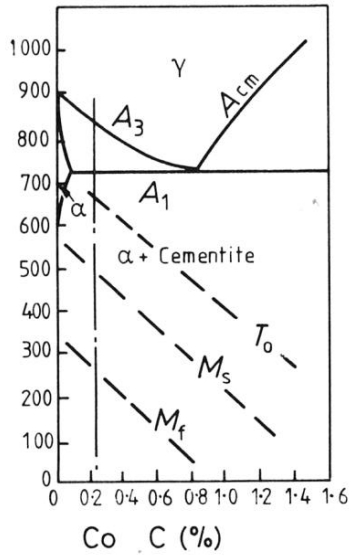
T_0 est la température pour laquelle les énergies de Gibbs de l'austénite et de la martensite sont égales.

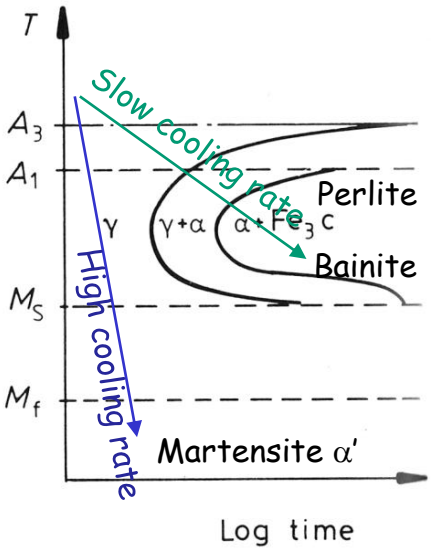
$M_s < T_0$ car une réserve d'énergie chimique est requise pour créer les dislocations requises pour accommoder la distorsion de réseau.



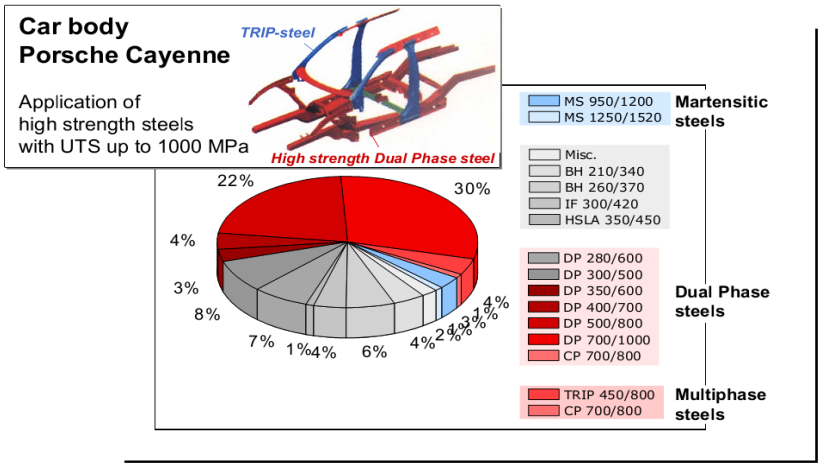
$T_1 > T_0 > T_2$



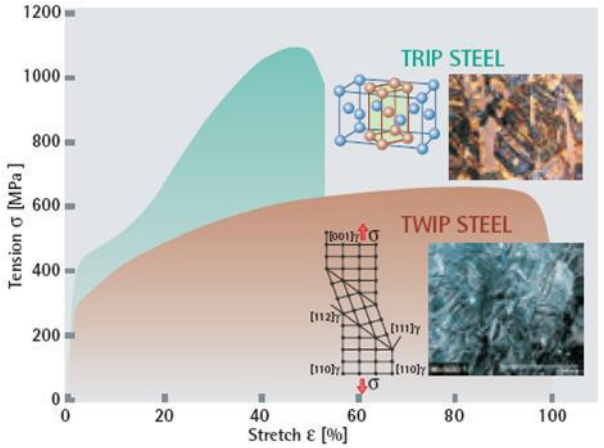




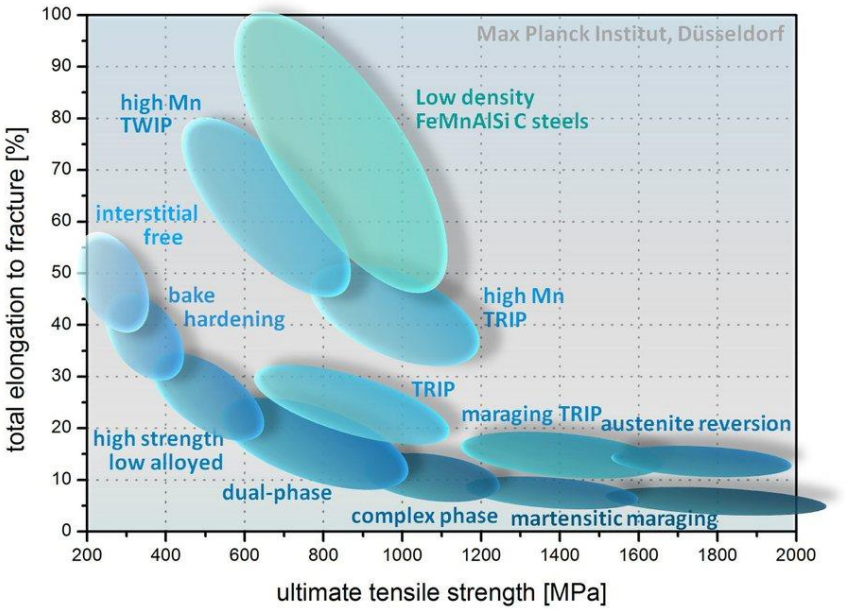
2. Martensite dans les aciers



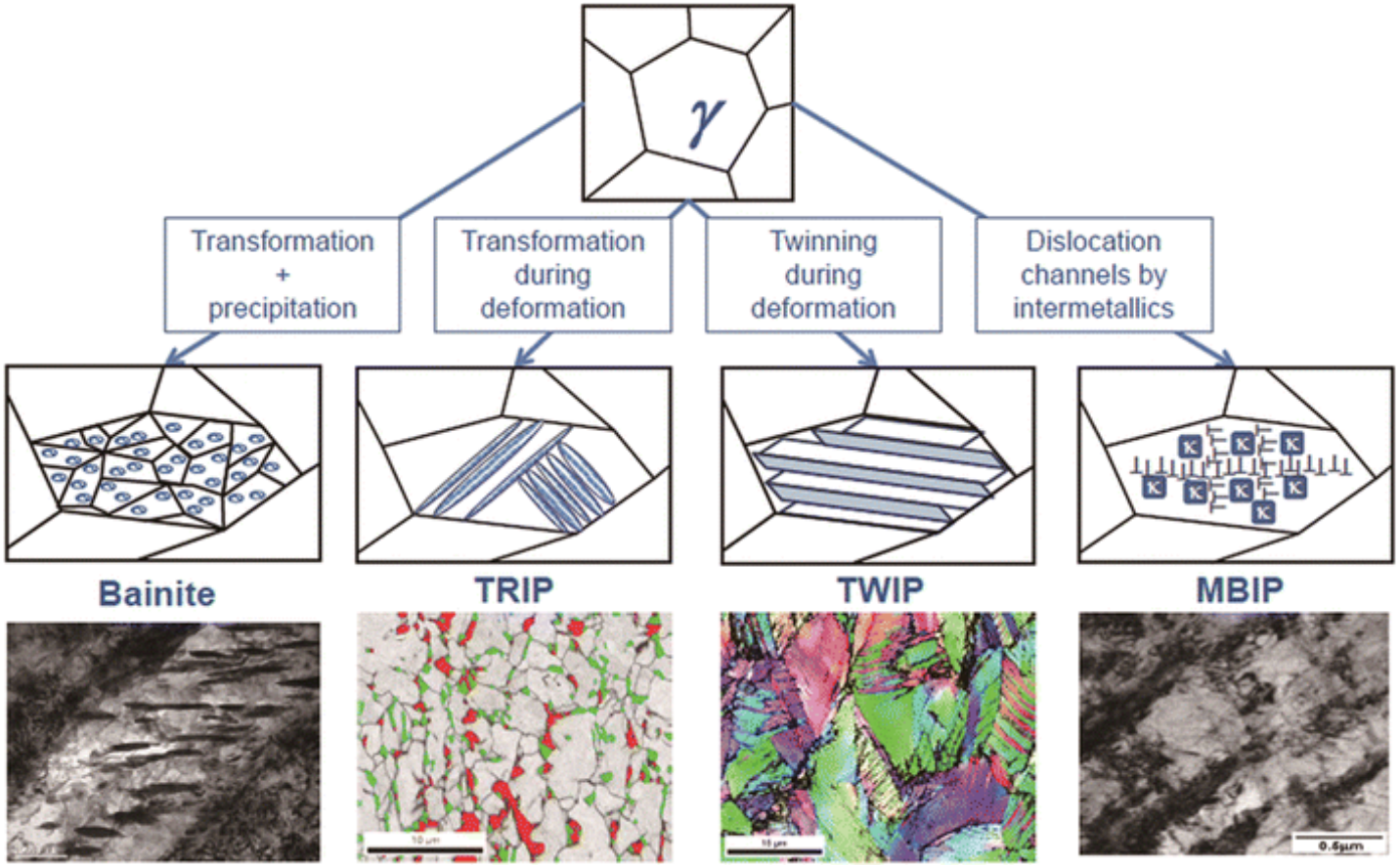
Fraction of different steel grades in a car body (Porsche Cayenne)



The façade of the Capital Gate in Abu Dhabi was constructed by Waagner-Biro Stahlbau AG with GRAITEC Advance Steel, the 3D-Software for steel constructions



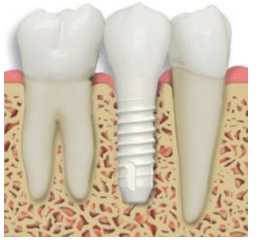
2. Martensite dans les aciers

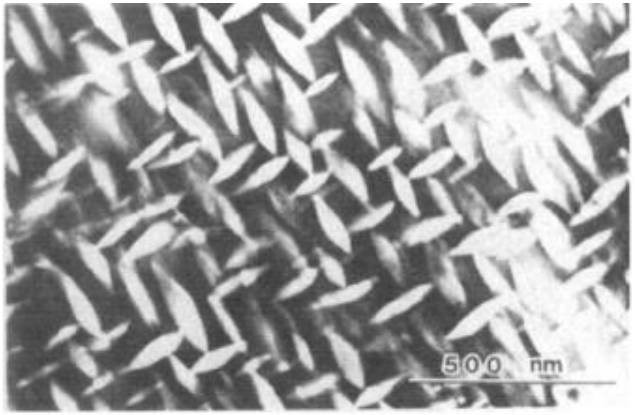


TRIP Transformation induced plasticity ($\gamma \rightarrow \alpha'$ and/or ε)
TWIP Twinning induced plasticity ($\gamma \rightarrow \gamma$-twin)
MBIP Microband-induced plasticity ($\gamma \rightarrow \gamma$ + shear bands)

3. Martensite dans les céramiques

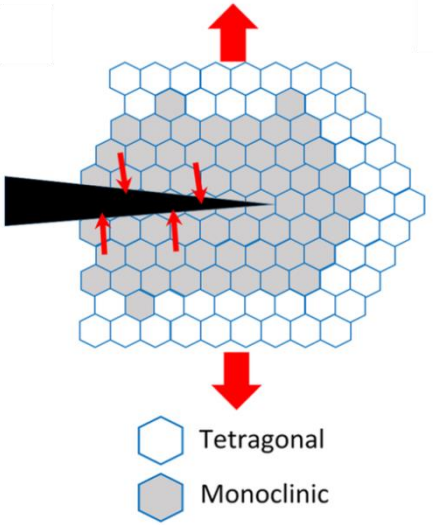
Certaines céramiques présentent une transformation martensitique; c'est le cas par exemple de la zircone (ZrO_2) partiellement stabilisée (PSZ) par ajout d'autres oxydes comme CaO, MgO, ou Y_2O_3

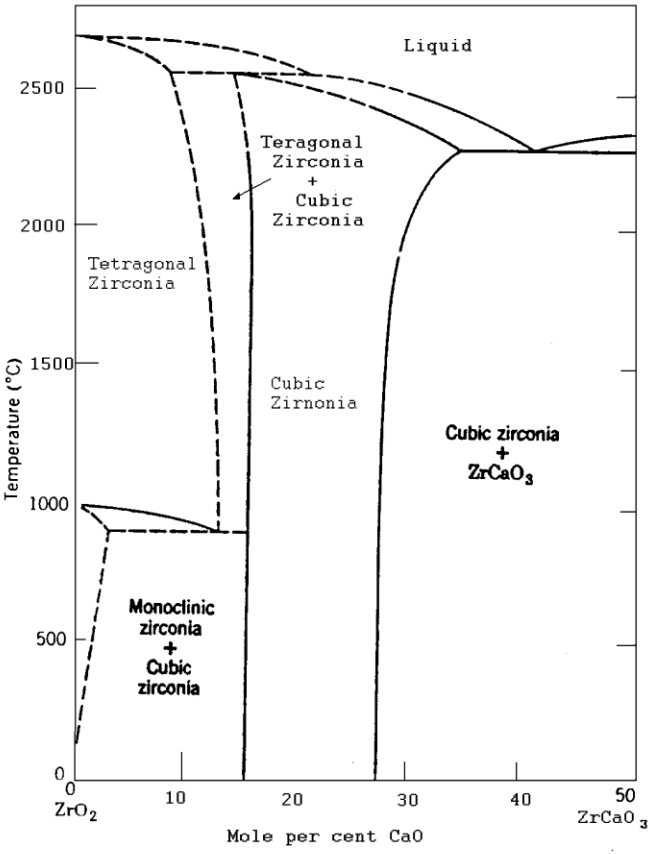




A.G. Evans and R.M. Cannon, Acta Metal. **34** (1986) 761

P. Palmero et al. Materials **2014**, *7*(7), 5012-5037





Les transformations au refroidissement dans ZrO_2-Y_2O_3 sont $cubique \rightarrow tétragonal \rightarrow monoclinique$.

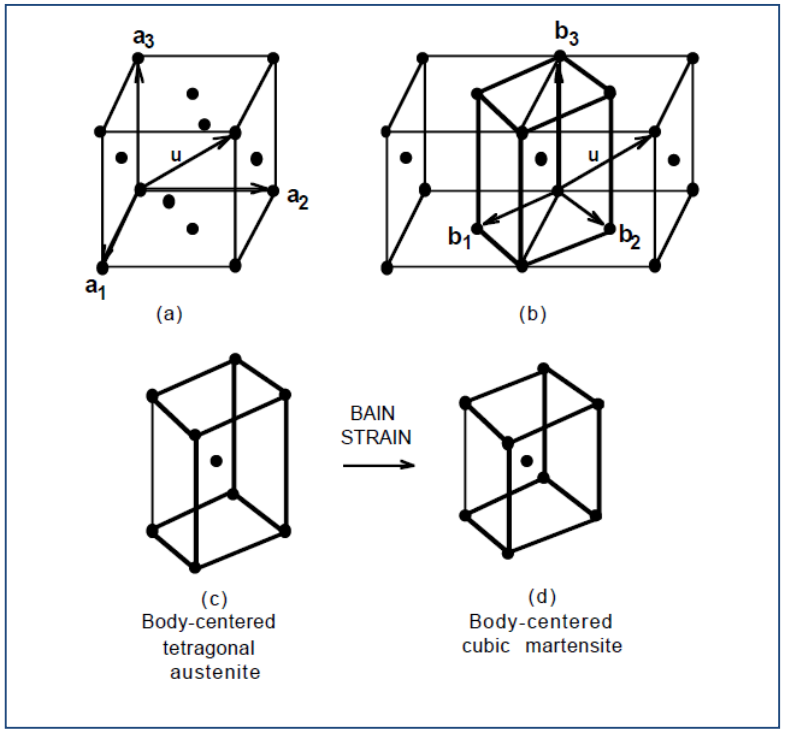
Cette série de transformations permet de dissiper l'énergie en point de fissure et donc de ralentir/bloquer sa propagation. De plus, le changement de volume a tendance a « boucher » la fissure.

4. Phenomenological Theory of Martensite Crystallography

Born with fcc → bcc martensite (in steels)
Bain 1924; Greninger & Troiano 1949

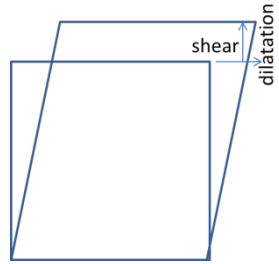
Version 1: Bowles & Mackenzie 1954

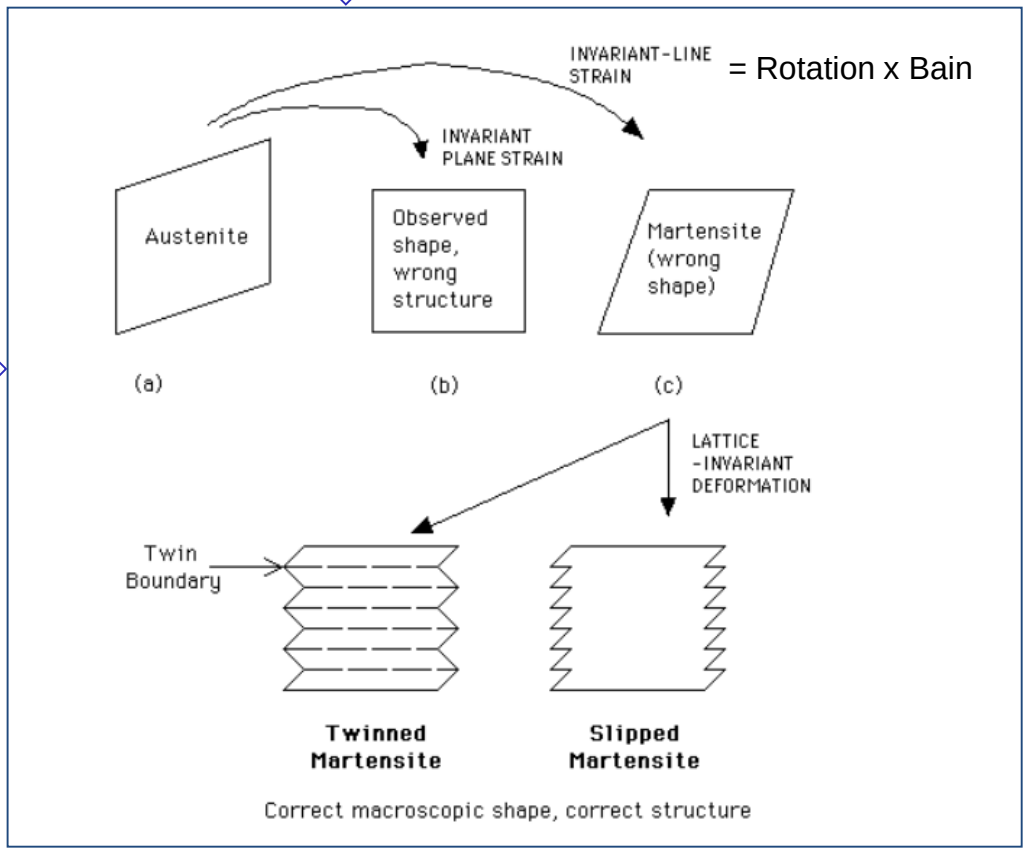
Bain distortion (from crystallography)



From HKDH Bhadeshia

Invariant plane strain
IPS (from morphology)





4. PTMC

The Bain strain **B** converts the structure of the parent phase into that of the product; although it achieves the correct lattice, the Bain strain does not give the correct orientation relationship nor does it ensure a glissile interface. When combined with an appropriate rigid body rotation **R**, the net homogeneous lattice deformation **RB** is an invariant–line strain (step a to c in Fig. 3). However, the observed shape deformation is an invariant–plane strain $\mathbf{P_1}$ (step a to b in Fig. 3), but this gives the wrong crystal structure. If, however, a second homogeneous shear $\mathbf{P_2}$ is combined with $\mathbf{P_1}$ (step b to c), then the correct structure is obtained but the wrong shape since

$$\mathbf{P_1 P_2 = RB}$$

These discrepancies are all resolved if the shape changing effect of $\mathbf{P_2}$ is cancelled macroscopically by an inhomogeneous lattice–invariant deformation, which may be slip or twinning as illustrated in Fig. 3.

My criticisms

PTMC

- The PTMC starts by the end (the versatile shapes and HPs).
- It was and still is phenomenological (how do the atoms move?).

B

- Bain OR nearly never observed.

R

- Rigid body rotation = free parameter
- No physical meaning. Is like the remainder of a division.

P_1

- It brings the fcc/bcc volume change
- It is an average lattice distortion (see version 2).
- The habit plane depends too much on the alloy and martensite morphology

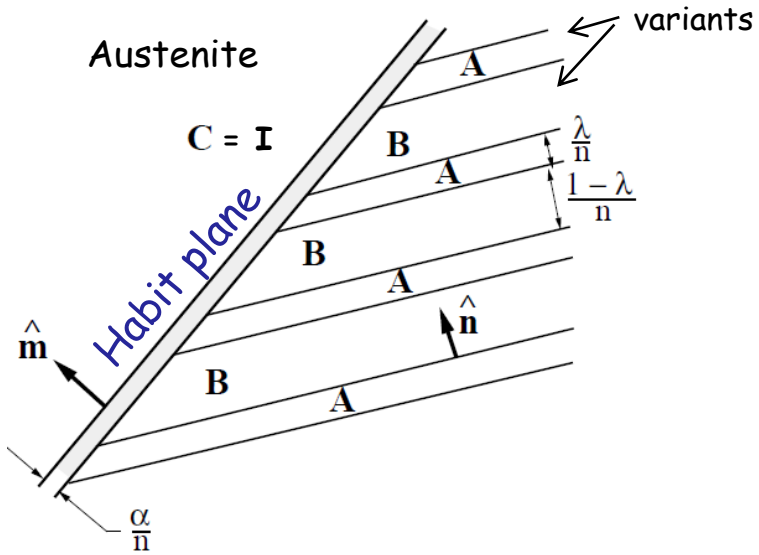
P_2

- Physically ok: Slip by dislocations or nanotwins.
- Two many degrees of freedom.
- Multiple shear mode required to explain some habit planes.

Version 2: Wechsler, Lieberman & Read 1953

Mathematically equivalent to version 1

"Modern" mathematized form:
Ball & James, Pitteri, Zanzotto, Bhattacharya

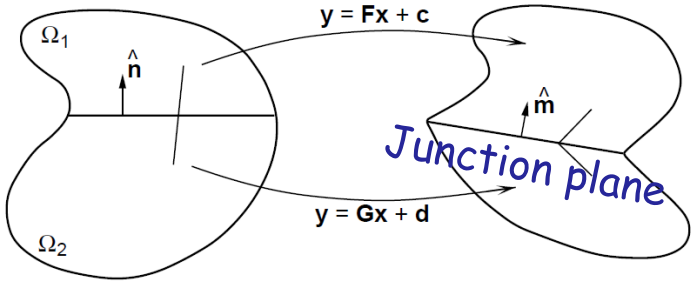


$$\lambda \mathbf{F}_A + (1-\lambda)\mathbf{F}_B = \mathbf{IPS}$$

with $\mathbf{F}_A$ and $\mathbf{F}_B$ two distortion variants

The volume change should be conserved: $\det(\mathbf{F}_A) = \det(\mathbf{F}_B) = \det(\mathbf{IPS})$

Compatibility condition:



The interface plane (n) between the two variants is distorted similarly by **F** and **G**, **F** and **G** are said rank-one connected:

$$\mathbf{F}_A - \mathbf{F}_B = \boldsymbol{a} \otimes \boldsymbol{n}$$

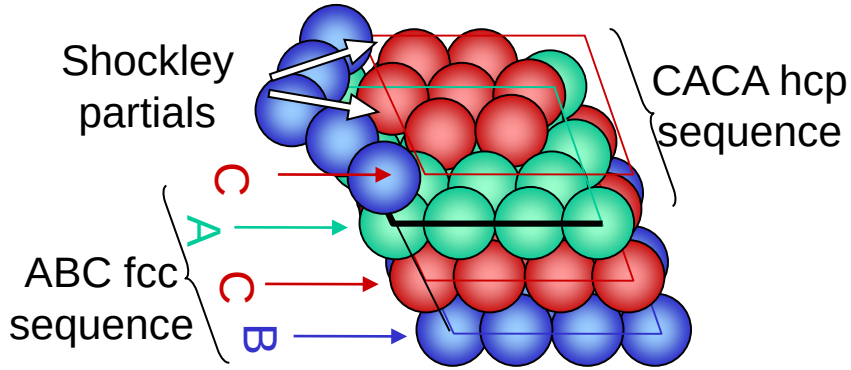
The junction planes between the variants (called twins) and the habit planes can be calculated only from the lattices parameters of the parent and daughter phases

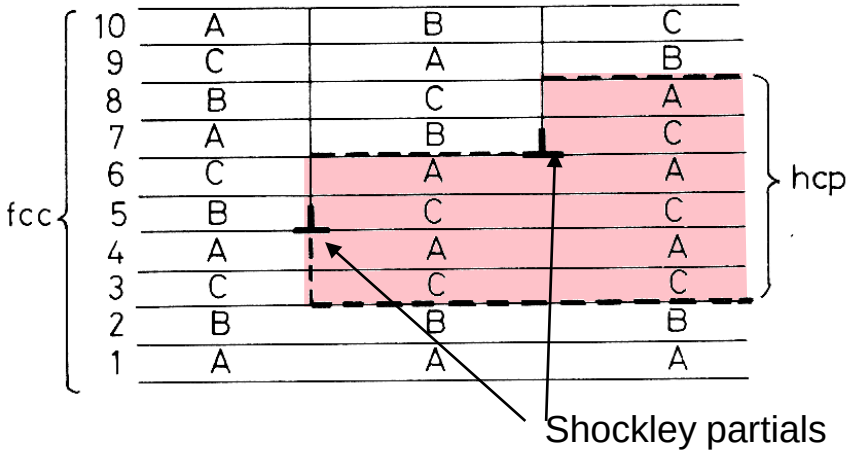
5. Dislocation models

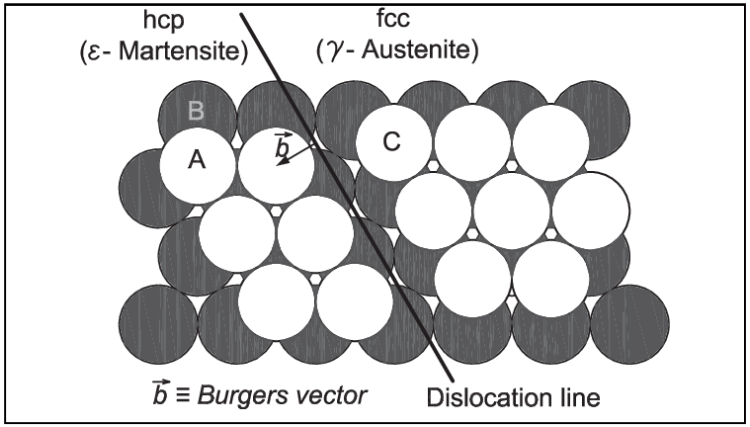
PTMC does not explain how martensite is formed from austenite at the atomic level. Thus, researchers have tried to develop alternative models over the last 40 years.

Dislocation/disconnection models

A simple case: the fcc-hcp transformation in Co
This case of martensitic transformation looks very much like deformation twinning. Considering (111) planes of the fcc structure of Co, transformation into the hcp phase and semi-coherent interfaces between the fcc and hcp phase can be obtained with **regular sequences of partial Shockley** dislocations introduced every two planes.







5. Dislocation models

There are probably more than 500 papers that use it in association with molecular dynamic simulations, but nobody could reply to this simple question:
Where do the dislocations come from ?

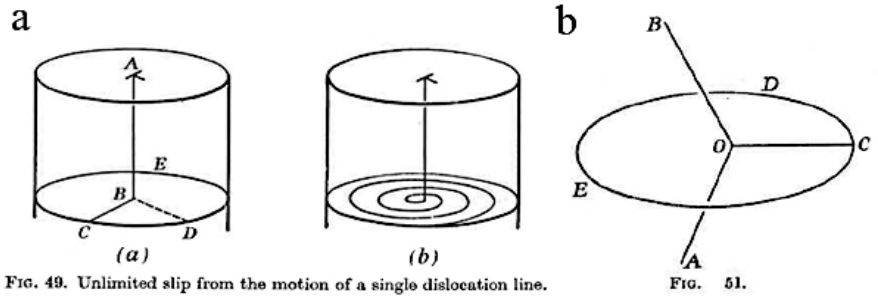
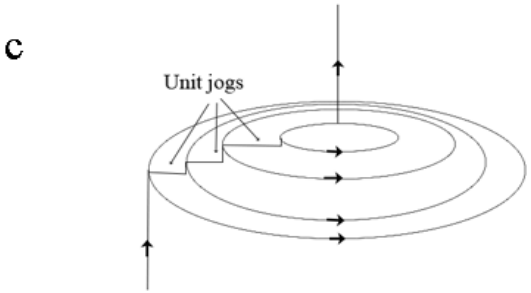


FIG. 49. Unlimited slip from the motion of a single dislocation line.

FIG. 51.



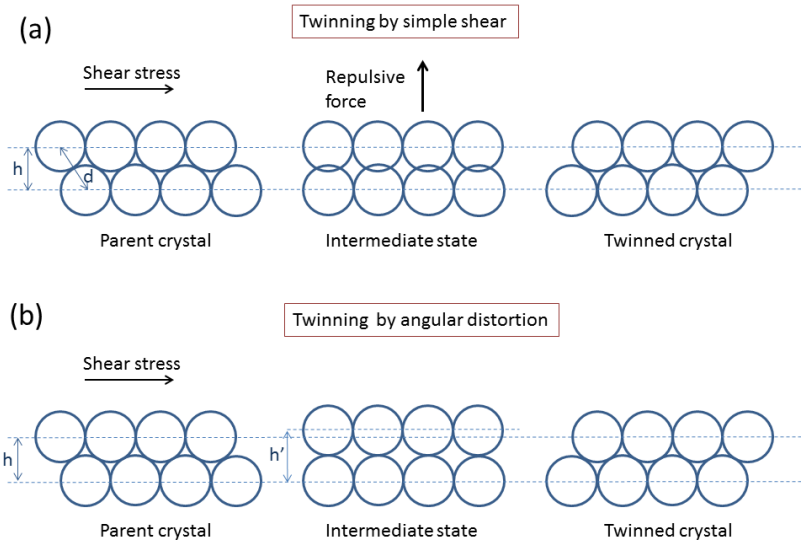
Schematic representation of twinning dislocations and **pole mechanism**.
(a) A early model made by Frank and Read explains the dislocation "multiplication" in a crystal, from Cottrell's book.
(b) This model was used by Cottrell to explain how dislocations can build twins.
(c) Scheme of the pole mechanism proposed by Venables.

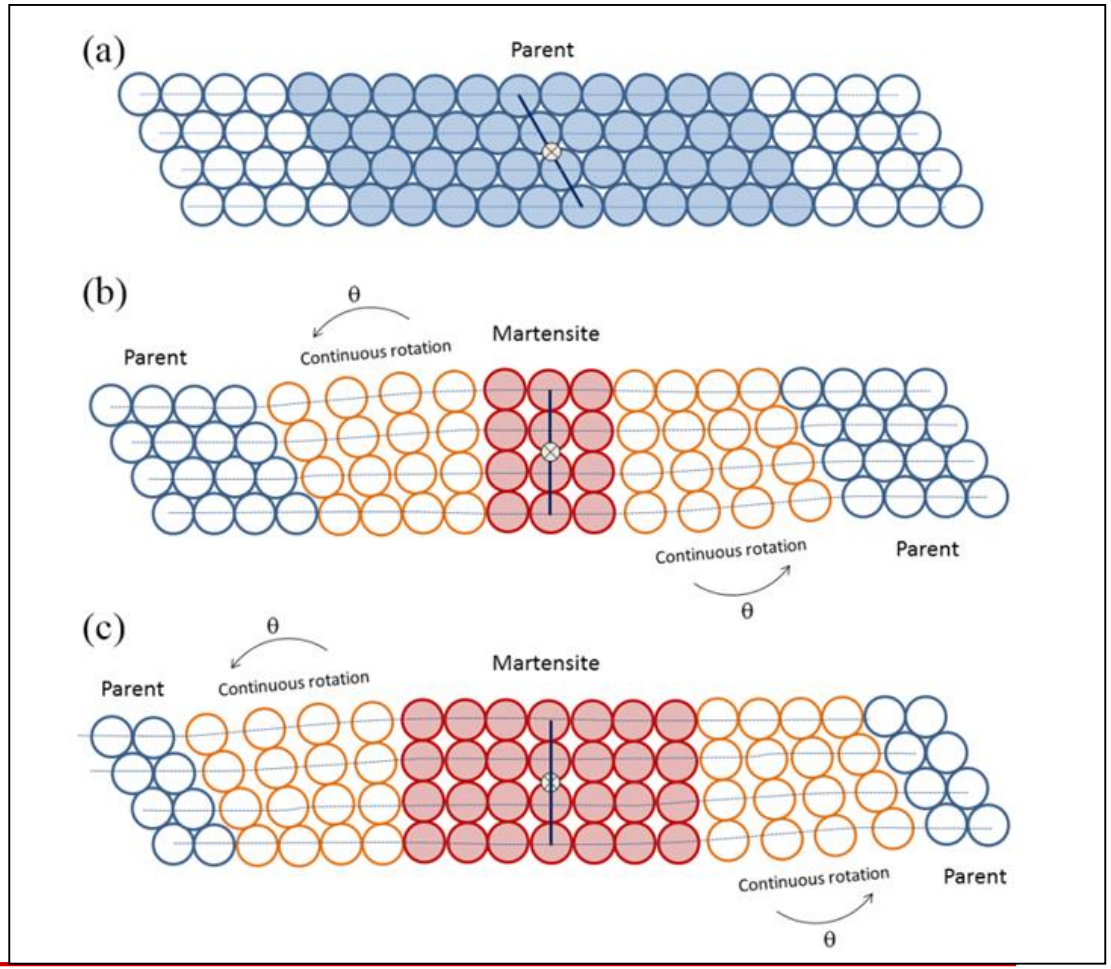
After more 50 years of TEM, **pole sources have never been observed**.
It seems that nowadays, we all agree to say that they do not exist

5. Alternative approach

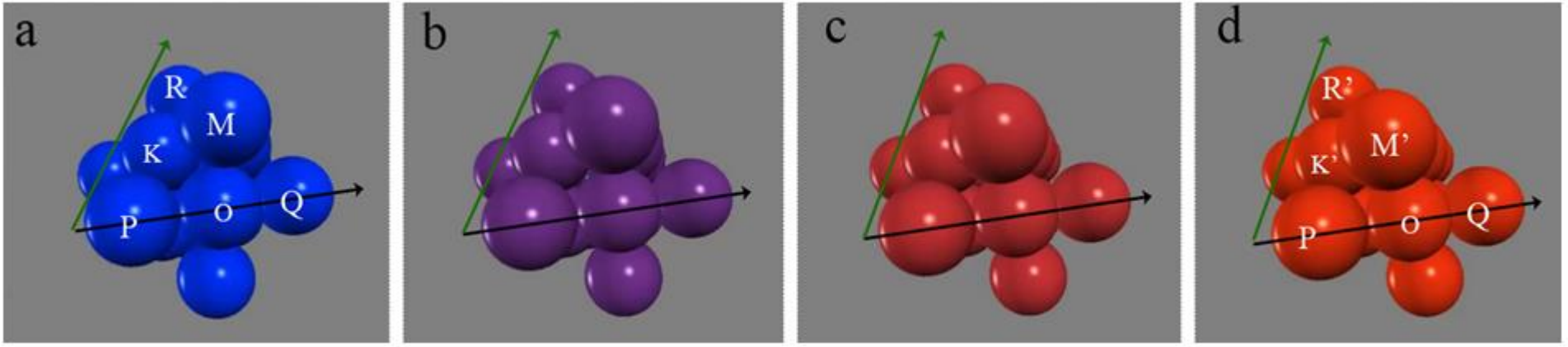
I propose a shift of paradigm: angular distortion instead of shear

My point of view: Dislocations are just accommodation defects generated by the formation of martensite in the surrounding austenite; they are not intrinsically essential to the transformation. In small free crystals, the transformation can be imagined without dislocation.





5. Alternative approach



Fcc-bcc distortion with KS OR with hard-spheres. The continuity is given by the angle between two dense directions, β = (PO, PK) that changes from 60° (fcc) , X = cos(β) = ½, to 70.5° (bcc), X = 1/3. C. Cayron Acta Mater. 96 (2015) 189–202. Movie at http://lmtm.epfl.ch/research.

Continuous fcc to bcc distortion matrix:

$$F^{\gamma}(\beta) = \begin{pmatrix} \frac{1}{\sqrt{6}}\sqrt{\frac{1-X}{1+X}}\left(\sqrt{2}X+2\sqrt{X}\right)+X & 1-X-\frac{1}{\sqrt{6}}\sqrt{\frac{1-X}{1+X}}\left(\sqrt{2}X+2\sqrt{X}\right) & \sqrt{\frac{1-X^2}{3}}-\frac{1}{\sqrt{6}}\sqrt{\frac{1-X}{1+X}}\left(\sqrt{2}X+2\sqrt{X}\right) \\ -\frac{1}{\sqrt{6}}\sqrt{\frac{1-X}{1+X}}\left(\sqrt{2}X+2\sqrt{X}\right)+X & 1-X+\frac{1}{\sqrt{6}}\sqrt{\frac{1-X}{1+X}}\left(\sqrt{2}X+2\sqrt{X}\right) & -\sqrt{\frac{1-X^2}{3}}+\frac{1}{\sqrt{6}}\sqrt{\frac{1-X}{1+X}}\left(\sqrt{2}X+2\sqrt{X}\right) \\ \frac{2}{\sqrt{6}}\sqrt{\frac{1-X}{1+X}}\left(\sqrt{2}X-\sqrt{X}\right) & -\frac{2}{\sqrt{6}}\sqrt{\frac{1-X}{1+X}}\left(\sqrt{2}X-\sqrt{X}\right) & 2\sqrt{\frac{1-X^2}{3}}-\frac{2}{\sqrt{6}}\sqrt{\frac{1-X}{1+X}}\left(\sqrt{2}X-\sqrt{X}\right) \end{pmatrix} \quad with\ X = Cos\beta$$

5. Alternative approach

Atomistic model of formation of the {225} habit planes in high carbon martensitic steels

A. Baur, C. Cayron, R. Logé, Scientific Reports (2017)

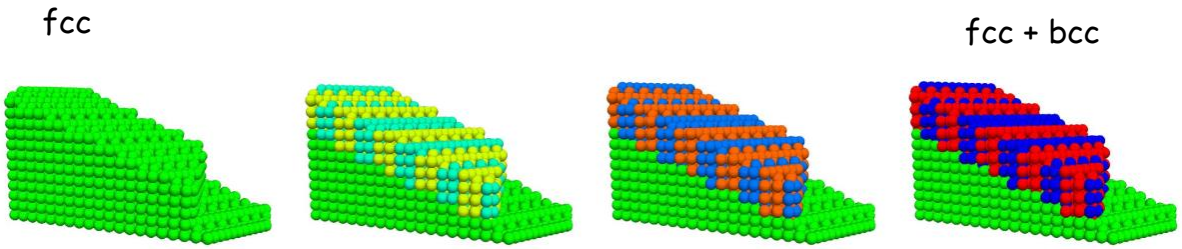
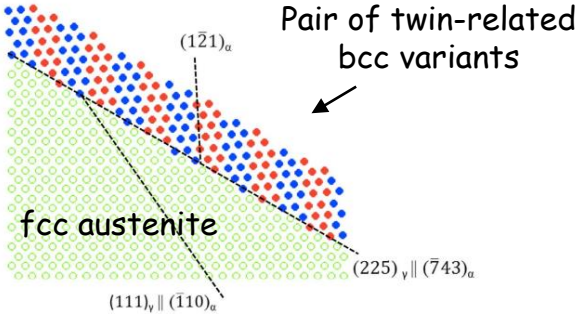
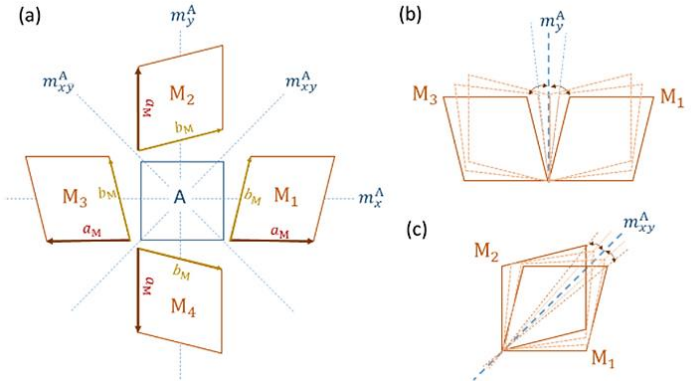


Figure 4. Snapshots of the $(225)_\gamma$ thin plate formation. Green dots: iron atoms in austenite. Blue and red dots: iron atoms in martensitic twin-related variants α_1 and α_3.



Prediction of the junction planes and habit planes in NiTi from correspondence and symmetries



C. Cayron, Crystals 12 (2022) 130.

The twin relations that links the variants are symmetry elements of the parent phase. They can be directly (with the complex machinery of PTMC) calculated by considering the inter-correspondence between the variants.

Summary

- Martensite transformation most generally imply a **lattice distortion** with or without atomic **shuffles**.
- In ideal pure shuffle transformations, there is no lattice distortion.
- The **mysteries of martensite**: what are the atomic displacements, how to predict the parent-martensite orientation relationship, how to explain the odd habit planes, ?
- The classical Phenomenological Theory of Martensite Crystallography (**PTMC**) tries to solve these questions. It combines the Bain (stretch distortion), an invariant plane strain (that gives the habit plane of martensite), an additional simple shear that can be dislocations or twins, and a “free” rotation. In modern PTMC, the twins are not anymore an input; they result from compatibility conditions between the variants.
- The **dislocation models** assume that partial dislocations can generate the martensite.
- **These theories can be criticised**: PTMC does not explain how the atoms move, and the dislocation theories do not explain where the dislocations come from? It is possible to reverse the approach and assume that the dislocations are the consequence of the lattice distortion and not the cause. This is an axis of research of your teacher.