Shape Memory Alloys

: An Overview & Nanoscale Characteristics

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Current status of Structural Materials

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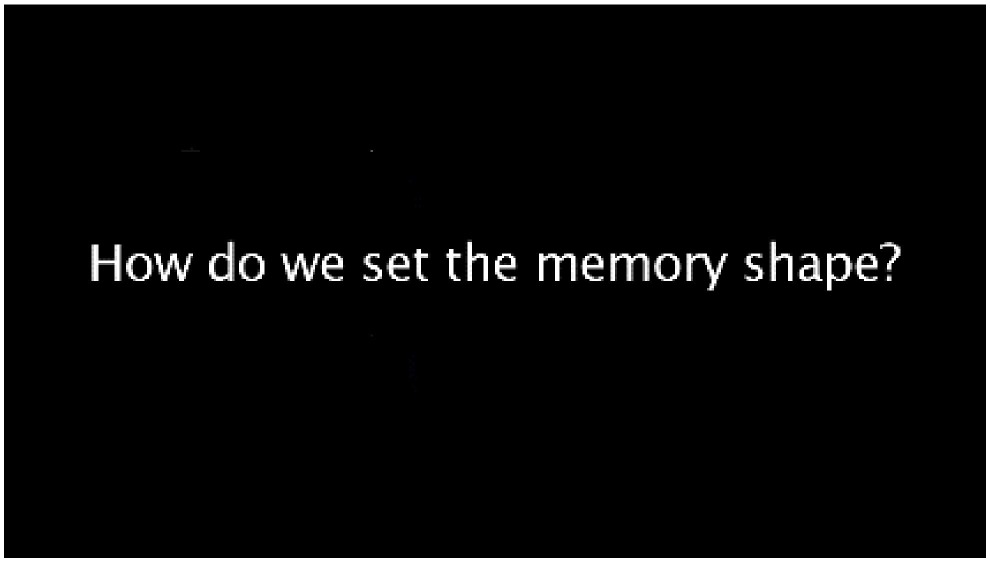
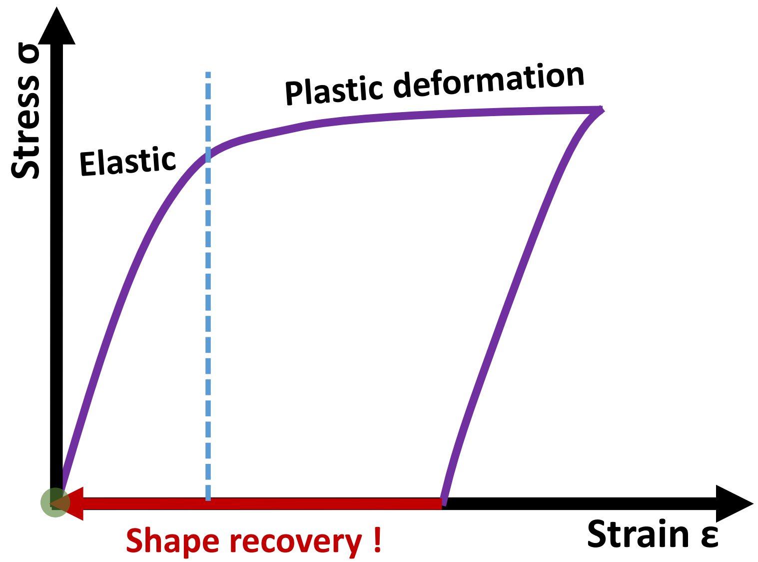
- Shape Memory Alloys
  - Origin of SME : Thermoelastic martensitic transformation
  - Type of SME : one-way / two-way SME
  - Research trend of SMA
    - Alloy design / Orientation effect / Size effect at the nanoscale

Concept of Shape Memory Alloys





High recovery strain through Phase transformation

Origin of SME : Thermoelastic martensitic transformation

Study of reversible martensitic transformation (1949)

Cu-system (1953) → NiTi system (1963)

Martensitic transformation
- **Thermoelastic**
- Non-thermoelastic

▶ Driving force from austenite to martensite

$$\Delta G = \pi r^2 t \Delta g_c + \pi r^2 t A + \pi r^2 t B + 2\pi r^2 \sigma \approx 0$$

- $\pi r^2 t \Delta g_c$: Chemical free energy
- $\pi r^2 t A$: Elastic strain energy
- $\pi r^2 t B$: Plastic strain energy
- $2\pi r^2 \sigma$: Interface energy between A-M

Hiroyasu Funakubo, «Shape Memory Alloys» (1984)

Origin of SME : Thermoelastic martensitic transformation

$$\pi r^2 tB + 2\pi r^2 \sigma \approx 0$$

- $\pi r^2 tB$: **Plastic strain energy**
- $2\pi r^2 \sigma$: **Interface energy between A-M**

✓ good coherency A-M

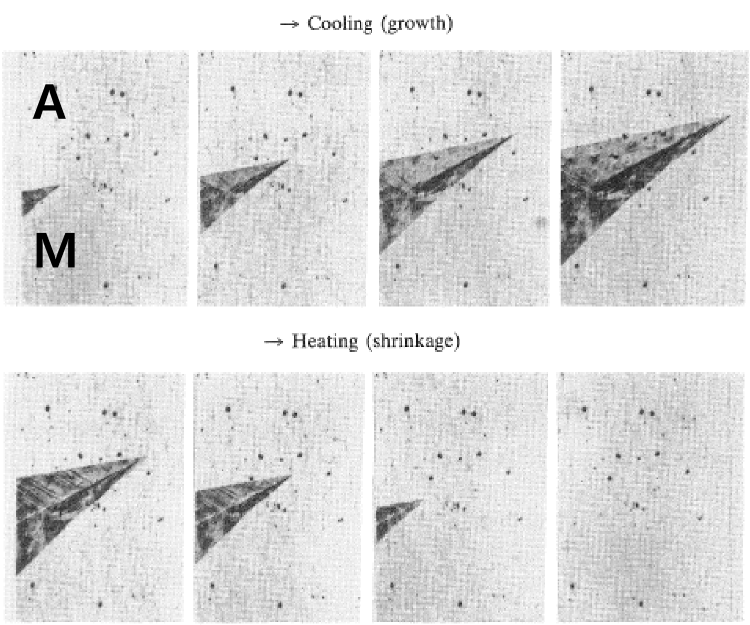
✓ Structural change ↓

✓ volume change ↓

✓ SME : Martensitic transformation and reverse transformation through **specific path with preferred variant**

✓ **Ordered phase** with super-lattice, there is specific path with preferred variant depending on atomic bonding

→ Parent (austenite) has an ordered structure ex. B2, $L2_1$



$$\Delta G = \pi r^2 t \Delta g_c + \pi r^2 t A$$

- **Cooling** : Equilibrium between chemical free energy difference and non chemical (elastic-strain) free energy
- **Heating** : Shrinkage of martensite until equilibrium

Hiroyasu Funakubo, «Shape Memory Alloys» (1984)

Type of Shape Memory Effect

Shape Memory Effect

One-way SME

- **Super-elasticity**

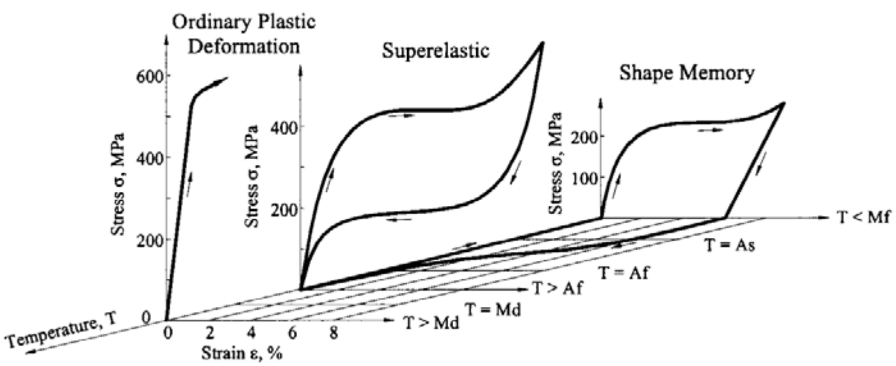
  T > A_f

- **Shape memory effect (Heat treatment)**

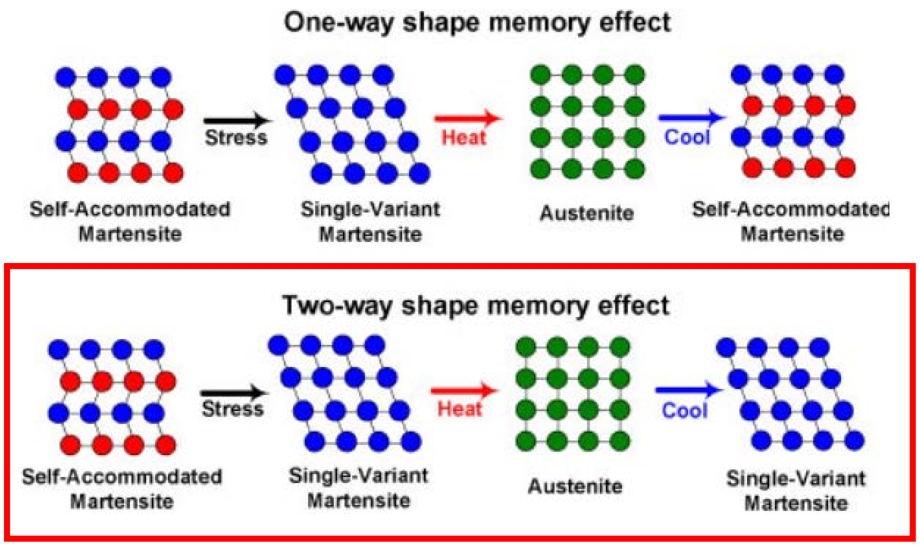
  T < A_f

Two-way SME

- **Shape change through temperature change**

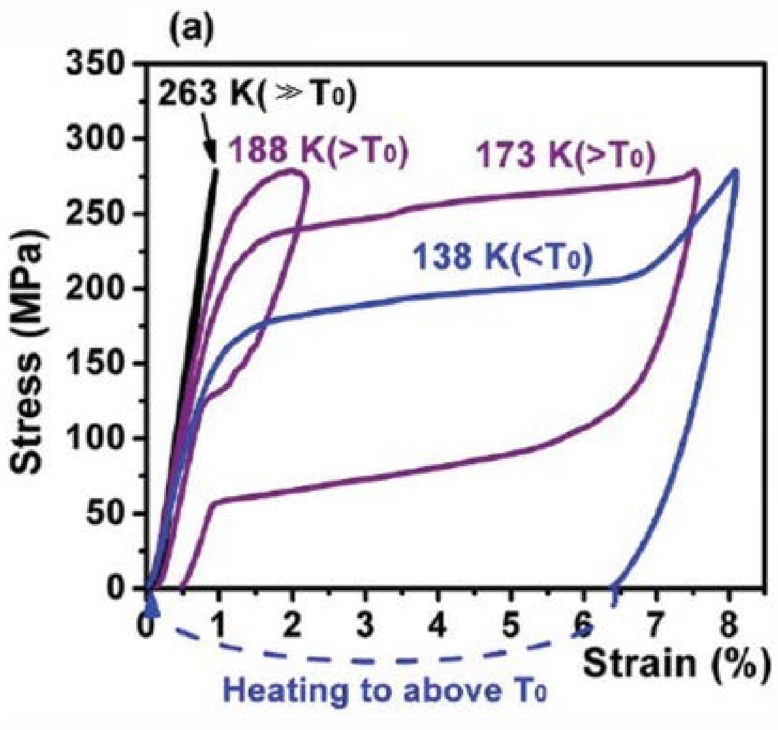


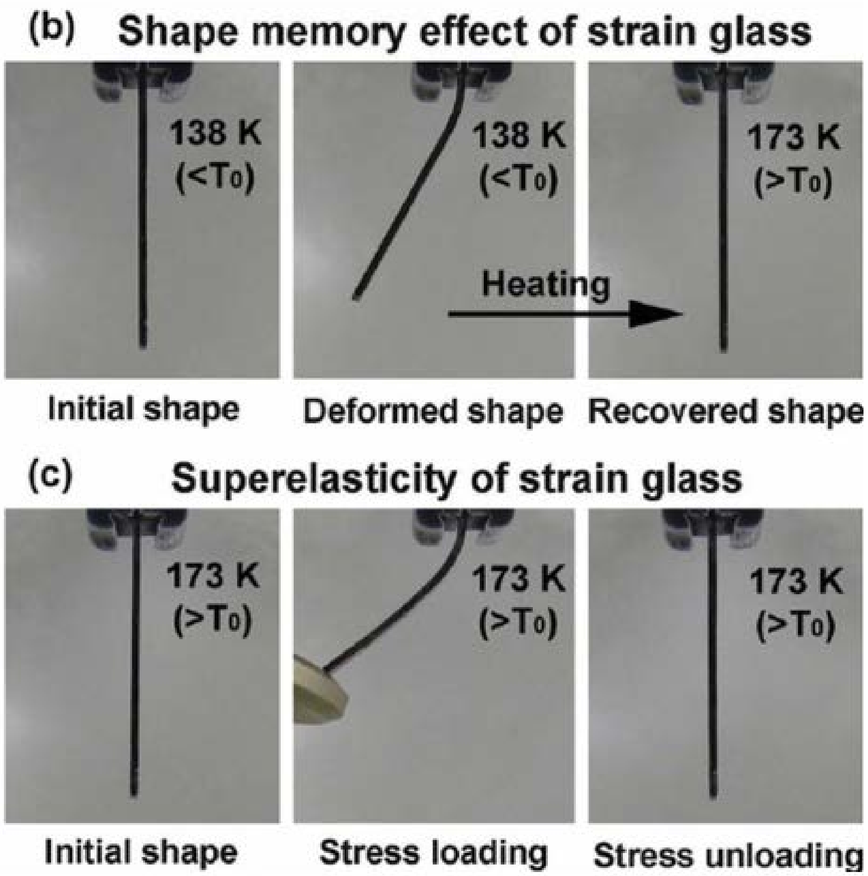
R. DesRoches et al., Journal of structural engineering 130(1) (2004) 38-46.



J Ma, I Karaman & R.D. Noebe, Internatinal Materials Reviews 55 (2010)

One way SME : Super-elasticity & SME of SMA





Yu Wang et al., Physical Review Letters 97 (2006) 225703.

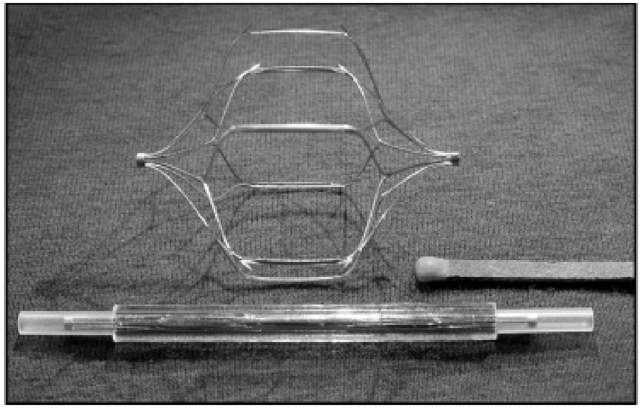
- **Super-elasticity**

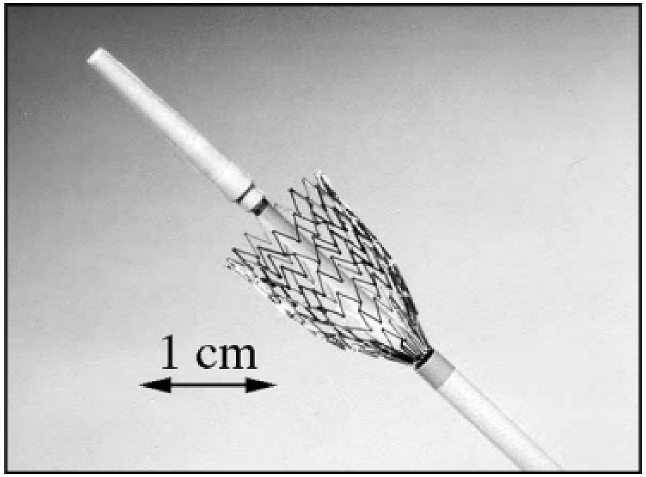
T > A_f

N. Pandis et al., Semianr in Orthodontics 16 (2010) 249-257.

- **Shape Memory Effect**

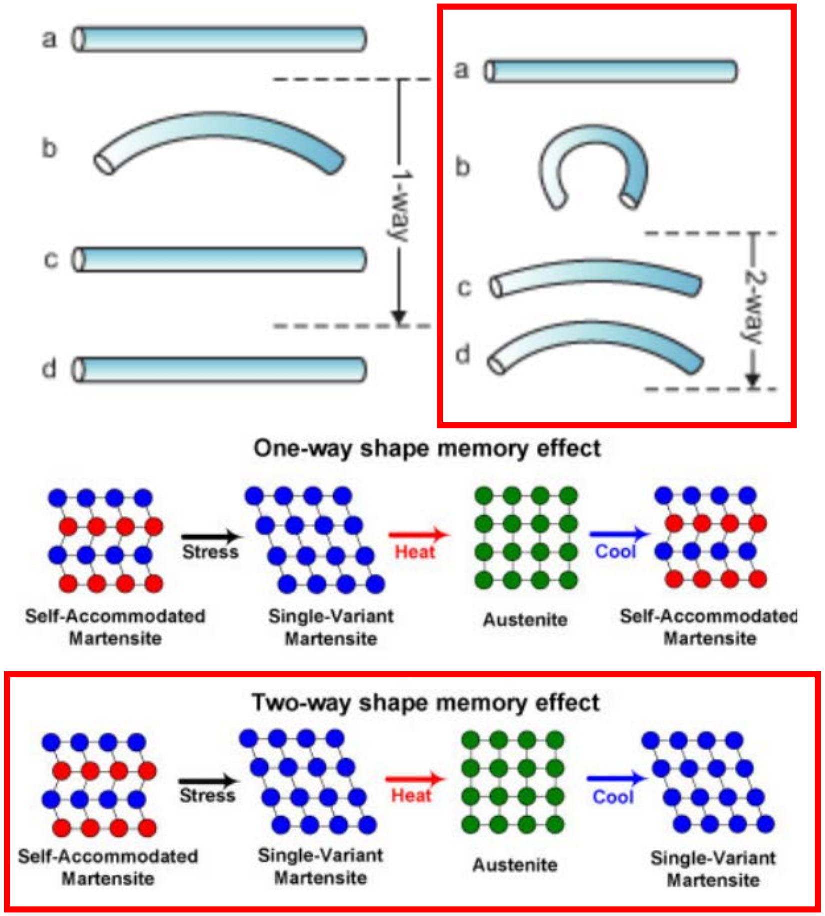
T > A_f





T.W. Duerig, «The use of superelasticity in modern medicine», MRS bulletin (2002)

https://www.youtube.com/watch?v=xhykVMFDULk



J Ma, I Karaman & R.D. Noebe, Internatinal Materials Reviews 55 (2010)

https://en.wikipedia.org/wiki/Shape-memory_alloy

Biomedical application as temperature sensitive sensor / grabber

Research trend to control characteristics of SMA (1) Finding system

- ✓ Thermoelastic Martensitic transformation
- ✓ Ordered phase as parent austenite phase

TABLE I.1
Data for Alloys which Exhibit a Complete SME.

Alloy	Composition	M_s (°C)	Transformation Temperature Hysteresis (°C)	Type of Transformation*	Ordered or Disordered
AgCd	44~49at.%Cd	−190~−50	~15	B2→M2H	ordered
AuCd	46.5~50at.%Cd	30~100	~15	B2→M2H	ordered
CuAlNi	14~14.5wt.%Al 3~4.5wt.%Ni	−140~100	~35	DO_3→2H	ordered
CuAuZn	23~28at.%Au 45~47at.%Zn	−190~40	~ 6	L21→M18R	ordered
CuSn	~15at.%Sn	−120~30		DO_3→2H or18R	ordered
CuZn	38.5~41.5wt.%Zn	−180~−10	~10	B2→9R or M9R	ordered
CuZnX (X=Si, Sn, Al, Ga)	few wt.% ×	−180~100	~10	B2→9R or M9R DO_3→18R or M18R	ordered
InTl	18~23at.%Tl	60~100	~ 4	FCC→FCT	disordered
NiAl	36~38at.%Al	−180~100	~10	B2→M3R	ordered
TiNi	49~51at.%Ni	−50~100	~30	B2→B19	ordered
FePt	~25at.%Pt	~−130	~ 4	$L1_2$→ ordered BCT	ordered
FePd	~30at.%Pd	~−100		FCC→FCT→BCT	disordered
MnCu	5~35at.%Cu	−250~180	~25	FCC→FCT	disordered

* FCT means face centered tetragonal lattice; BCT means body centered tetragonal. For other symbols see section 1

Hiroyasu Funakubo, «Shape Memory Alloys» (1984)

- **Previous approach to control the SMA properties : Alloy design**

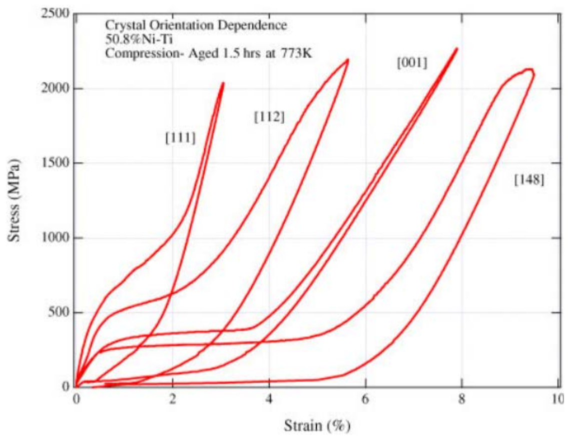
➡ Control the phase stability (austenite)

NiTi Based SMAs	M_f	M_s	A_s	A_f	Reference
$Ti_{50}Ni_{50}$	15	55	80	89	[49]
$Ti_{49.5}Ni_{50.5}$	−78	−19	9	53	[56]
$Ti_{49}Ni_{51}$	−153	−114	−89	−40	[4]
$Ti_{49}Ni_{51}Cu_{10}$	8	30	35	50	[56]
$Ti_{50}Ni_{40}Cu_{10}$	21	41	53	67	[56]
$Ti_{44}Ni_{47}Nb_9$	−175	−90	−85	−35	[45]
$Ti_{42.2}Ni_{49.8}Hf_8$	50	69	111	142	[57]
$Ti_{40.7}Ni_{49.8}Hf_{9.5}$	61	90	118	159	[57]
$Ti_{40.2}Ni_{49.8}Hf_{10}$	103	128	182	198	[57]
$Ti_{35.2}Ni_{49.8}Hf_{15}$	95	136	140	210	[57]
$Ti_{30.2}Ni_{49.8}Hf_{20}$	127	174	200	276	[57]
$Ti_{48}Ni_{47}Zr_5$	20	65	75	138	[58]
$Ti_{43}Ni_{47}Zr_{10}$	45	100	113	165	[58]
$Ti_{38}Ni_{47}Zr_{15}$	100	175	175	230	[58]
$Ti_{33}Ni_{47}Zr_{20}$	205	275	265	330	[58]
$Ti_{50}Pd_{50}$	550	563	580	591	[49]
$Ti_{50}Ni_{20}Pd_{30}$	208	241	230	241	[49]
$Ti_{50}Ni_{10}Pd_{40}$	387	403	419	427	[49]
$Ti_{50}Ni_5Pd_{45}$	467	486	503	509	[49]
$Ti_{50}Ni_{45}Pt_5$	10	29	36	49	[49]
$Ti_{50}Ni_{40}Pt_{10}$	−8	18	−27	36	[49]
$Ti_{50}Ni_{30}Pt_{20}$	241	300	263	300	[49]
$Ti_{50}Ni_{20}Pt_{30}$	537	619	626	702	[49]

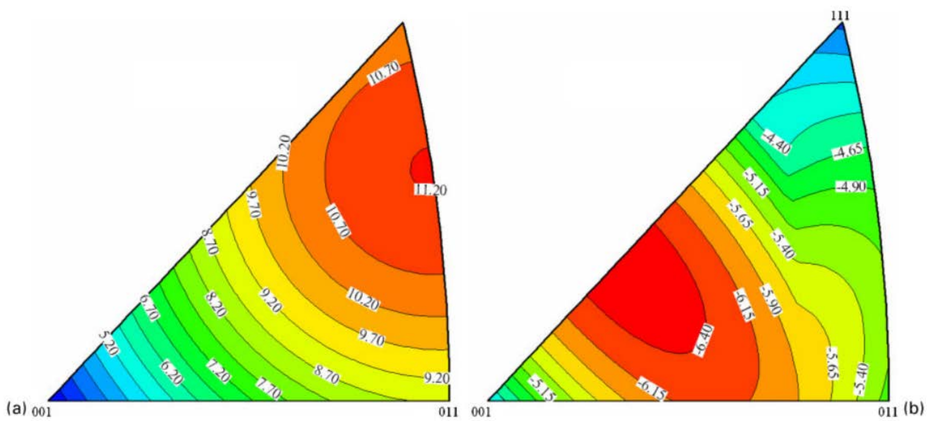
P.K. Kumar and D.C. Lagoudas, « Introcutction of Shape Memory Alloys» (2008)

Research trend to control characteristics of SMA (3) Orientation effect

- **Mechanical response depending on the orientation**



- **Maximum transformation strain depending on the orientation**



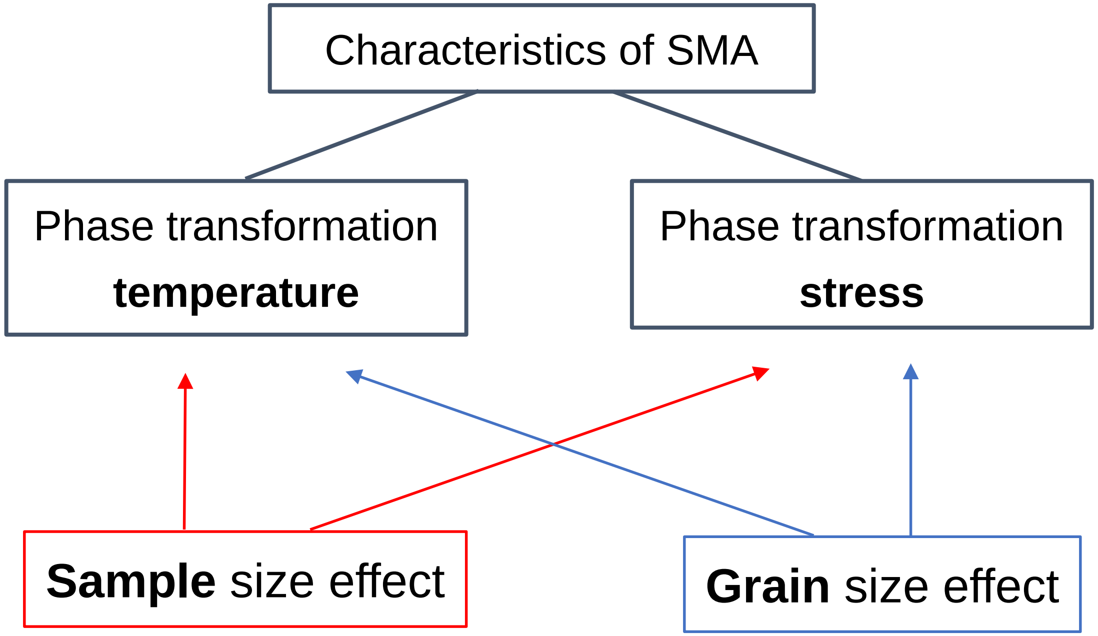
Under tensile stress　　Under compressive stress

J Ma, I Karaman & R.D. Noebe, Internatinal Materials Reviews 55 (2010)

Research trend to control characteristics of SMA (4) Size effect

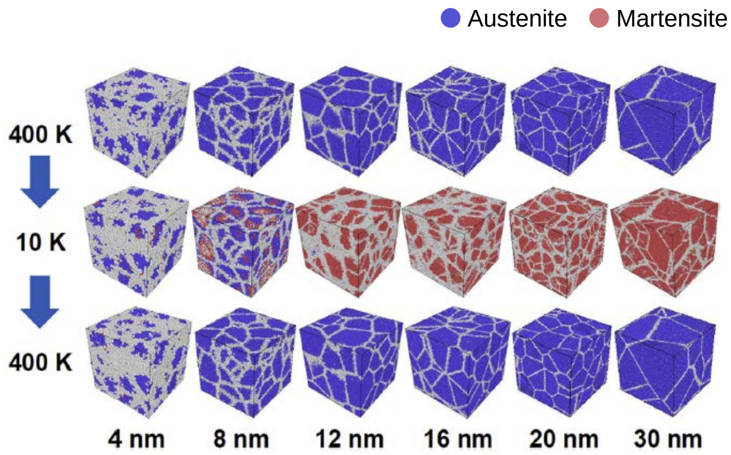
- **New approach : Abnormal behavior at the nanoscale**

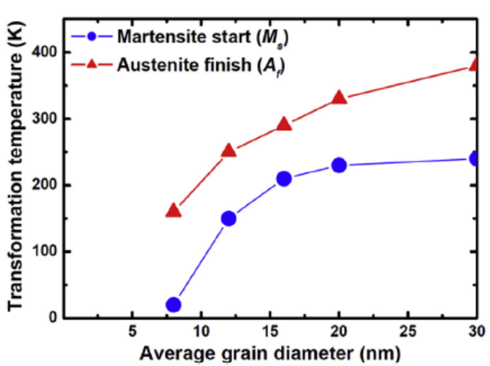
  ➡ Surface area to volume ratio increases



Size effect on phase transformation temperature

Grain size effect

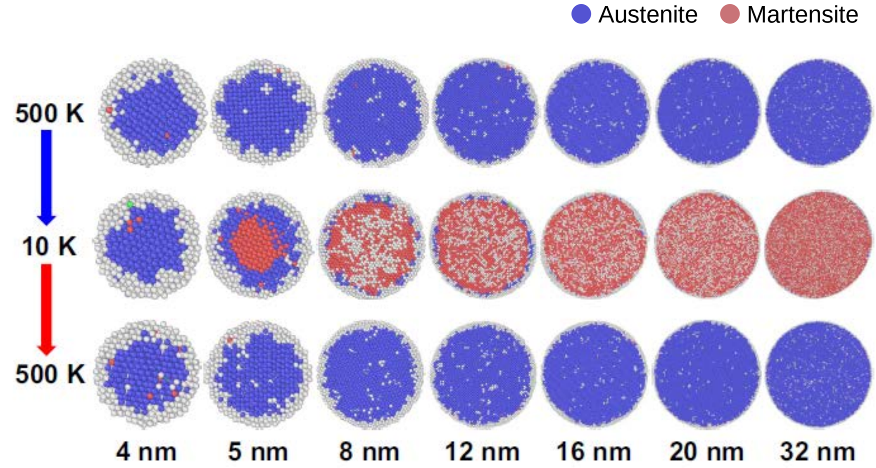


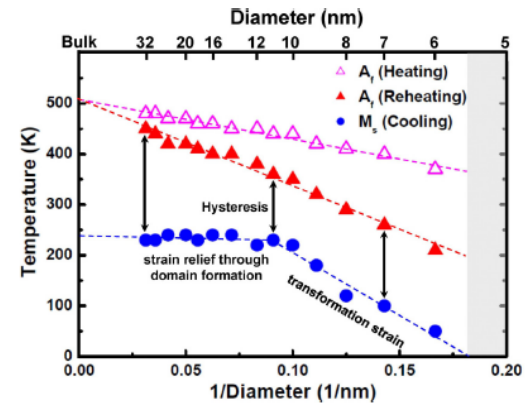


1. austenite over-stabilization : $\gamma_{\text{auestenite}} < \gamma_{\text{martensite}}$
2. Grain boundaries work as energy barrier

W.S. Ko et al., Acta Materialia 123 (2017) 90-101

Sample size effect



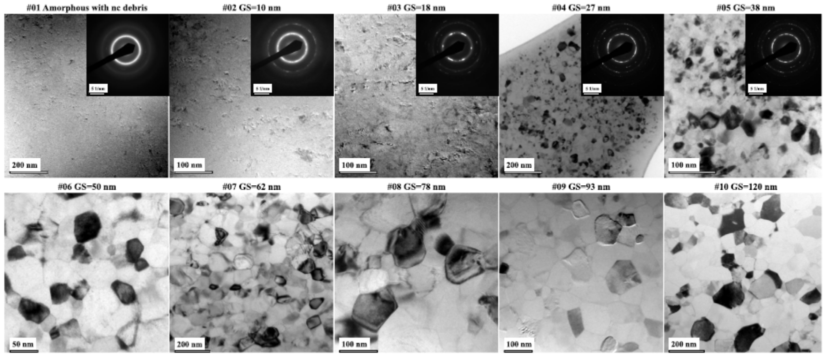


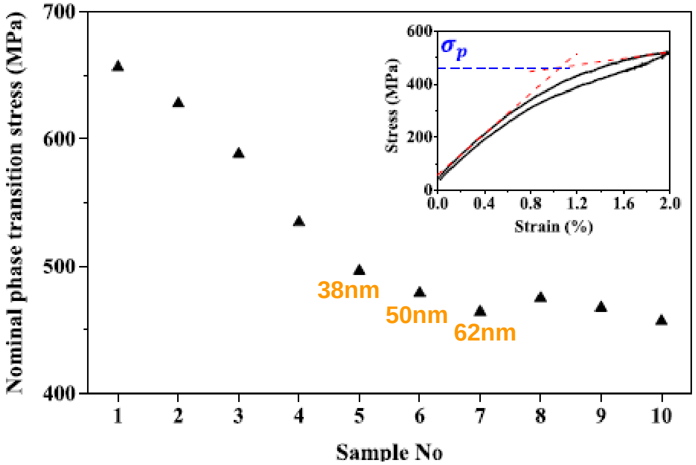
1. austenite over-stabilization : $\gamma_{auestenite} < \gamma_{martensite}$

W.S. Ko et al., Physical Review Materials 2 (2018) 030601

Size effect on phase transformation stress

Grain size effect



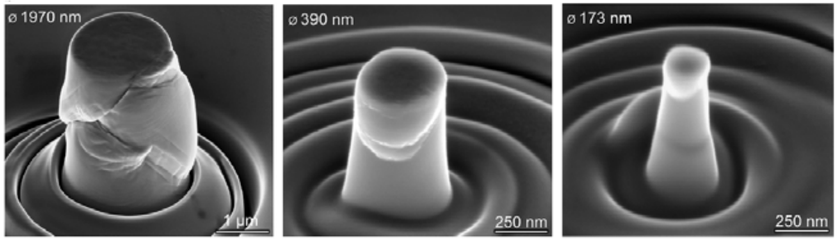


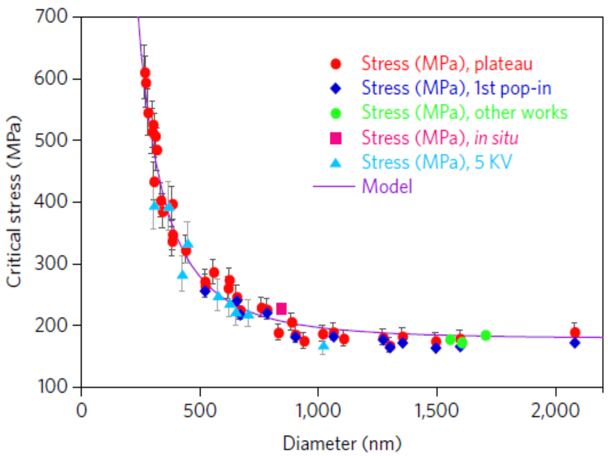
Transformation strain mechanism :

Grain boundaries work as mechanical constraints.

Minglu Xia et al., Meterials Letters 211 (2018) 352-355

Sample size effect





Dislocation starvation

↓

Homogeneous nucleation

↓

Critical stress for PT increases

J.F. Gomez-Cortes et al., Nature nanotechnology 12 (2017) 790-796

Summary

- Origin of SME : Thermoelastic martensitic transformation

- Type of SME : one-way / two-way SME

- Research trend of SMA

  - ✓ Searching alloy system
  - ✓ Alloy design using additional element
  - ✓ Orientation effect
  - ✓ Size effect at the nanoscale

- Industrial / Biomedical / Electrical Applications

Thank you for your kind attention

Type of Martensitic Transformation

Martensitic transformation

Athermal Isothermal