Study to control characteristic temperature of shape memory nanoparticles based on size dependency

Current Status of Structural Materials

2020. 04. 20

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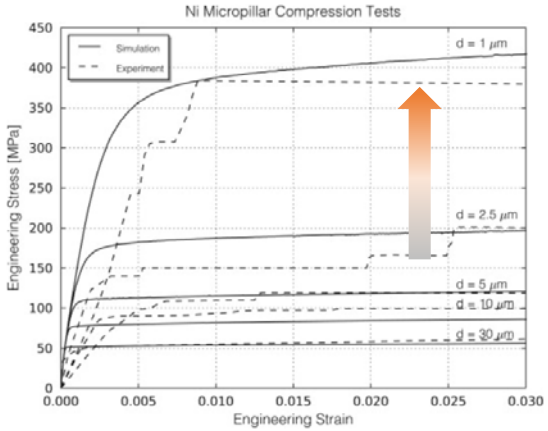
Contents

- Review : Size effect of nanoscale Shape memory alloys
- Novel fabrication method of SMA nanoparticles
- Mechanical behavior of fabricated SMA nanoparticles depending on size

Size effect of Metallic materials

- **“Smaller is stronger” in crystalline materials**



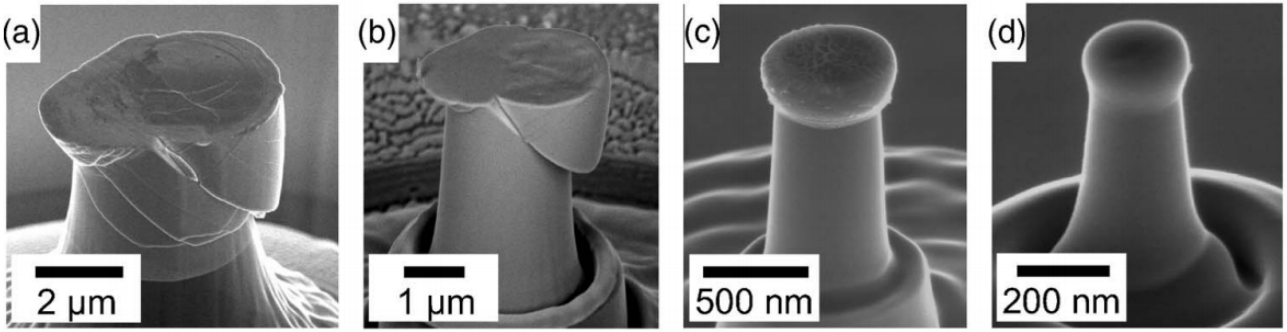
d = 1μm

→ Dislocation (Defect) starvation for smaller sample

d = 30μm

Ni Single crystal, Journal of the Mechanics and Physics of Solids 60 (2012) 1432-1446

- **Brittle to ductile transition in Metallic Glasses**



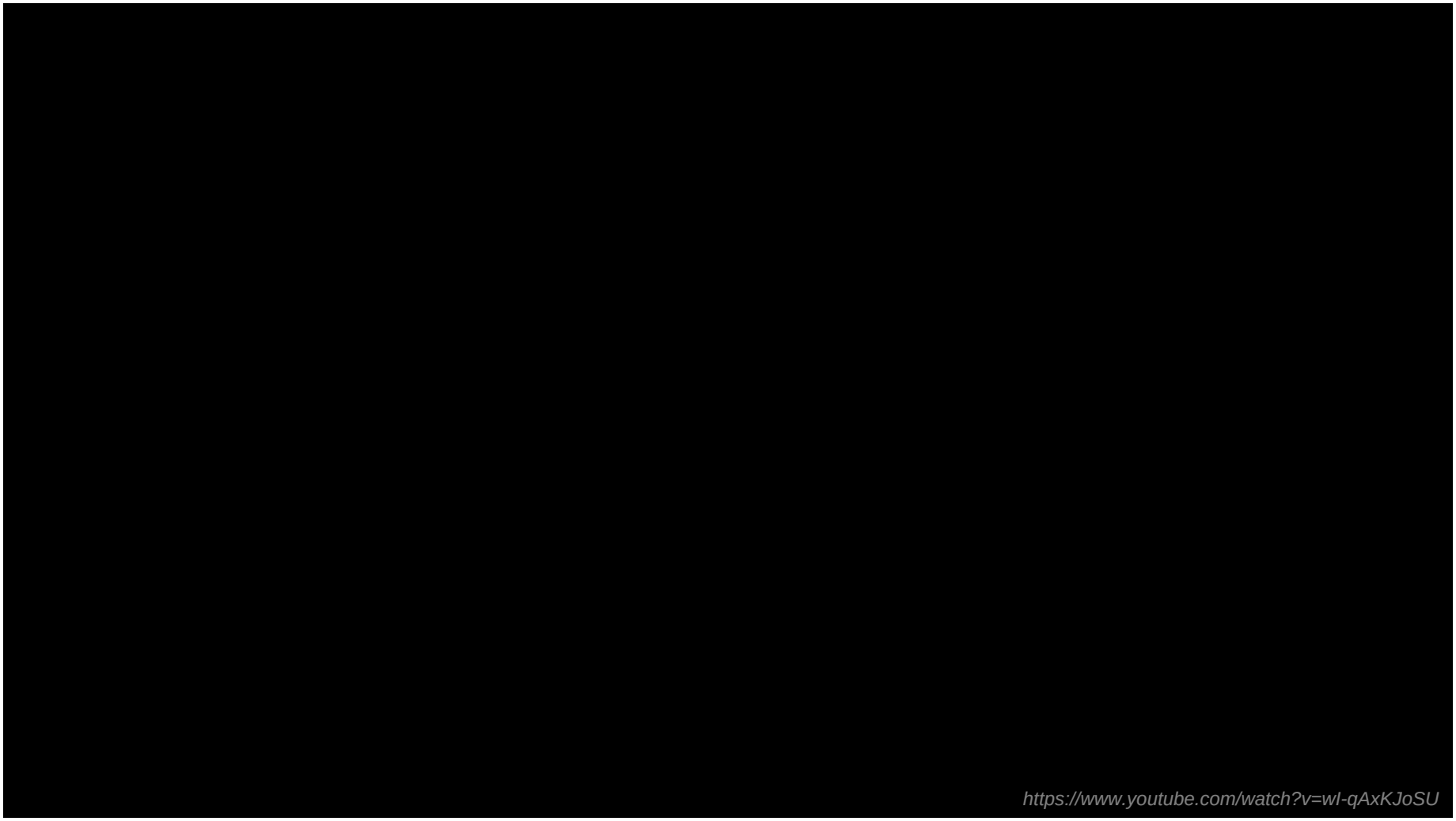
d = 3.61μm **1.84μm** **0.44μm** **0.14μm**

→ Sample size induced transition in deformation mode

: Shear band propagation → homogeneous flow

Volkert et al., J. Appl. Phys. 103 (2008)

Shape Memory Alloys : Shape memory effect & Superelasticity

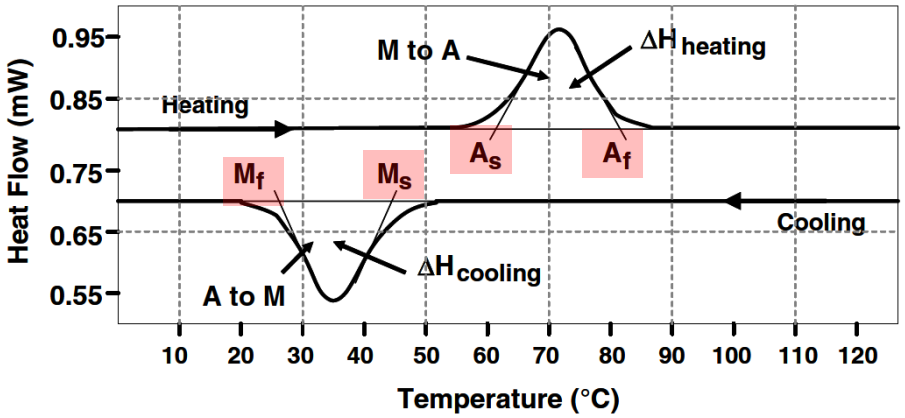


One of important current research issues on SMA is

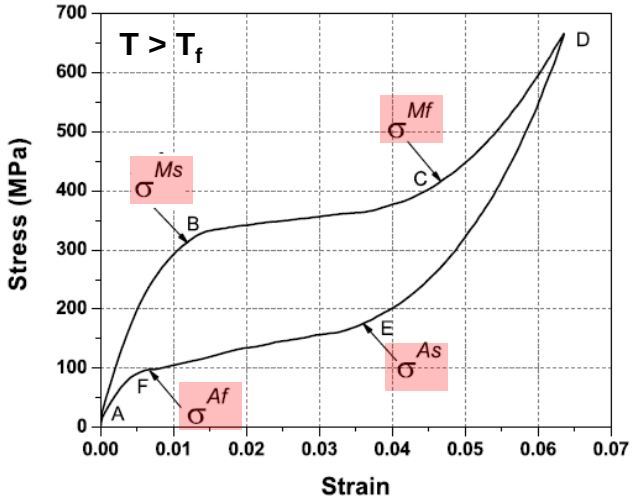
to change characteristic temperature and stress.

Characteristic temperature / stress of shape memory alloys

Thermally-induced phase transformation



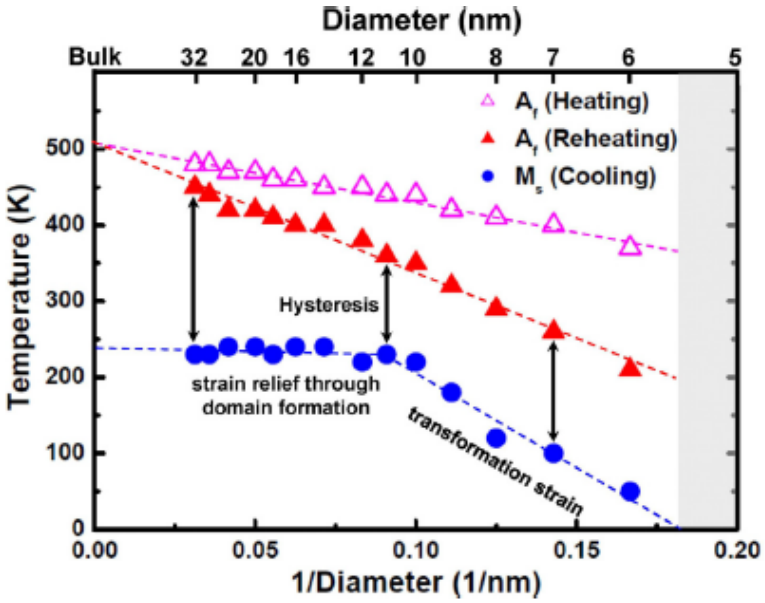
Stress-induced phase transformation

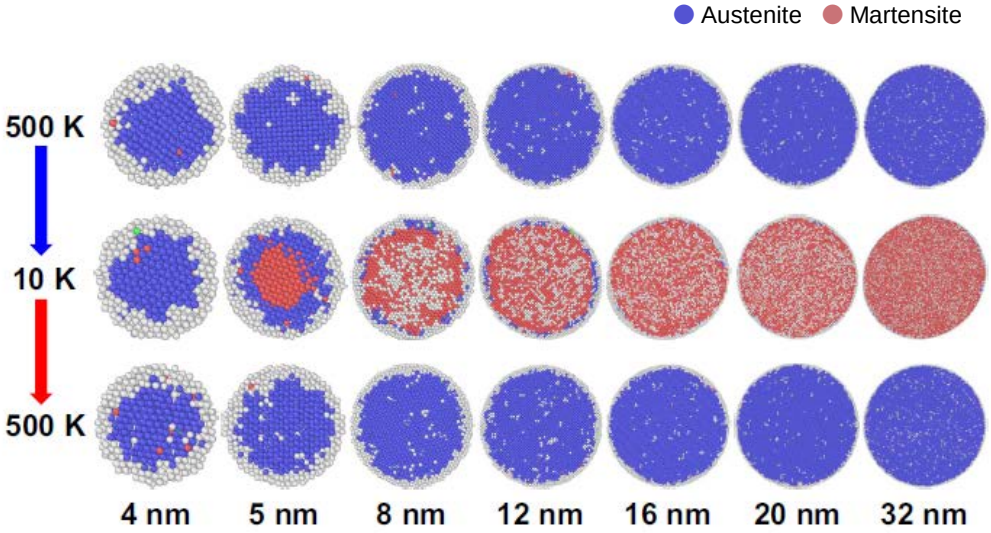


P.K. Kumar and D.C. Lagoudas, « Introcutction of Shape Memory Alloys» (2008)

- **Previous approach to control the SMA properties : Alloy design**
  - ➡ Control the phase stability (austenite)
- **New approach : Abnormal behavior at the nanoscale**
  - ➡ Surface area to volume ratio increases

Effect of sample size on phase transformation temperature



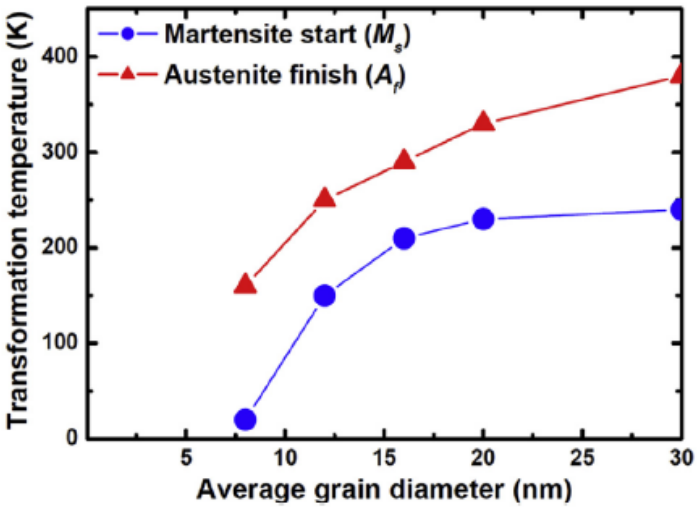


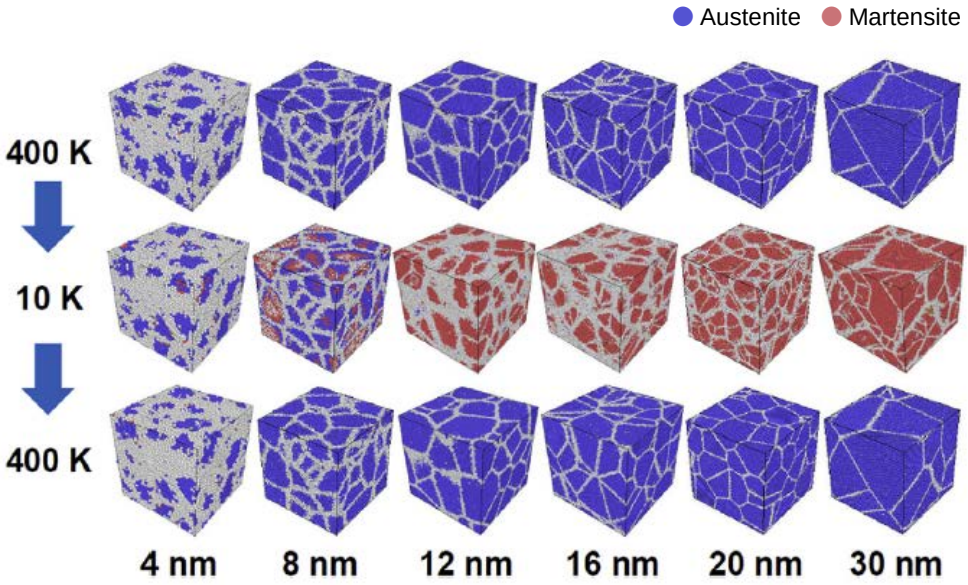
W.S. Ko et al., Physical Review Materials 2 (2018) 030601

∵ **austenite over-stabilization :** $\gamma_{auestenite} < \gamma_{martensite}$

As the sample size decreases, transformation temperatures decrease.

Effect of grain size on phase transformation temperature





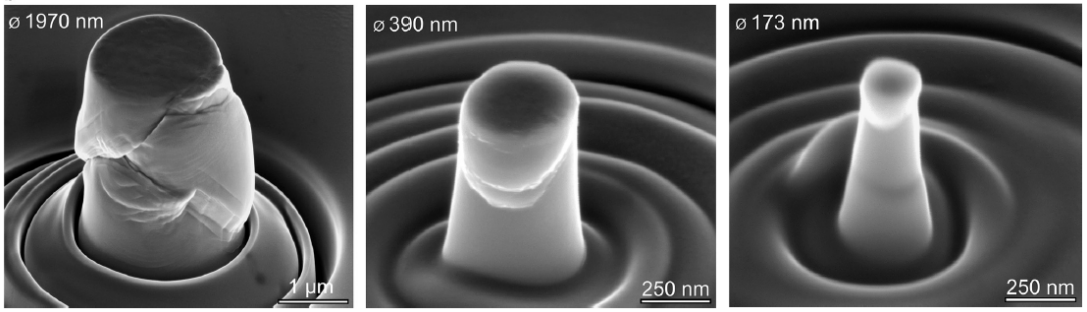
W.S. Ko et al., Acta Materialia 123 (2017) 90-101

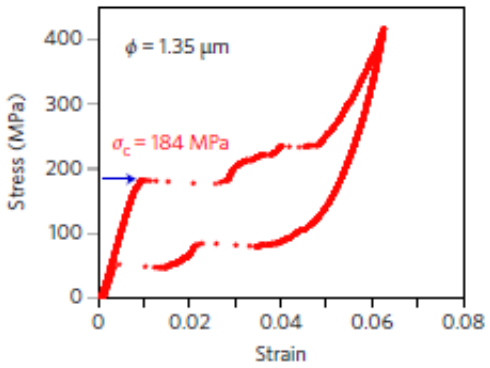
∵ **1. austenite over-stabilization :** $\gamma_{auestenite} < \gamma_{martensite}$

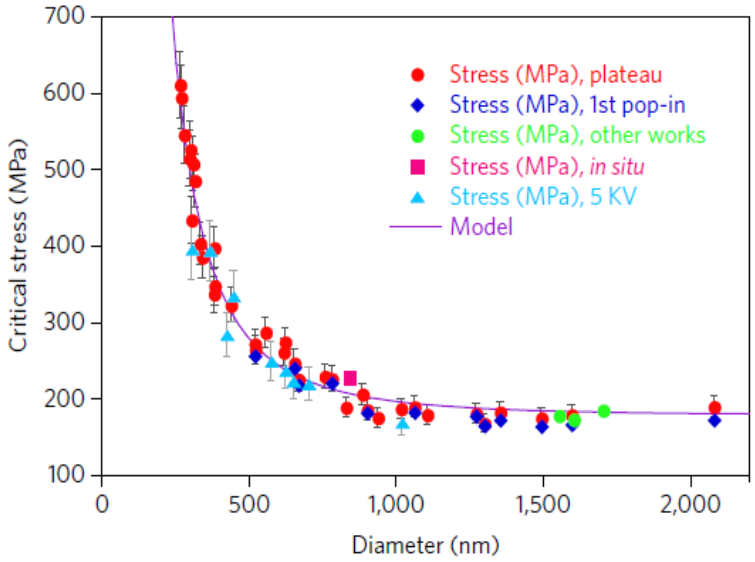
2. Grain boundaries work as energy barrier

As the grain size decreases, transformation temperatures decrease.

Effect of sample size on phase transformation stress







∵ **Dislocation starvation**

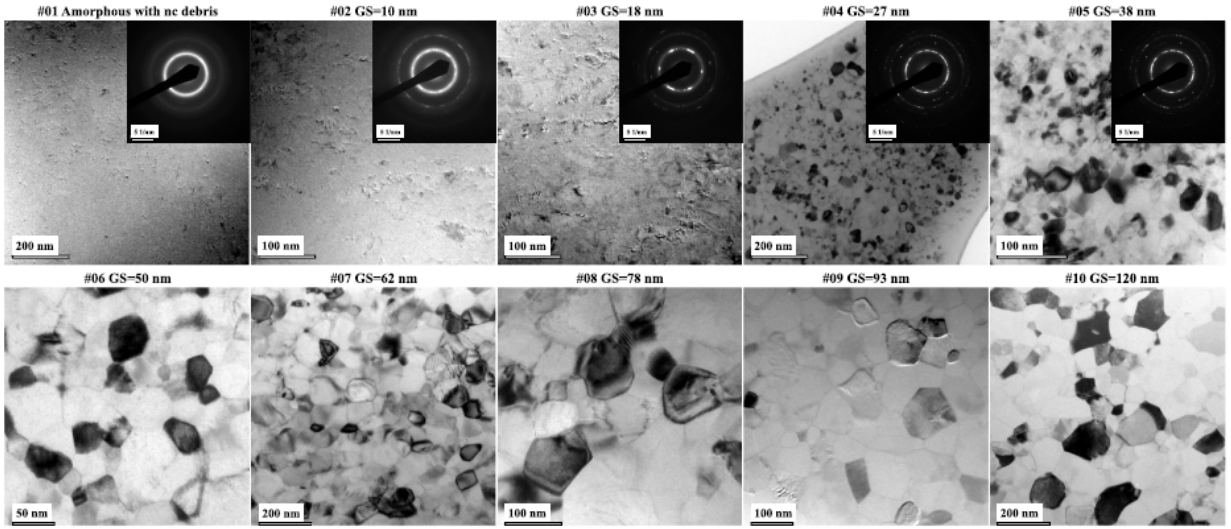
Homogeneous nucleation

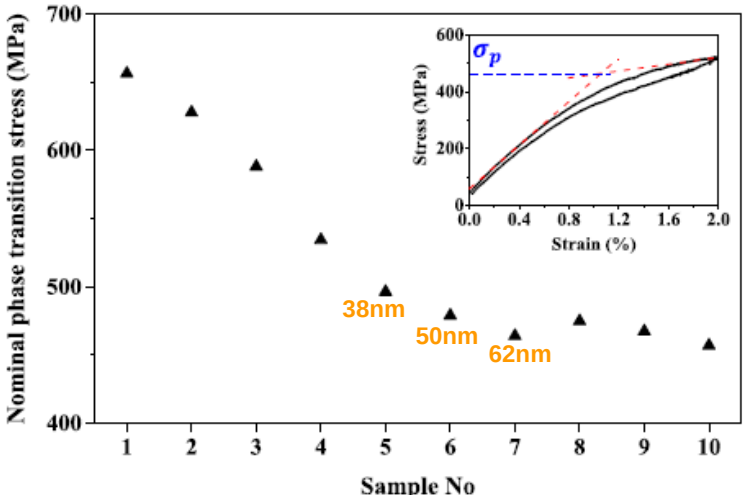
Critical stress for PT increases

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

As the sample size decreases, transformation stress increases.

Effect of grain size on phase transformation stress





∵ **Transformation strain mechanism :**

Grain boundaries work

as mechanical constraints.

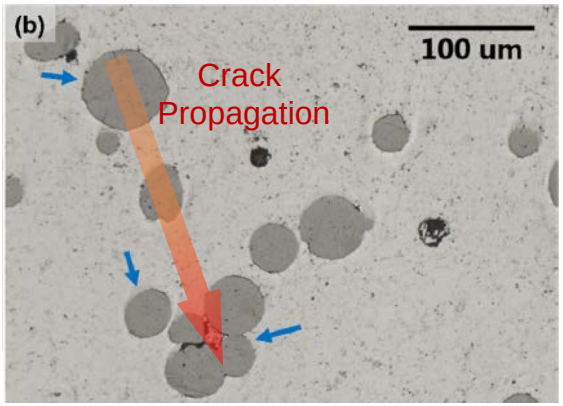
Minglu Xia et al., Meterials Letters 211 (2018) 352-355

As the grain size decreases, transformation stress increases.

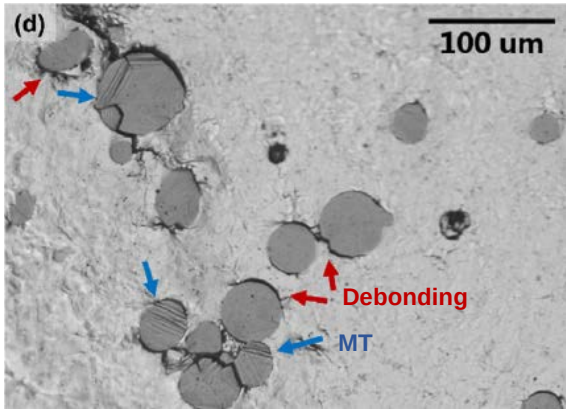
Summary of SMA size effect

	Phase transformation **temperature**	Phase transformation **stress**
Sample size effect	Sample size ↓ PT temperature ↓	Sample size ↓ PT stress ↑
Grain size effect	Grain size ↓ PT temperature ↓	Grain size ↓ PT stress ↑

- **Shape memory alloy as second phase in composite materials : multiple stress**



Stress at the crack tip induced **martensitic transformation**

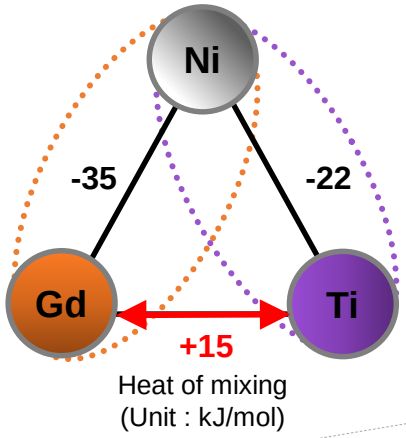


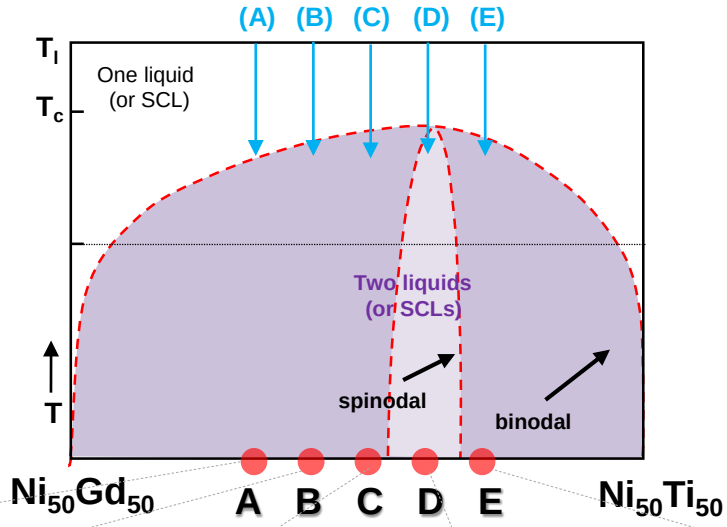
Al Matrix + $Ni_{43}Co_7Mn_{39}Sn_{11}$ SMA Particles

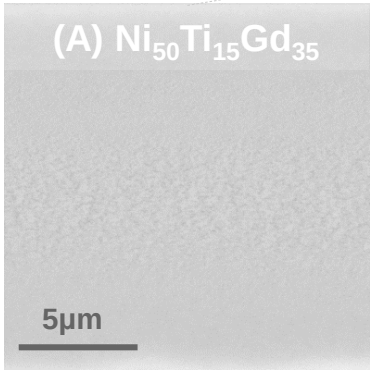
N.E. Bartam, I. Karaman, MSE A 751 (2019) 201-213.

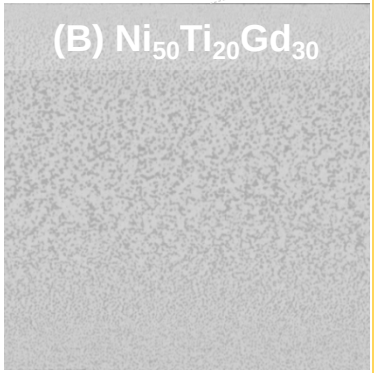
Need to study size effect of isotropic polycrystalline SMA particles

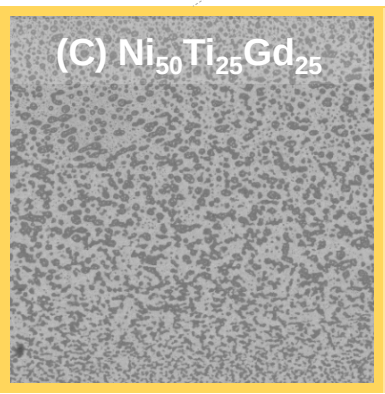
Microstructure of Ni-Ti-Gd system

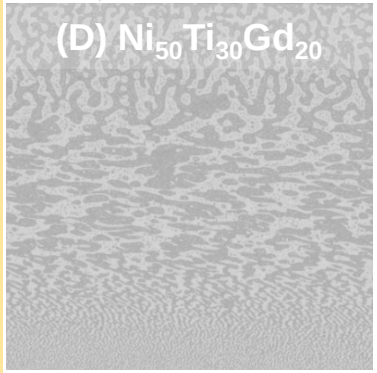


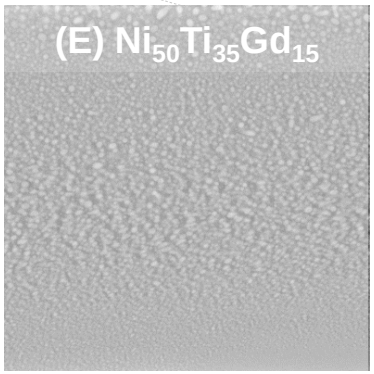












Select $Ni_{50}Ti_{25}Gd_{25}$ as precursor alloy

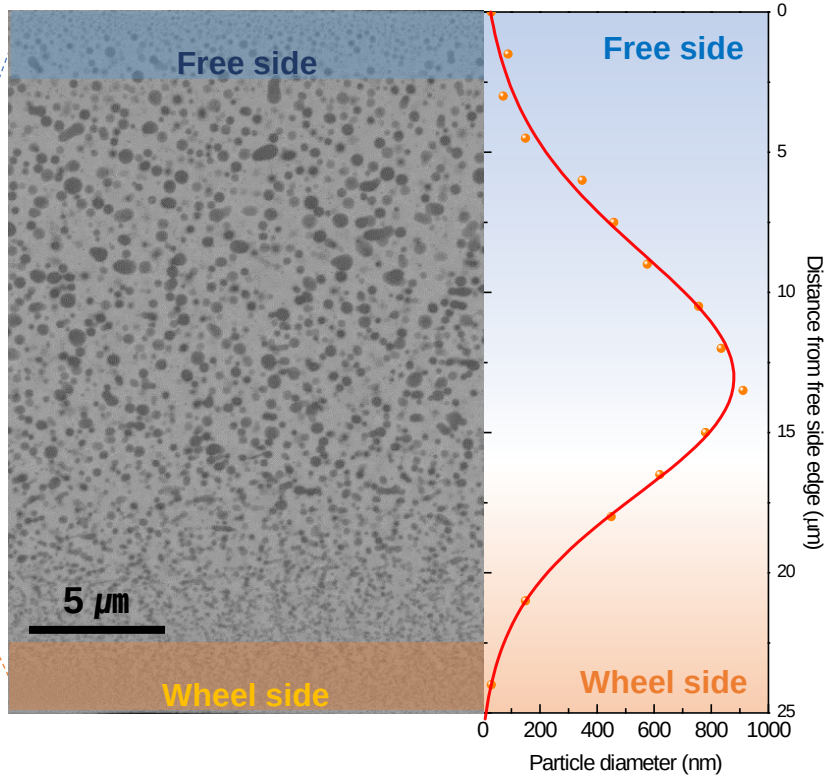
Selective dissolution from phase separated ribbon

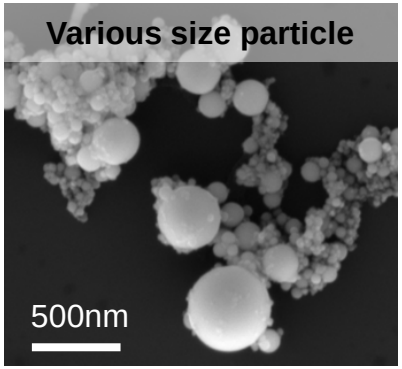
- **0.1M nitric acid + Crushed ribbon → Ultra-sonication**

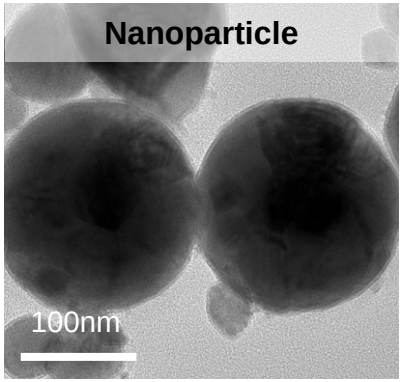
Melt - spun ribbon

Free side
: Cooled on Ar atmosphere

Wheel side
: relatively high cooling rate by water cooled wheel



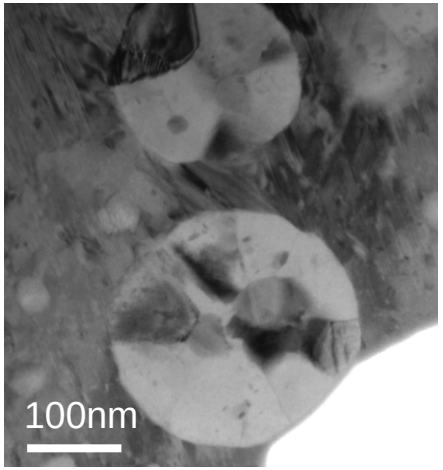


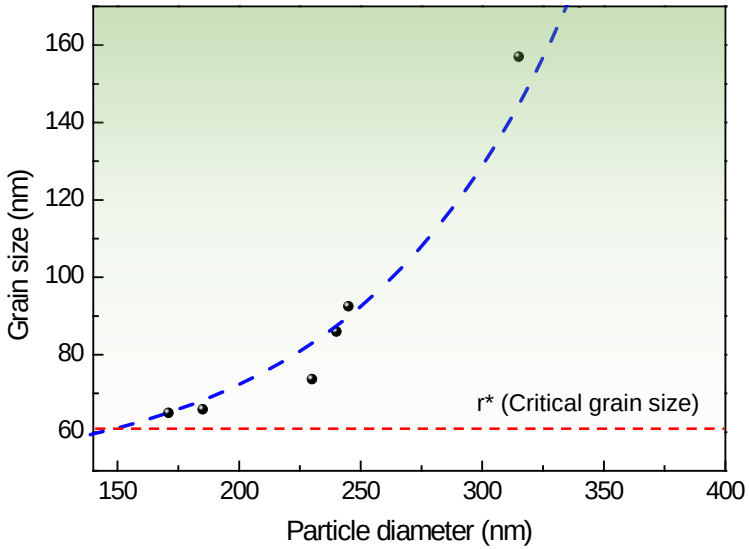


Dealloyed particles have an average size distribution from 100nm to 1000nm.

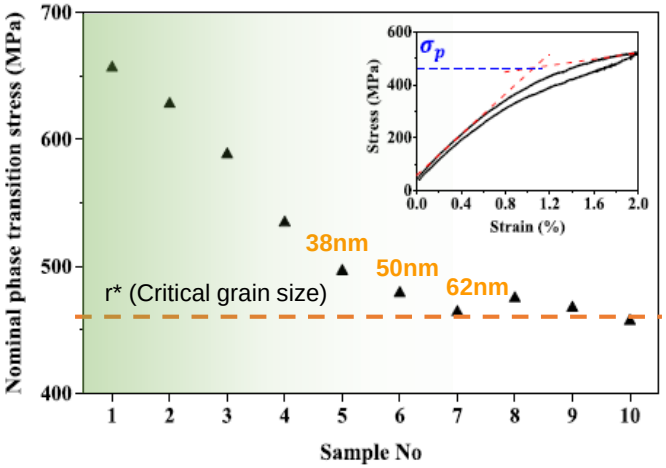
Analysis of grain size of particles

- **Relation between grain size and particle diameter**





- **Negligible of grain size effect**

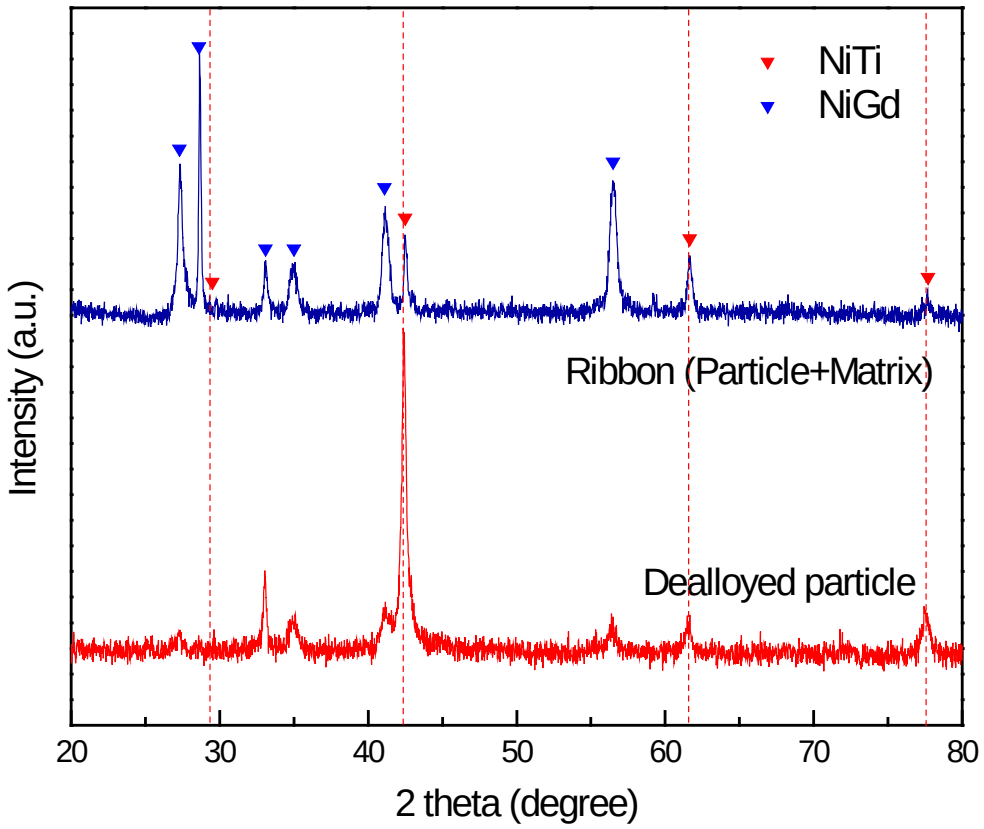


Minglu Xia et al., Meterials Letters 211 (1018) 352-355

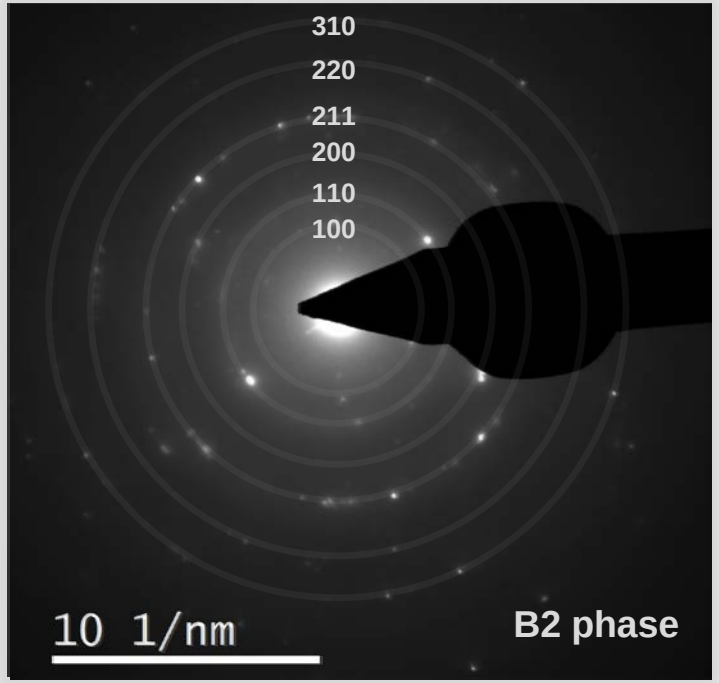
We focused only on
the sample size effect of
polycrystalline SMA nanoparticles.

Phase analysis before/after dealloying

- **XRD of ribbon / dealloyed particle**



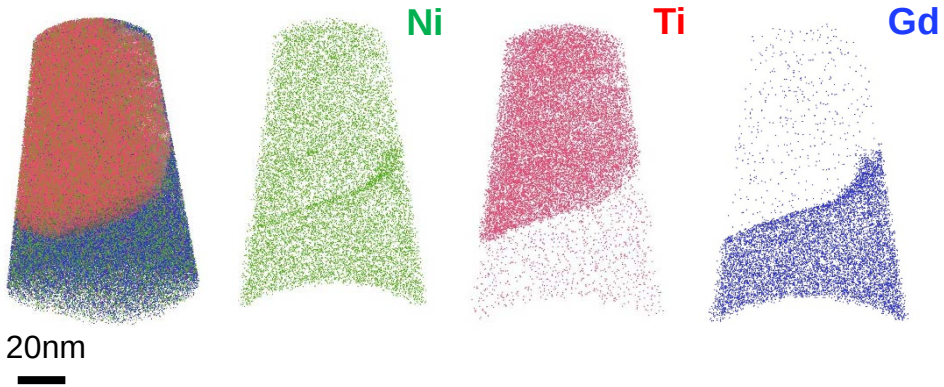
- **TEM diffraction pattern of dealloyed particle**



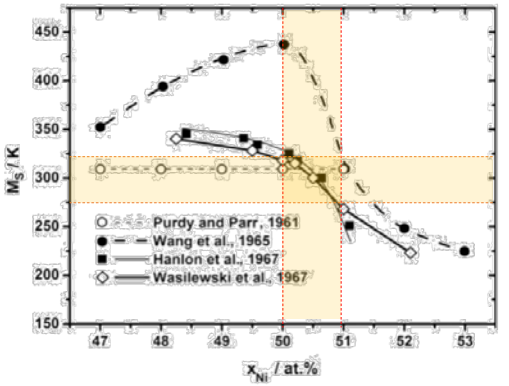
- (Before dealloying) **NiGd matrix** + **NiTi particles [B2]**
- (After dealloying) **NiTi particles [B2]**

Compositional analysis

- **Tomogram of atomic configuration**

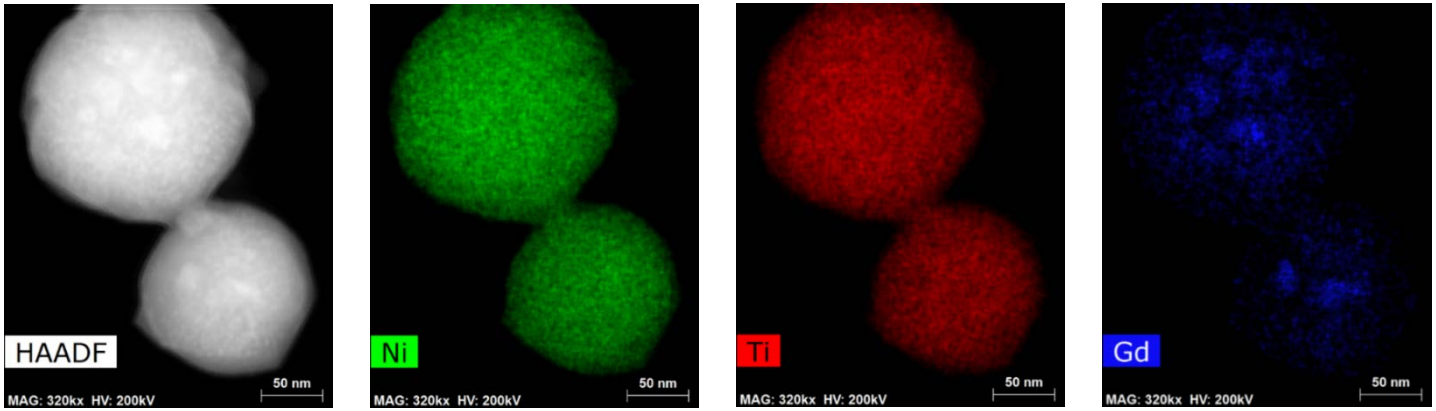


	Ni	Ti	Gd
Average (at.%)	51.224	47.556	0.600
Average (at.%)	59.392	1.158	36.998



- **STEM EDS mapping : $Ni_{50.07}Ti_{49.66}Gd_{0.25}$**

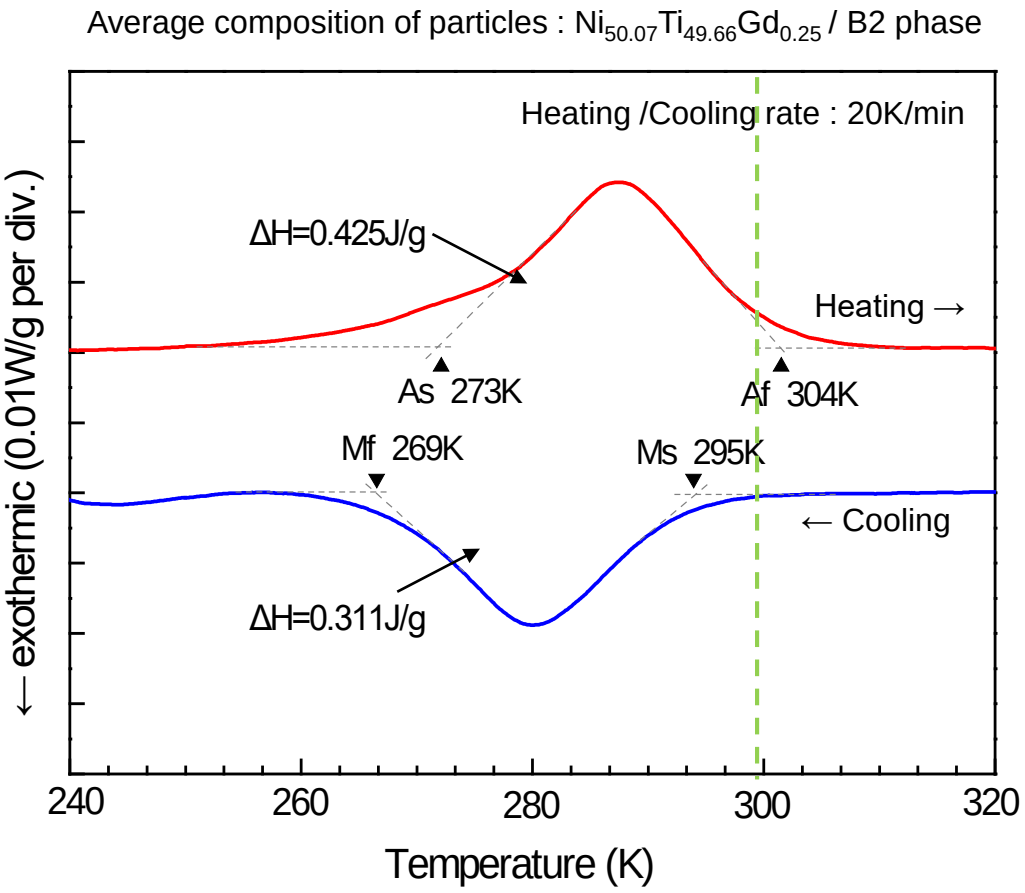
J. Frenzel et al., Acta Materialia 58 (2010) 3444–3458.



Droplet phases with composition similar to targeted composition (Nitinol)

Thermally-induced phase transformation

- **DSC result of dealloyed particles**



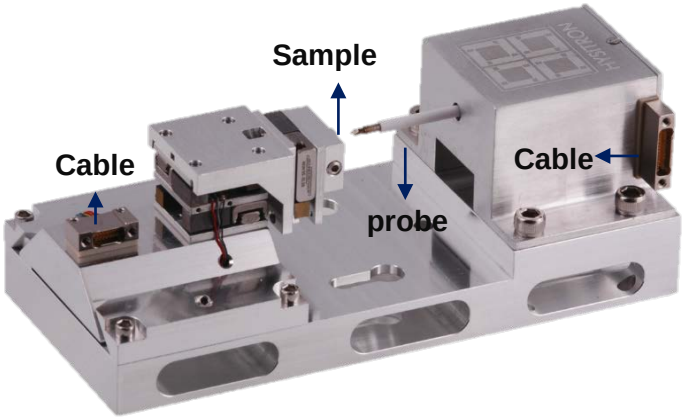
A_f ≈ Room temperature

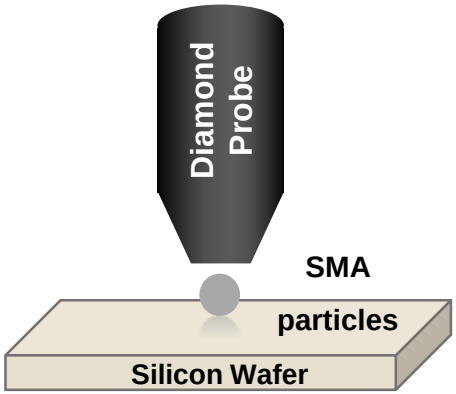
Possibility of superelastic behavior at RT

Stress-induced phase transformation

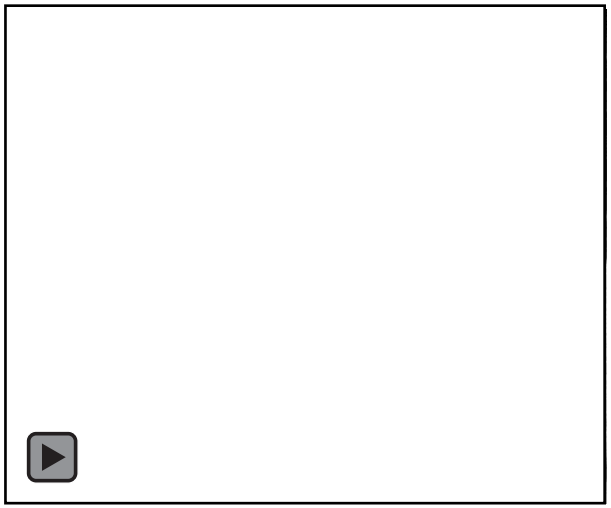
In-situ compression test in SEM

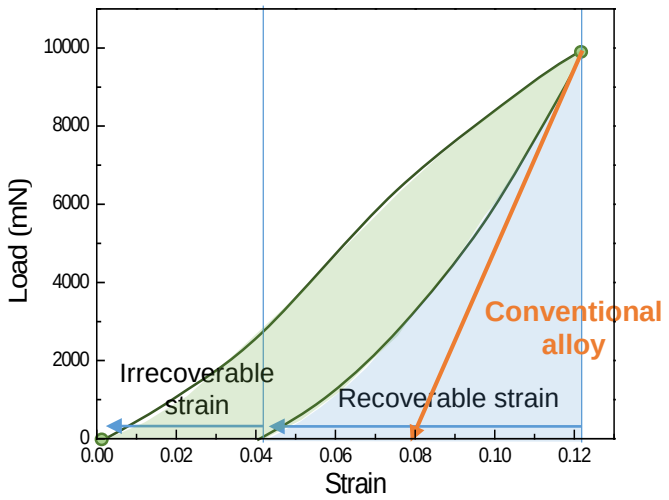
- Pico-indenter (PI 85)



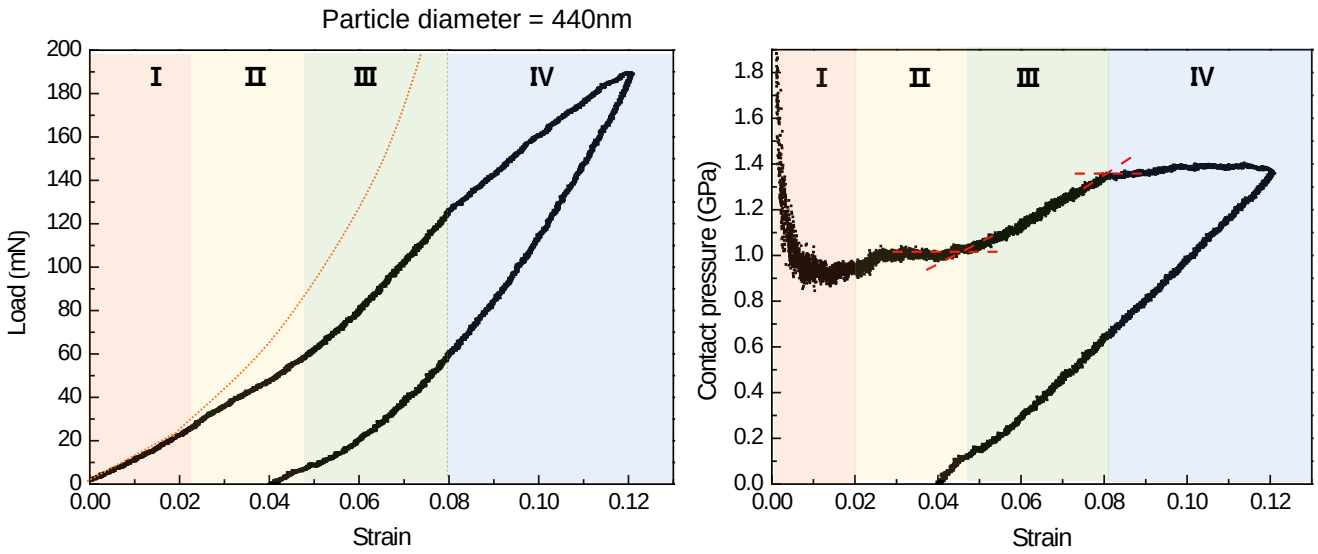


Mechanical response of compression





Deformation stages during parallel plate compression



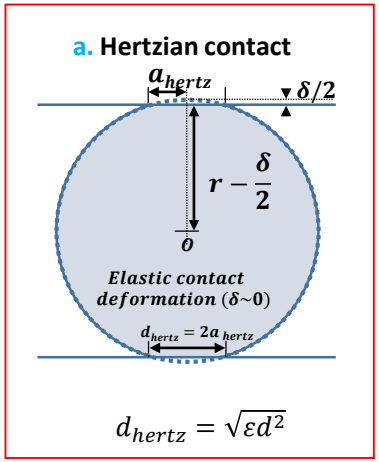
Ⅰ: Elastic deformation of auestenite

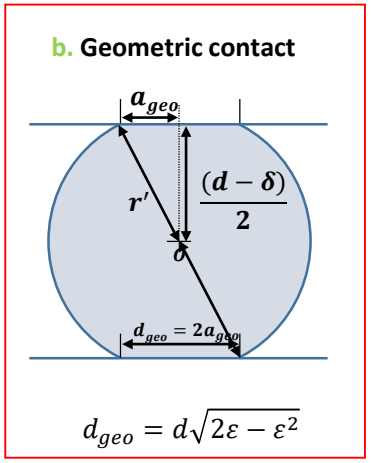
Ⅱ: Matensitic transformation

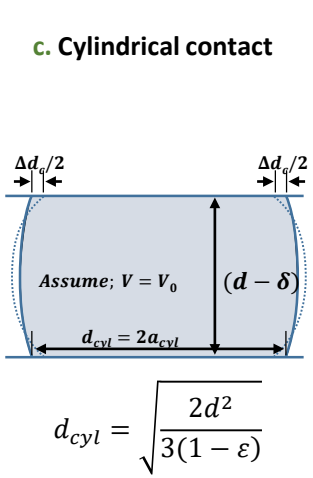
Ⅲ: Elastic deformation of martensite

Ⅳ: Plastic deformation of martensite

Geometric relations in the three contact diameter models

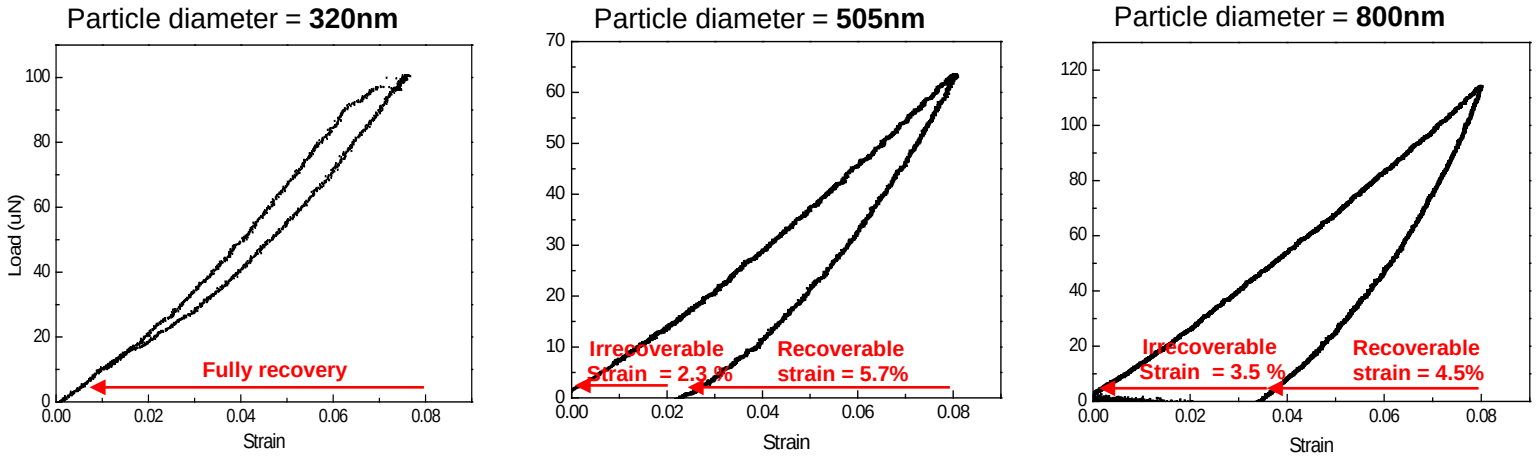




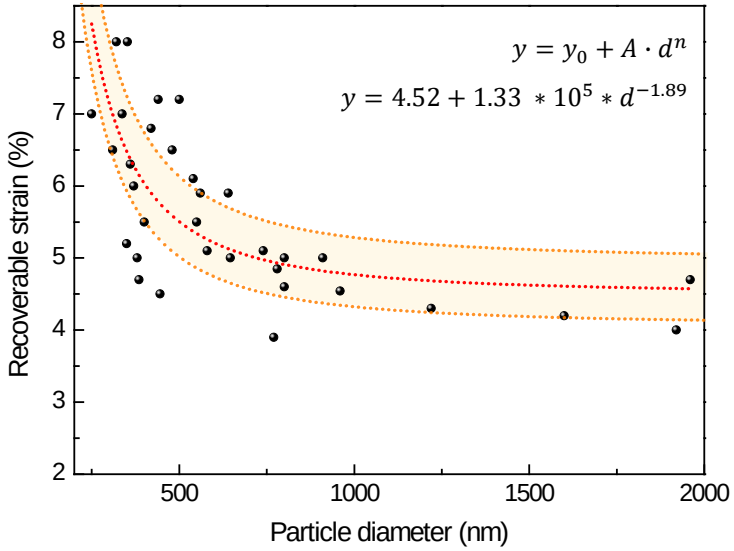


J. W. Kim et al., submitted (2019).

Mechanical response of PS-SMA NP depending on size

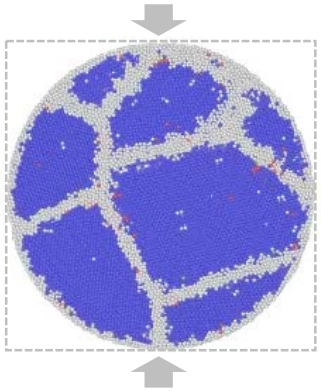


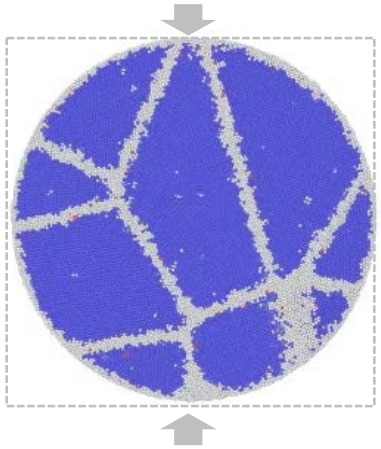
- **Recoverable strain of PS-SMA NP depending on size**

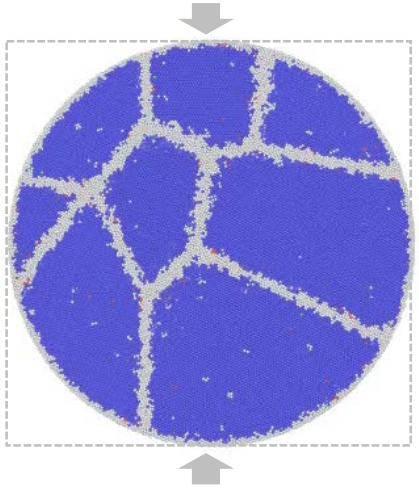


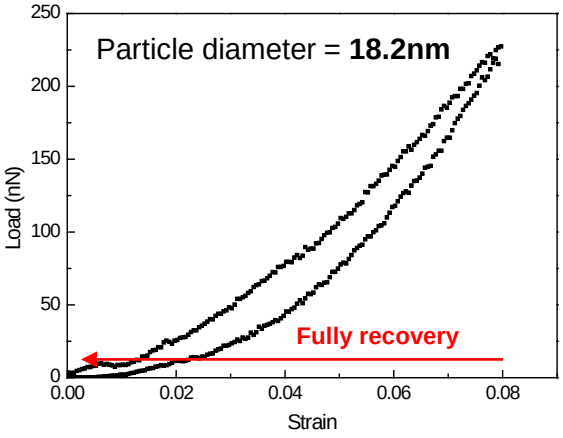
As sample size decreases ▶ Higher recoverable strain at R.T.

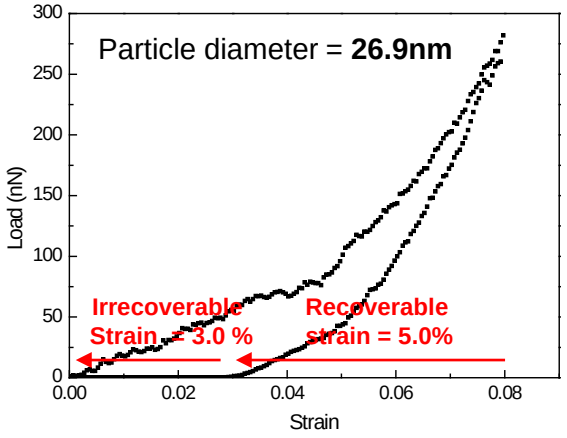
MD Simulation : Mechanical behavior of PS-SMA NP depending on size

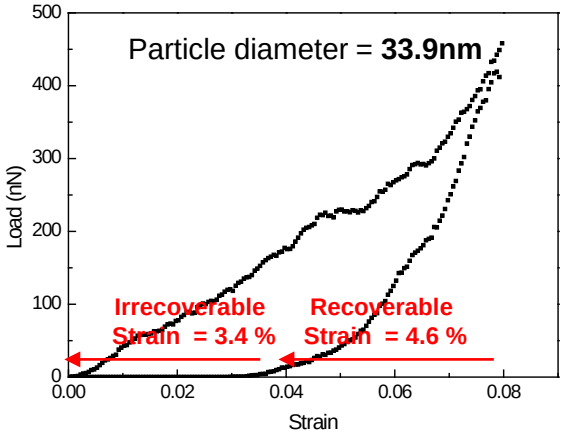










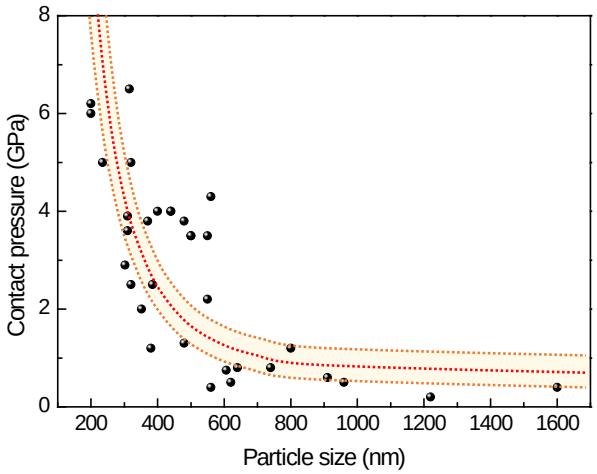


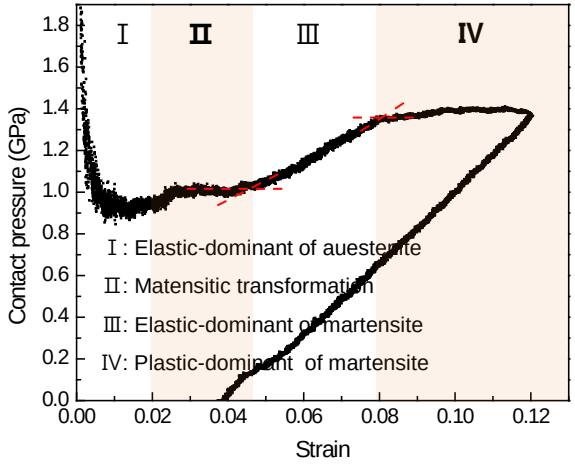
ε = 8% compression, Number of grains = 10

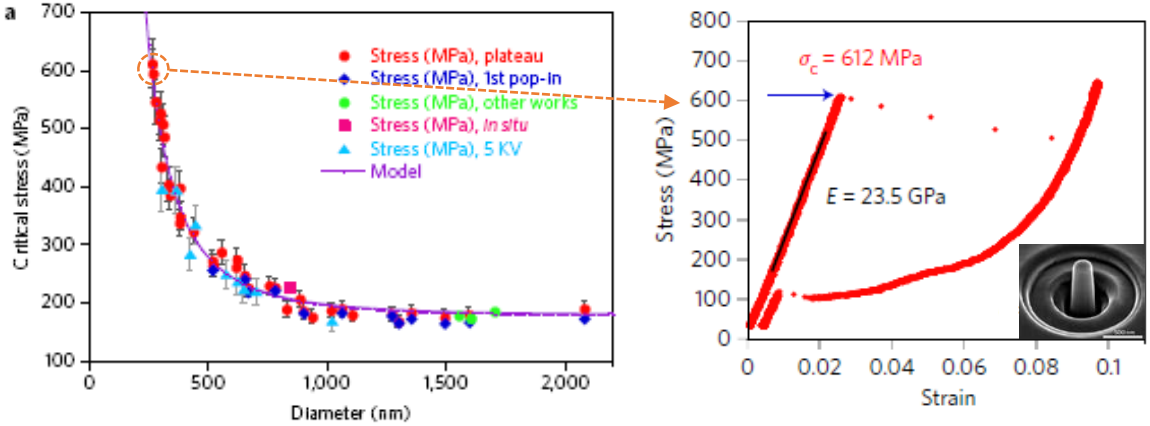
As sample size decreases ▶ Higher recoverable strain

Loading : Critical stress of PS-SMA NP depending on size

Critical stress for MT (Ⅱ)







All samples were fully recovered.

∵ M_s = 252 K, M_f = 242 K

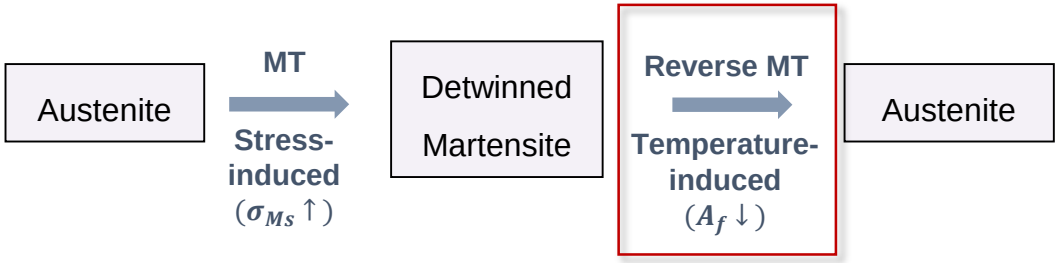
A_s = 273 K, A_f = 285 K < R.T.

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

Increase in critical stress for MT is not the cause of the difference of recoverable strain.

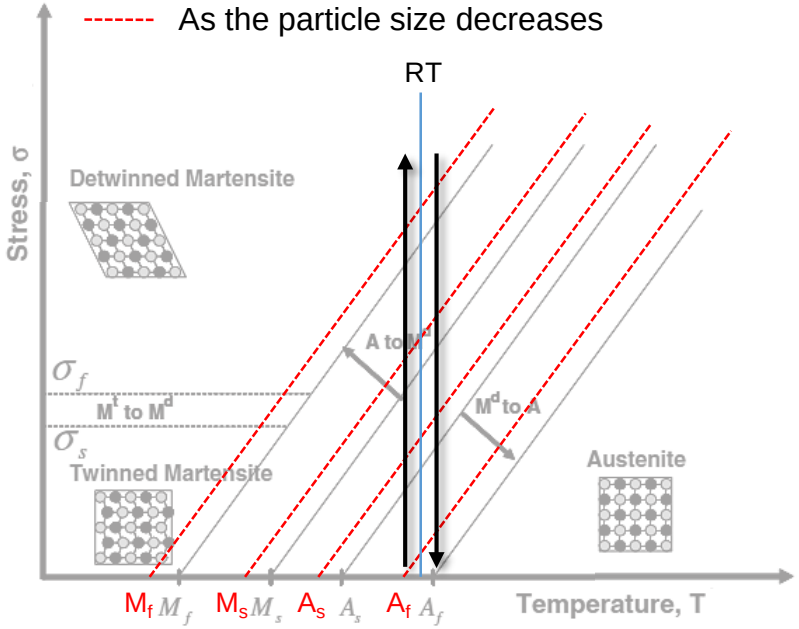
Size effect of SMA nanoparticle

- **Smaller particles are better recovered.**



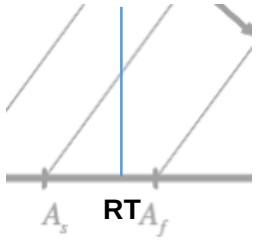
Reverse MT occurs favorably for the smaller size (lower A_s)

ε = 8% compression

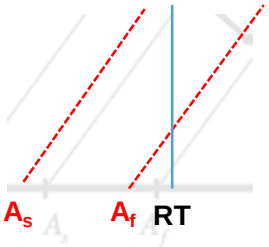


P. K. Kumar and D. C. Lagoudas, "Introduction to Shape Memory Alloys" (2008)

(D > D^c) A_s< RT< A_f



(D < D^c) A_s< A_f <RT

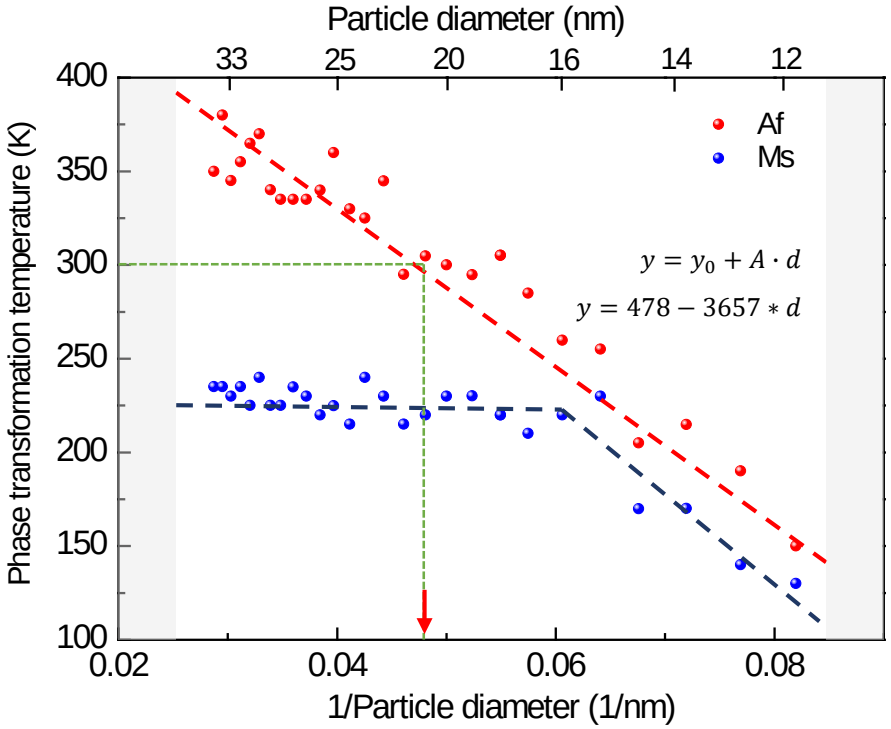


Reverse MT ↑

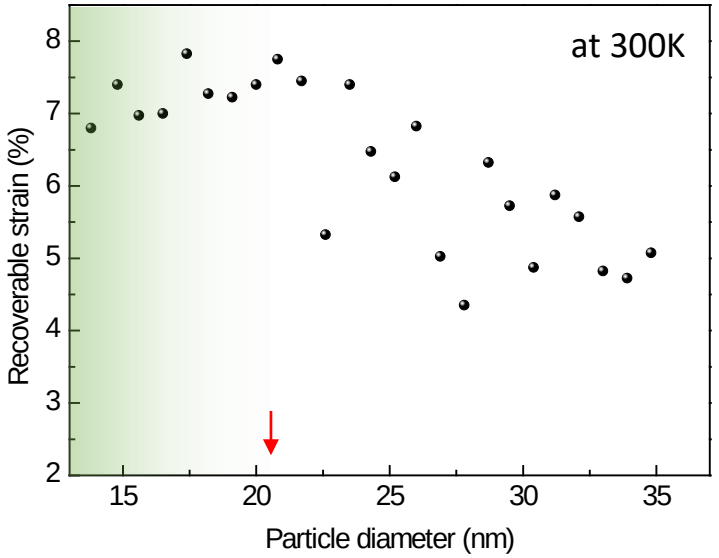
Recovery ↑

MD simulation : Recoverable strain of PS-SMA NP depending on size

Phase transformation temperature depending on size



Recoverable strain depending on size



As sample size decreases, the A_f temperature decreases.

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

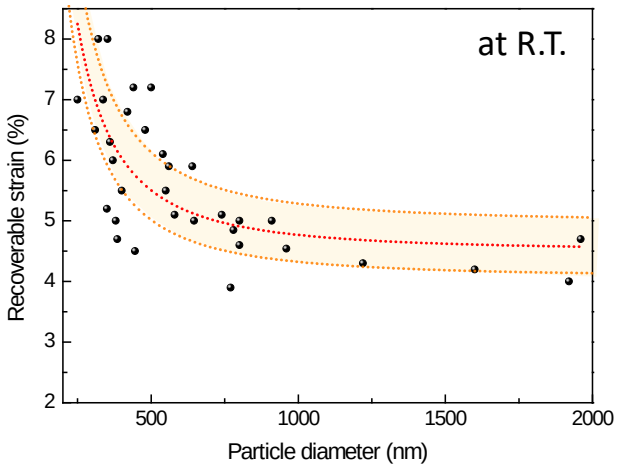
From the point where operating temperature is higher than A_f, recoverable strain tends to decrease.

Summary

Ⅰ. Novel Fabrication method of polycrystalline SMA nanoparticles

Positive heat of mixing between Ti-Gd → **Phase separation** phenomenon in Ni-Ti-Gd alloy system → Fabrication of SMA nanoparticles through **dealloying**

Ⅱ. Size effect of PS-SMA nanoparticles



The Smaller particle diameter,

the Larger recoverable strain & Recoverable work efficiency

The same tendency as MD simulation

As sample size decreases, the **critical temperature** where recoverable strain starts to decrease decreases.

Ⅲ. Findings of this study

- Experimental evidence of sample size effect on PT temperature for polycrystalline particles
- New approach to control the SMA properties: sample size control at the nanoscale

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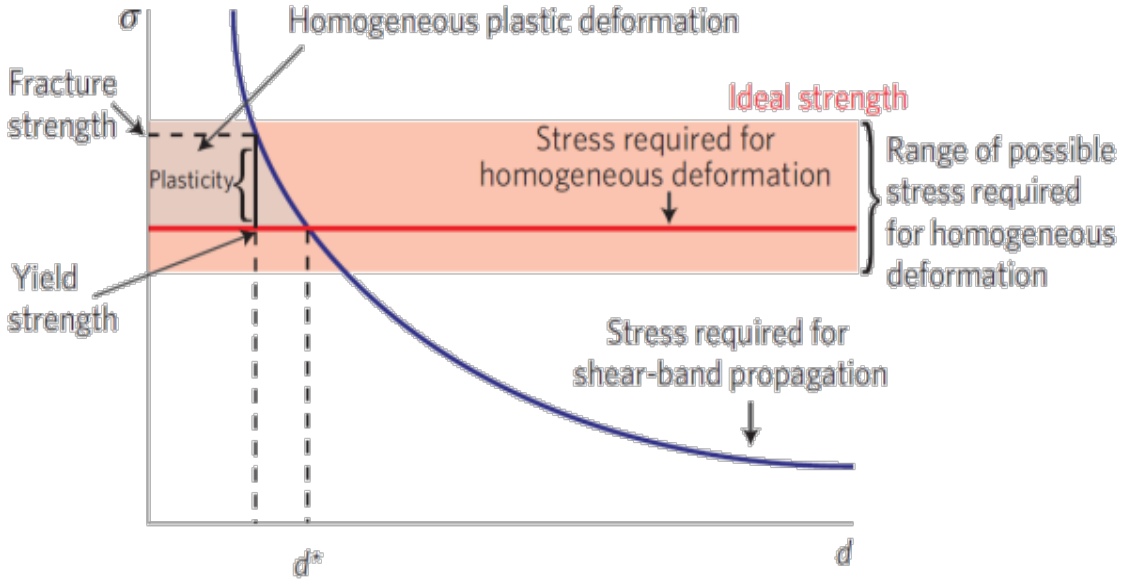
Thank you for your kind attention

Supplementary : Size effect of MG - Brittle to Ductile transition

Competition between deformation modes

Jang et al., Nat. Mater. 9 (2010)



For shear band formation,
elastic strain energy (3D energy source) should be bigger than **Surface energy** (2D energy sink).

Wang et al., Acta Mater. 60 (2012) 5370.
Yabari et al., Phys. Rew. B 82 (2010) 172202.